Technical Report

TR-14-03

Waste form and packaging process report for the safety assessment SR-PSU

Svensk Kärnbränslehantering AB

March 2014

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co

Box 250, SE-101 24 Stockholm
Phone +46 8 459 84 00

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Preface

This report compiles information on processes in the waste form and packaging that are relevant for the long-term safety of the low- and intermediate level waste repository SFR in Forsmark. It forms part of the SR-PSU safety assessment, which supports SKB´s licence application to extend and continue to operate SFR.

This report has been compiled and edited by Klas Källström, SKB, and Maria Lindgren, Kemakta Konsult AB. Experts have contributed to the report, as listed in Section 1.3.

The report has been reviewed by Jordi Bruno, Amphos 21, Russel Alexander, Bedrock Geosciences, Luc van Loon, PSI, and Kastriot Spahiu, SKB.

Stockholm, March 2014

Fredrik Vahlund
Project leader SR-PSU

Summary

The final repository for short-lived radioactive waste (SFR) located in Forsmark, Sweden is currently being used for the final disposal of low- and intermediate-level operational waste from Swedish nuclear facilities. SKB plans to extend the repository to host waste from the decommissioning of the nuclear power plants. The SR-PSU assessment of the long-term safety (post-closure safety) of the whole repository is an important part of the application for a licence to build the extension. This process report constitutes one of the main references supporting the Main report, which summarises the long-term safety for SFR.

Processes that are expected to take place in the near field of SFR in the period up to 100,000 years post-closure are systematically documented in two process reports, including an evaluation of the importance of each process within the SR-PSU and a suggestion of how the process should be handled in the SR-PSU activities. This report addresses processes related to the waste package, i.e. the waste form and packaging. The other process report for the near field treats the processes in the technical barriers in the repository. The process reports support the description of the repository long term reference evolution.

This report consists of two main chapters describing the waste form processes and the packaging processes respectively.

Sammanfattning

Slutförvaret för kortlivat radioaktivt avfall (SFR) i Forsmark, Sverige används för närvarande för slutlig deponering av låg- och medelaktivt driftavfall från svenska kärntekniska anläggningar. SKB planerar att bygga ut förvaret för att förvara avfall från rivning av kärnkraftverken. Analysen av långsiktig säkerhet SR-PSU (säkerhet efter förslutning) för hela förvaret är en viktig del av ansökan om att få bygga ut förvaret. Den här processrapporten utgör en av huvudreferenserna till huvudrapporten som summerar analysen av långsiktig säkerhet för SFR.

Processer som förväntas ske i närzonen i SFR under 100 000 år efter förslutning dokumenteras systematiskt i två processrapporter, vilken inkluderar utvärdering av varje process betydelse och förslag om hur processen ska hanteras inom SR-PSU. Den här rapporten behandlar processer för avfallskollin, dvs avfallsformen och emballage. Den andra processrapporten för närzonen behandlar de tekniska barriärerna i förvaret. Processrapporterna är en viktig del i underlaget för beskrivningen av förvarets referensutveckling.

Rapporten är indelad i två huvudkapitel som beskriver de relevanta processerna för avfallsformen samt avfallspaketen.

Contents

1 Introduction

1.1 Background

The final repository for short-lived radioactive waste (SFR) located in Forsmark, Sweden, is used for the final disposal of low- and intermediate-level operational waste from Swedish nuclear facilities. SKB plans to extend SFR to host waste from the decommissioning of the nuclear power plants and other nuclear facilities. Additional disposal capacity is needed also for operational waste from nuclear power units in operation since their operation life-times have been extended compared with what was originally planned.

The SFR repository includes waste vaults underground together with buildings above ground that include a number of technical installations. The underground part is situated at 60 metres depth in the rock and is located below the Baltic Sea. The existing facility (SFR 1) comprises five waste vaults with a disposal capacity of approximately 63,000 m^3. The extension (SFR 3[1]) will have a disposal capacity of 108,000 m^3 in five new waste vaults plus one new vault for nine boiling water reactor pressure vessels, see Figure 1-1.

The long-term post closure safety of the whole SFR has been assessed and documented in the SR-PSU Main report with supporting documents, see Section 1.2. The Main report is part of SKB's licence application to extend and continue to operate SFR. The present report is a main reference and describes thermal, hydraulic, mechanical and chemical processes in the waste form and packaging that are relevant for the long-term safety of SFR.

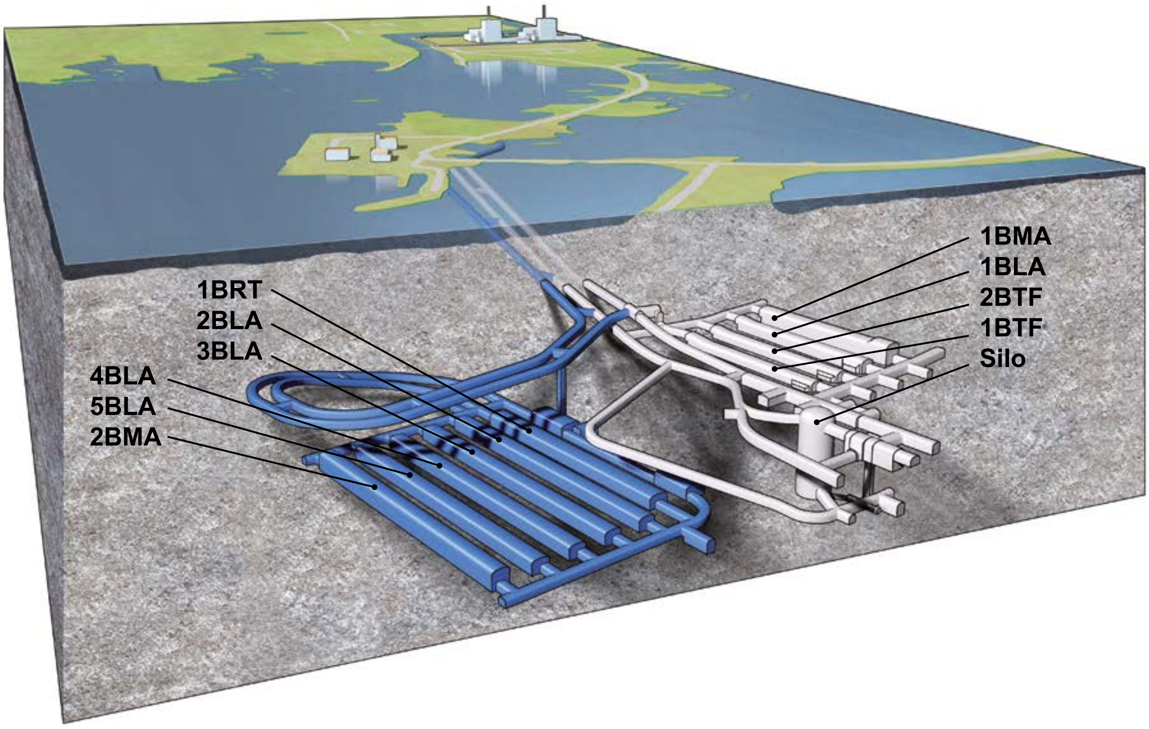

Figure 1-1. *Schematic illustration of SFR. The grey part is the existing repository (SFR 1) and the blue part is the planned extension (SFR 3). The waste vaults in the figure are the silo for intermediate-level waste, 1–2BMA vaults for intermediate-level waste, 1–2BTF vaults for concrete tanks, 1–5BLA vaults for low-level waste and the BRT vault for reactor pressure vessels.*

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[1] The extension is called SFR 3 since the name SFR 2 was used in a previous plan to build vaults adjacent to SFR 1 for disposal of reactor core components and internal parts. The current plan is to dispose of this waste in a separate repository.

1.2 Report hierarchy in the SR-PSU safety assessment

The applied methodology for the long-term safety comprises ten steps and is described in Chapter 2 of the Main report of SR-PSU. Several of the steps carried out in the safety assessment are described in more detail in supporting documents, so called Main references that are of central importance for the conclusions and analyses in the Main report. The full titles of these reports together with the abbreviations by which they are identified in the following text together with short comments on the report contents are given in Table 1-1.

There are also a large number of additional references. The additional references include documents compiled within SR-PSU, but also documents compiled outside of the project, either by SKB or equivalent organisations as well as in the scientific literature. Additional publications and other documents are referenced in the usual manner.

A schematic illustration of the safety assessment documents is shown in Figure 1-2.

1.3 This report

The long term safety assessment for SFR (SR-PSU) is performed according to a developed methodology including ten steps (see Chapter 2 in the Main report (SKB 2014k)). This report focuses on assessment Step 4 – Description of internal processes.

The purpose of this process report is to document the scientific knowledge and handling of the processes in the waste form and the packaging that has been identified to be relevant for the long term safety in a previous assessment step, Step 1 – Handling of FEP's (features, events and processes).

The documentation of the processes is not exhaustive from a scientific point of view, since such a treatment is neither necessary for the purposes of the safety assessment nor possible within the broad scope of the assessment. However, it must be sufficiently detailed to justify the handling of each process in the safety assessment and the associated uncertainties. The handling approaches established in this report will be used in subsequent steps in the applied assessment methodology, namely the analysis of the reference evolution, Step 7, and in the analyses of scenarios, Step 9.

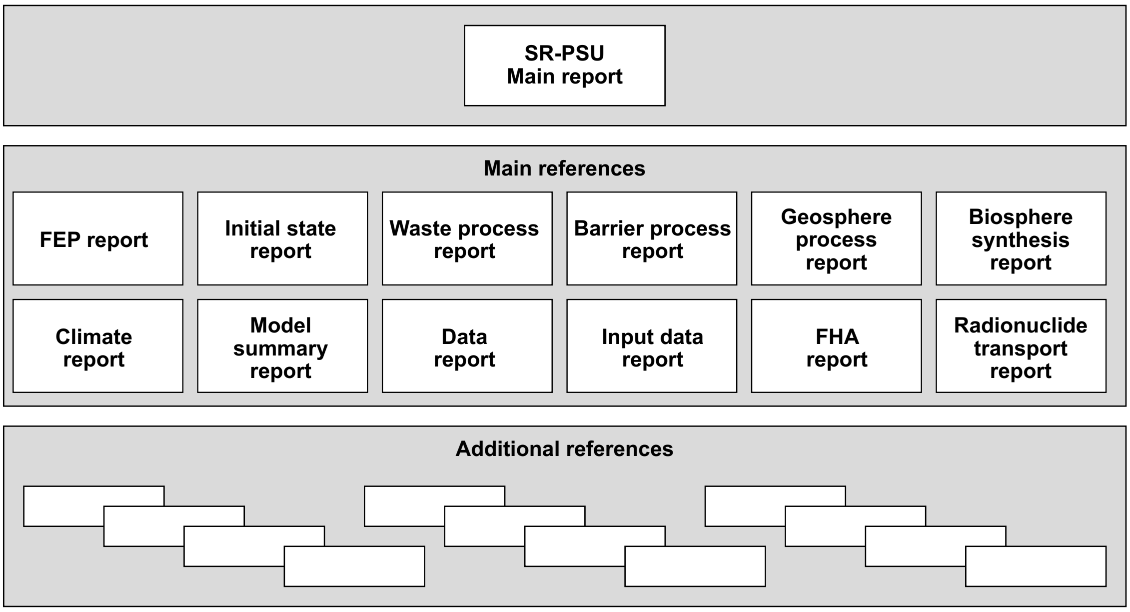

Figure 1-2. The hierarchy of the Main report, Main references and additional references in the SR-PSU long-term safety assessment. The additional references either support the Main report or any of the Main references.

Table 1-1. Main report and Main references in the SR-PSU long term safety assessment. All reports are available at www.skb.se

Abbreviation used when referenced in this report	Text in reference list	Comment on content
Main report	**Main report, 2014**. Safety analysis for SFR. Long-term safety. Main report for the safety assessment SR-PSU. SKB TR-14-01, Svensk Kärnbränslehantering AB.	This document is the main report of the SR-PSU long-term post-closure safety assessment for SFR. The report is part of SKB´s licence application to extend and continue to operate SFR.
Barriers process report	**Engineered barriers process report**, **2014**. Engineered barrier process report for the safety assessment SR-PSU. SKB TR-14-04, Svensk Kärnbränslehantering AB.	Describes the current scientific understanding of the processes in the engineered barriers that have been identified in the FEP processing as potentially relevant for the long-term safety of the repository. Reasons are given in the process report as to why each process is handled a particular way in the safety assessment.
Biosphere synthesis report	**Biosphere synthesis report**, **2014**. Biosphere synthesis report for the safety assessment SR-PSU. SKB TR-14-06, Svensk Kärnbränslehantering AB.	Describes the handling of the biosphere in the safety assessment. The report summarises site description and landscape evolution, FEP handling, exposure pathway analysis, the radionuclide model for the biosphere, included parameters, biosphere calculation cases and simulation results.
Climate report	**Climate report**, **2014**. Climate and climate-related issues for the safety assessment SR-PSU. SKB TR-13-05, Svensk Kärnbränslehantering AB.	Describes the current scientific understanding of climate and climate-related processes that have been identified in the FEP processing as potentially relevant for the long-term safety of the repository. The report also describes the climate cases that are analysed in the safety assessment.
Data report	**Data report, 2014.** Data report for the safety assessment SR-PSU. SKB TR-14-10, Svensk Kärnbränslehantering AB.	Qualifies data and describes how data, including uncertainties, that are used in the safety assessment are quality assured.
FEP report	**FEP report, 2014.** FEP report for the safety assessment SR-PSU. SKB TR-14-07, Svensk Kärnbränslehantering AB.	Describes the establishment of a catalogue of features, events and processes (FEPs) that are of potential importance in assessing the long-term functioning of the repository.
FHA report	**FHA report**, **2014**. Handling of future human actions in the safety assessment SR-PSU. SKB TR-14-08, Svensk Kärnbränslehantering AB.	Describes radiological consequences of future human actions (FHA) that are analysed separately from the main scenario, which is based on the reference evolution and less probable evolutions.
Geosphere process report	**Geosphere process report**, **2014**. Geosphere process report for the safety assessment SR-PSU. SKB TR-14-05, Svensk Kärnbränslehantering AB.	Describes the current scientific understanding of the processes in the geosphere that have been identified in the FEP processing as potentially relevant for the long-term safety of the repository. Reasons are given in the process report as to why each process is handled a particular way in the safety assessment.
Initial state report	**Initial state report**, **2014**. Initial state report for the safety assessment SR-PSU. SKB TR-14-02, Svensk Kärnbränslehantering AB.	Describes the conditions (state) prevailing in SFR after closure. The initial state is based on verified and documented properties of the repository and an assessment of the evolution during the period up to closure.
Input data report	**Input data report**, **2014**. Input data report for the safety assessment SR-PSU. SKB TR-14-12, Svensk Kärnbränslehantering AB.	Describes the activities performed within the SR-PSU safety assessment and the input data used to perform these activities.
Model summary report	**Model summary report**, **2014**. Model summary report for the safety assessment SR-PSU. SKB TR-14-11, Svensk Kärnbränslehantering AB.	Describes the calculation codes used in the assessment.
Radionuclide transport report	**Radionuclide transport report**, **2014**. Radionuclide transport and dose calculations for the safety assessment SR-PSU. SKB TR-14-09, Svensk Kärnbränslehantering AB.	Describes the radionuclide transport calculations carried out for the purpose of demonstrating fulfilment of the criterion regarding radiological risk.
Waste process report	**Waste process report, 2014.** Waste form and packaging process report for the safety assessment SR-PSU. SKB TR-14-03, Svensk Kärnbränslehantering AB.	Describes the current scientific understanding of the processes in the waste and its packaging that have been identified in the FEP processing as potentially relevant for the long-term safety of the repository. Reasons are given in the process report as to why each process is handled in a particular way in the safety assessment.

The following nomenclature from the IAEA safety glossary (IAEA 2007) is used in the report:

Package, waste: The product of conditioning that includes the waste form and any container(s) and internal barriers (e.g. absorbing materials and liner), as prepared in accordance with requirements for handling, transport, storage and/or disposal.

Waste form: Waste in its physical and chemical form after treatment and/or conditioning (resulting in a solid product) prior to packaging. The waste form is a component of the waste package.

Packaging: The assembly of components necessary to enclose the radioactive contents completely. It may, in particular, consist of one or more receptacles, absorbent materials, spacing structures, radiation shielding and service equipment for filling, emptying, venting and pressure relief; devices for cooling, absorbing mechanical shocks, handling and tie-down, thermal insulation; and service devices integral to the package. The packaging may be a box, drum, or similar receptacle, or may also be a freight container, tank, or intermediate bulk container.

1.4 Identification and description of processes

1.4.1 Identification of processes

This is the first time SKB has compiled a process report for the waste packages in SFR. However, many of the FEPs evaluated in this report have been evaluated in the SAR-08 safety assessment (SKB 2008b), which was based on the FEPs identified in the SAFE safety assessment report (SKB 2001b). This is further explained in the FEP report (SKB 2014d).

For the SR-PSU safety assessment the FEP lists and databases have been revisited. This is further described in the FEP report that also includes the databeses (SKB 2014d). A complete list of processes described in the SR-PSU process reports can be found in the above mentioned FEP report (SKB 2014d).

The original FEP analysis for SFR was carried out within the SAFE project and addressed the first 10,000 years post closure. The emphasis was on identifying the FEPs and interactions between processes that will affect the future evolution of the repository. The work was carried out with the aid of an interaction matrix, a method based on systematic and documented expert judgements, with a focus on identifying interactions between different processes. The contents of the matrix were cross-checked against the NEA FEP database version 1.0 (NEA 1997). This was later used as the basis for the FEP analysis in the SAR-08 safety assessment. In this assessment, the FEPs were revisited and checked for their validity and the possible need of updates due to new information and/or changed conditions.

For SR-PSU, a renewed FEP processing has been performed using all project FEPs in the international NEA FEP database (version 2.1). In addition, since many projects included in the NEA FEP database concern high level waste, FEPs from two additional projects for L/ILW waste have been evaluated. These were Olkiluoto L/ILW Hall in Finland and Rokkasho 3 in Japan (both in preliminary unpublished versions). This has resulted in lists of FEPs that are mapped (related) to system processes. These FEP lists have been checked in order to ensure that all relevant aspects of a process are addressed in the process descriptions and handled appropriately in the SR-PSU assessment. The handling of each FEP has been documented in tables created for this purpose. The tables are provided in the SR-PSU FEP report (SKB 2014d) and the handling is also documented in the SKB FEP database.

In general, these checks showed that all relevant NEA project FEPs were already covered by the process descriptions and included in existing plans for handling the relevant processes in the SR-PSU assessment.

1.4.2 Structure for process descriptions

All processes, see Table 1-2, are described for the waste form (Section 3) and steel and concrete packaging (Section 4), separately. All process descriptions use a document template, with the following structure:

Overview/general description

The background knowledge relevant to the process is the following:

Dependencies between process and system component variables

For each process considered, a table is used to identify how the process is influenced by the specified set of physical variables and how the process influences the variables. The handling of each influence in SR-PSU is also indicated in the table, and a more extensive description of the influences and handling are given in the text.

The physical variables that define the state of the system are given in Section 2.1.2 and Section 2.2.2.

Boundary conditions

The boundary conditions for each process are discussed with reference to the waste form or packaging. The processes for which boundary conditions need to be described are, in general, related to transport of material or energy across the boundaries. For example, for chemical processes occurring within the waste form, the boundary conditions are the relevant transport processes occurring in the waste form, i.e. advection and diffusion.

Model studies/experimental studies

Model and experimental studies of the process are summarised. This documentation constitutes the major source of information for many of the processes.

Natural analogues/observations from nature

If relevant, natural analogues and/or observations from nature that contribute to the present understanding of the process are documented.

Time perspective

The timescale or timescales on which the process occurs are documented, if such timescales can be defined.

Handling in the safety assessment SR-PSU

The handling of the process in the safety assessment SR-PSU is described. Typically, the process is:

- Defined as irrelevant on the basis of the information given.
- Defined as irrelevant provided that a certain condition is fulfilled.
- Included in the modelling.

The following aspects are also addressed, although no prescribed format is given:

- Time periods over which the process is relevant.
- Handling of boundary conditions, especially spatially and/or temporally variable chemical or hydraulic conditions.
- Handling of the interactions between the process and the specified waste form variables, and coupling to other processes within the system.

The information compiled has also been used to map all processes to their handling, see Chapter 5.

Table 1-2. Processes and experts responsible for the process documentation.

Process		Expert author, affiliation
3.	**Waste form processes**	
3.1	**Radiation related processes**	
3.1.1	Radioactive decay	Maria Lindgren, Kemakta Konsult AB
3.1.2	Radiation attenuation/heat generation	Maria Lindgren, Kemakta Konsult AB
3.1.3	Radiolytic decomposition of organic material	Lars Olof Höglund, Kemakta Konsult AB
3.1.4	Water radiolysis	Marie Wiborgh, Kemakta Konsult AB
3.2	**Thermal processes**	
3.2.1	Heat transport	Martin Birgersson, Clay Technology
3.2.2	Phase changes/freezing	Martin Birgersson, Clay Technology
3.3	**Hydraulic processes**	
3.3.1	Water uptake and transport during unsaturated conditions	Lars Olof Höglund, Kemakta Konsult AB
3.3.2	Water transport under saturated conditions	Lars Olof Höglund, Kemakta Konsult AB
3.4	**Mechanical processes**	
3.4.1	Fracturing	Peter Cronstrand, Vattenfall PC
3.5	**Chemical processes**	
3.5.1	Advective transport of dissolved species	Magnus Sidborn, Kemakta Konsult AB
3.5.2	Diffusive transport of dissolved species	Magnus Sidborn Kemakta Konsult AB
3.5.3	Sorption/uptake	Michael Ochs, BMG
3.5.4	Colloid formation and transport	Jordi Bruno, Amphos21
3.5.5	Dissolution, precipitation and recrystallisation	Lars Olof Höglund, Kemakta Konsult AB
3.5.6	Degradation of organic materials	Mireia Grivé, Amphos21, Klas Källström, SKB
3.5.7	Water uptake/swelling	Mark Elert, Kemakta Konsult AB
3.5.8	Microbial processes	Birgitta Kalinowski, SKB, Karsten Pedersen, University of Göteborg
3.5.9	Metal corrosion	Lara Duro, Amphos21
3.5.10	Gas formation and transport	Lara Duro, Amphos21
3.6	**Radionuclide transport**	
3.6.1	Speciation of radionuclides	Klas Källström, SKB, Michael Ochs, BMG
3.6.2	Transport of radionuclides in the water phase	Per-Gustav Åstrand, Facilia AB
3.6.3	Transport of radionuclides in the gas phase	Lara Duro, Amphos21
4.	**Steel and concrete packaging**	
4.1	Thermal processes	
4.1.1	Heat transport	Martin Birgersson, Clay Technology
4.1.2	Phase changes/freezing	Martin Birgersson, Clay Technology
4.2	**Hydraulic processes**	
4.2.1	Water uptake and transport during unsaturated conditions	Lars Olof Höglund, Kemakta Konsult AB
4.2.2	Water transport under saturated conditions	Lars Olof Höglund, Kemakta Konsult AB
4.3	**Mechanical processes**	
4.3.1	Fracturing/deformation	Peter Cronstrand, Vattenfall PC
4.4	**Chemical processes**	
4.4.1	Advective transport of dissolved species	Magnus Sidborn, Kemakta Konsult AB
4.4.2	Diffusive transport of dissolved species	Magnus Sidborn, Kemakta Konsult AB
4.4.3	Sorption/uptake	Michael Ochs, BMG
4.4.4	Colloid transport and filtering	Jordi Bruno, Amphos21
4.4.5	Dissolution, precipitation and recrystallisation	Lars Olof Höglund, Kemakta Konsult AB
4.4.6	Microbal processes	Birgitta Kalinowski, SKB, Karsten Pedersen, University of Göteborg
4.4.7	Metal corrosion	Lara Duro, Amphos21
4.4.8	Gas formation and transport	Lara Duro, Amphos21
4.5	**Radionuclide transport**	
4.5.1	Speciation of radionuclides	Klas Källström, SKB, Michael Ochs, BMG
4.5.2	Transport of radionuclides in the water phase	Per-Gustav Åstrand, Facilia AB
4.5.3	Transport of radionuclides in the gas phase	Lara Duro, Amphos21

Handling of uncertainties in SR-PSU

The handling of the uncertainties associated with the understanding and handling of the process are summarised.

Uncertainties in mechanistic understanding: The uncertainty in the general understanding of the process is discussed based on the available documentation and with the aim of addressing whether the basic scientific mechanisms governing the process are understood to the level necessary for the suggested handling.

Model simplification uncertainties: In most cases, the quantitative representation of a process will contain simplifications. These may be a significant source of uncertainty in the description of the system evolution. These uncertainties are discussed and approaches to addressing them are identified including alternative models or alternative approaches to simplification of a particular conceptual model.

Input data and data uncertainties: The set of input data necessary to quantify the process for the suggested handling is documented. The further treatment of important input data and input data uncertainties is described in a separate report, the Data report (SKB 2014c), to which reference is made if relevant.

Adequacy of references supporting the handling in SR-PSU

Under this heading, statements are provided concerning the adequacy of the references in a quality assurance perspective. These statements are restricted to the references supporting the selected handling and are, together with the arguments and justifications for the selected handling provided in the preceding subsections, evaluated in the factual review of the process report.

References

A list of references used in the process documentation is given at the end of the report.

1.4.3 Participating experts

The experts involved in assembling the basic information for each process are documented in Table 1-1. A SR-PSU list of experts is required by the SR-PSU QA plan, see further the SR-PSU Main report (SKB 2014k). The sub-sections “Handling in the safety assessment SR-PSU” and “Uncertainties” have been produced by SKB, in collaboration with the relevant expert(s).

2 Definition of system components

2.1 Waste form

For the purpose of the process descriptions, the waste form is defined as stabilised and non stabilised waste and the void inside the packaging. The outer boundary of the waste form is defined as the inter-face between the waste form and the packaging. The waste form system can be divided into two different categories:

- Non stabilised wastes, e.g. wastes deposited in the BTF ILW (Intermediate Level Waste) rock caverns and wastes deposited in the BLA LLW (Low Level Waste) rock caverns as well as in the BRT (reactor pressure vessel rock cavern).
- Stabilised wastes, e.g. wastes deposited in the BMA (ILW) rock caverns and in the silo (ILW).

There are many different waste package types in SFR, but the packaging and the waste matrices, i.e. treatment methods, are quite similar. The different treatment methods are:

- Cement solidification. Ion-exchange resins or sludge are mixed with concrete in drums or moulds.
- Cement stabilisation. Trash and scrap metal are placed in moulds and concrete is poured over them.
- Bitumen stabilisation. Ion-exchange resins are dried and mixed with bitumen and then poured into moulds or drums.
- De-watering. Wet ion-exchange resin is pumped into a concrete tank and water is removed by vacuum suction.

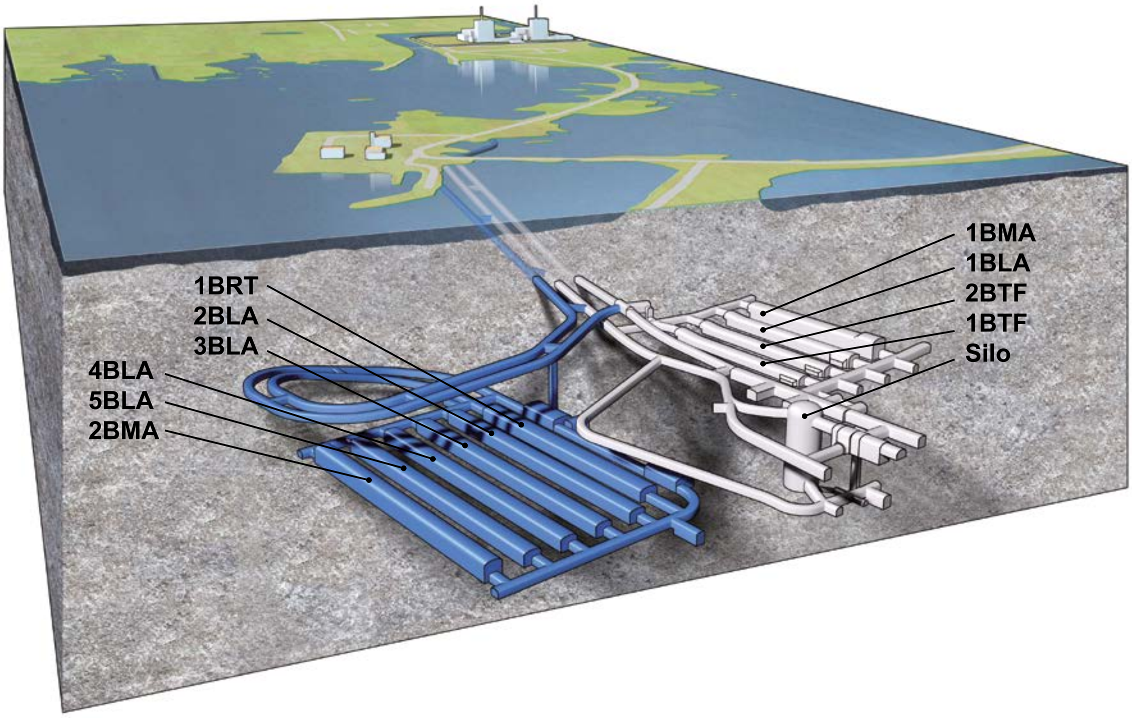

Figure 2-1. *Schematic picture showing the SFR repository. Caverns in withe colour belongs to the existing facility where as caverns in blue are part of the extension.*

2.1.1 Initial state of the waste form

The initial state of the waste form is defined at the time the repository closes. This is because operational waste will have been deposited in SFR for a long time before the repository is finally closed. Additionally, some of the waste deposited in the repository has been stored in its final packaging for long periods at the original site, e.g. at a nuclear power plant. The initial state of the waste form is further described in the Initial state report (SKB 2014g).

2.1.2 Definition of waste form variables

The waste form is described by the variables in Table 2-1. The description applies to the waste and its matrices, including porosities and fractures in the waste form.

Table 2-1. Variables for the waste form and their definition.

Variable	Definition
Geometry	Volume and dimensions of the waste form and voids inside the packaging.
	Porosity and pore characteristics of the waste form.
	Amount and characteristics of fractures in the waste form.
Radiation intensity	Intensity of alpha, beta and gamma radiation.
Temperature	Temperature
Hydrological variables	Magnitude, direction and distribution of water flow.
	Degree of water saturation.
	Water pressure.
	Aggregation state (water and/or ice).
Mechanical stresses	Stress and strain in waste form.
Radionuclide inventory	Inventory of radionuclides as a function of time within the waste package.
	Type, amount, chemical and physical form.
Material composition	Amount and surface characteristics of the materials inside the waste package (excluding radionuclides).
	Type and amount of chemicals (including decontamination chemicals).
	Type and amount of organic materials and other substances that can be used by microbes as nutrients and energy sources.
	Types and amount of microbes and bacteria and other types of biomass.
Water composition	Composition of water including radionuclides.
	Redox, pH, ionic strength, concentration of dissolved species, type and amount of colloids and/or particles, amount and composition of dissolved gas.
	Types and amount of microbes and bacteria and other types of biomass.
	Density and viscosity.
Gas variables	Amount and composition including radionuclides.
	Volume, pressure and degree of saturation.
	Magnitude, direction and distribution of gas flow.

2.2 Steel and concrete packaging

The system component steel and concrete packaging constitutes all packaging materials used in SFR. There are basically six different kinds of packaging:

- Steel drums. Standard 200-litre drums. The dimensions differ slightly but the drums are approximately 90 cm high and have a diameter of 60 cm. In the BMA caverns and the silo, the drums are handled four by four on a steel plate or in a steel box. Both types are custom made for the system. In the BTF the drums are handled one by one.
- Concrete moulds. A concrete cube with the side 1.2 m. The walls usually have a thickness of 10 cm, but can also be 25 cm. The moulds are deposited in the BMA rock caverns and in the silo. Some moulds that contain low activity wastes are used to build stabilisation walls in 1BTF.
- Steel moulds. Steel cubes with the same outer dimensions as the concrete moulds, but with 5 or 6 mm thick walls. The steel moulds can hold approximately 70% more waste than the concrete moulds but offer considerably less radiation shielding. The steel moulds are used in the BMA's and the silo.
- Concrete tanks. The tanks have the length of 3.3 m, width of 1.3 m and height of 2.3 m. The walls are 15 cm thick. The concrete tanks have a drain in the bottom of the tank. Concrete tanks are used in 1BTF and 2BTF.
- ISO-containers. Standard containers, usually with the dimensions 6.1 × 2.5 × 1.3 m or 6.1 × 2.5 × 2.6 m, but other dimensions can also be used. The containers can hold drums, boxes or bales. There can also be no inner package, just piled scrap metal. The containers are used in the BLA rock caverns.
- Steel boxes. These boxes are primarily used inside the ISO-containers.
- Odd' Waste. Large components such as heat exchangers, large pieces from the biological shielding etc could be disposed in SFR.

Radiation related processes are judged to have no influence in the packaging, except for radioactive decay – see corresponding chapter for the waste form 3.1. Therefore these processes are omitted in Chapter 4.

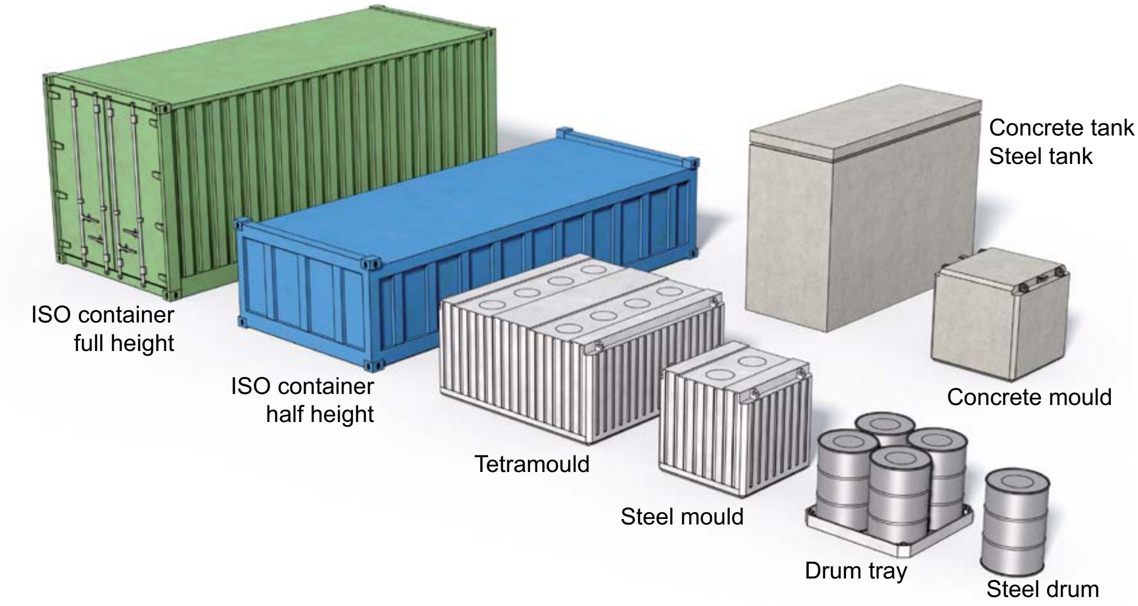

Figure 2-2. The different waste packages used in SFR.

2.2.1 Initial state of the packaging

The initial state of the steel and concrete packaging is defined at the time the repository is closed. Over the operational period of the repository, both aerobic and anaerobic corrosion of steel packaging may have taken place. Alteration of cement minerals may have taken place due to uptake of CO_2 from the atmosphere and intruding saline water. The initial state of the steel and concrete packaging is further described in the Initial state report (SKB 2014g).

2.2.2 Definition of the steel and concrete packaging variables

All variables for the steel and concrete packaging is defined in Table 2-2.

Table 2-2. Variables for steel and concrete packaging and their definition.

Variable	Definition
Geometry	Volume and dimensions of the packaging.
	Porosity and pore characteristics of the packaging.
	Amount and characteristics of fractures in the packaging.
Temperature	Temperature
Hydrological variables	Magnitude, direction and distribution of water flow.
	Degree of saturation.
	Water pressure.
	Aggregation state (water and/or ice).
Mechanical stresses	Stress and strain in packaging.
Material composition	Amount, composition and surface characteristics of the materials in the packaging.
	Type and amount of chemicals.
	Extent of cement hydration in concrete.
	Type and amount of organic materials and other substances that can be used by microbes as nutrients and energy sources.
	Types and amount of microbes and bacteria and other types of biomass.
Water composition	Composition of water including radionuclides.
	Redox, pH, ionic strength, concentration of dissolved species, type and amount of colloids and/or particles, amount and composition of dissolved gas.
	Types and amount of microbes and bacteria and other types of biomass.
	Density and viscosity.
Gas variables	Amount and composition including radionuclides.
	Volume, pressure and degree of saturation.
	Magnitude, direction and distribution of gas flow.

3 Waste form processes

3.1 Radiation related processes

3.1.1 Radioactive decay

Overview/general description

Radioactive decay releases ionising radiation (α-, β-, γ- and neutrons) and changes the radionuclide inventory of radioactive waste over time. During the radioactive decay of a parent radionuclide, a daughter product is created. When a daughter product is radioactive, further decay takes place until the final, stable daughter in the decay chain is reached.

This process is of fundamental importance, since it describes how the radiotoxicity of the waste evolves over time. The chemical properties of the daughter products may differ from those of the parent nuclides, which may affect their release mechanisms and migration properties. The energy liberated during decay is converted for the most part into heat (Section 3.1.2), however the effect of radioactive decay on the temperature in the repository is negligible (Section 3.1.2).

Dependencies between process and waste form variables

Table 3-1 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Table 3-1. Direct dependencies between the process "Radioactive decay" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No.	Not relevant.	No.	Not relevant.
Radiation intensity	No.	Not relevant.	Yes. The radiation intensity is a product of radioactive decay.	The radiation intensity is calculated from the radioactive decay of the inventory of radionuclides.
Temperature	No.	Not relevant.	Yes. Most of the decay energy is transformed into heat.	Radioactive decay has a negligible influence on the temperature , see Section 3.1.2 "Radiation attenuation/heat generation".
Hydrological variables	No.	Not relevant.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes. The radionuclide inventory defines radioactive decay.	The radionuclide inventory is used to quantify radioactive decay.	Yes. Radioactive decay both consumes and produces radionuclides.	The radionuclide inventory is calculated as a function of time.
Material composition	No.	Not relevant.	No.	Not relevant.
Water composition	No.	Not relevant.	Yes. Radioactive decay will affect the concentration of solution-phase radionuclides. Radioactive decay ultimately produces stable isotopes.	The concentration of radionuclides in water within the waste form is accounted for in the radionuclide transport modelling. The stable isotopes have a negligible influence on the water compostion.
Gas variables	No.	Not relevant.	Yes. Radionuclides, e.g. H-3 and C-14, might be present in the gas phase. Indirect effects also occur via radiolytic gas production, see Section 3.1.2 and Section 3.1.4.	Negligible compared to other processes influencing the gas composition.

Boundary conditions

There are no boundary conditions of relevance for this process. The initial condition is the radionuclide inventory in the waste form at the time of deposition of the waste in the repository.

Model studies/experimental studies

Many thorough experiments investigating radioactive decay have been carried out. The theoretical understanding of the process is therefore good and fully sufficient for the needs of the safety assessment.

Natural analogues/observations from nature

Radioactive substances occur naturally. During the first few decades of the 20th century, the study of these radioactive substances developed our understanding of radioactivity.

Time perspective

The time taken for half of the atoms of a certain radionuclide to decay is called the half-life. The half-lives of various radionuclides vary from fractions of a second to millions of years. The process of radioactive decay is therefore of importance during all phases of the repository.

Handling in the safety assessment SR-PSU

The process is included in model calculations of radionuclide transport. The process is also included in the calculations of the amounts of radiolytic gases likely to be present see Section 3.5.10.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The mechanistic understanding of the process is sufficient for the needs of the safety assessment.

Model simplification uncertainties

The radioactive decay can be calculated as a function of time with great accuracy when the nuclide content is known.

Input data and data uncertainties

The half-lives of the relevant radionuclides are generally known accurately. The most important exception to this is Se-79. In recent years, the half-life reported for Se-79 has ranged from 1.1×10^6 years (Jiang et al. 1997) to 1.24×10^5 years (He et al. 2000). The most recently published data are 2.80×10^5 years (He et al. 2002), 3.77×10^5 (Bienvenue et al. 2007) and 3.27×10^5 (Jörg et al. 2010).

Uncertainties associated with the inventory at deposition and radionuclide half-lives are discussed further in the Data report (SKB 2014c).

Adequacy of references supporting the handling in SR-PSU

All data used are published in peer-reviewed journals or result from careful reviews of published data.

3.1.2 Radiation attenuation/heat generation

Overview/general description

Radiation from radioactive decay will interact with the waste form and other materials within the repository. Energy is thereby transferred to the materials and the radiation is attenuated. Most of the energy transferred is converted into thermal energy, i.e. heat is generated. The thermal energy, or heat, that is generated is called residual or decay heat and is dependent on the radionuclide content of the waste. However, the radionuclide content of SFR wastes is low therefore the anticipated heat arising from decay and attenuation is also low. Additionally, the shielding effect of the waste and packaging means that radiation intensity outside the package is negligible.

In the safety assessment SAFE, heat generation due to corrosion of aluminium and radiolysis of water was calculated (Moreno et al. 2001). This showed that corrosion of aluminium generates more heat than radiolysis of water in BMA, 1BTF, 2BTF and BLA, while radiolysis of water dominates the heat generation in the silo. The highest heat generation calculated was in BLA, where a temperature increase of less than five degrees Celsius was predicted. Heat generation in the waste is hence judged to be of negligible importance and does not need to be evaluated further in the safety assessment.

Dependencies between process and waste form variables

Table 3-2 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Table 3-2. Direct dependencies between the process "Radiation attenuation/heat generation" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. The dimensions of attenuating materials determines the degree of attenuation.	Neglected. The heat generation from radiation attenuation is negligible in SFR.	No.	Not relevant.
Radiation intensity	Yes. Radiation intensity is the source of heat generated by radiation attenuation.	Neglected. The heat generation from radiation attenuation is negligible in SFR.	Yes. Attenuation lowers the radiation intensity.	Neglected, due to the low radiation intensity in general
Temperature	No.	Not relevant.	Yes. Most of the decay energy is transformed into heat, and thus increases the temperature of the attenuating material.	Neglected. The heat generation from radiation attenuation is negligible in SFR. Heat exchanges with the groundwater and the surrounding bedrock, lowering the effect on temperature further (SKB 2008b).
Hydrological variables	Yes. Water will influence radiation attenuation as it is an important attenuator.	Neglected. The heat generation from radiation attenuation is negligible in SFR.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes. The radionuclide inventory is the source of radiation, and thus influences the heat generated by radiation attenuation.	Neglected. The heat generation from radiation attenuation is negligible in SFR.	No.	Not relevant.
Material composition	Yes. Different materials have different attenuation properties.	Neglected. The heat generation from radiation attenuation is negligible in SFR.	No.	Not relevant.
Water composition	No.	Not relevant.	No.	Not relevant.
Gas variables	No.	Not relevant.	No.	Not relevant.

Boundary conditions

There are no relevant boundary conditions for this process other than the physical boundaries set by the geometries and materials of the components involved.

Model studies/experimental studies

The heat output is directly dependent on the radioactive decay process, as discussed in Section 3.1.1.

Natural analogues/observations from nature

Not applicable.

Time perspective

The process decreases in significance with time since the radionuclide inventory is dominated by short-lived radionuclides. Cobalt-60, with a half-life of 5.3 years, is the major contributor to the total decay energy (Pettersson and Elert 2001).

Handling in the safety assessment SR-PSU

Heat generation in the waste is negligible (Moreno et al. 2001) and thus will not be treated any further in the safety assessment.

Handling of uncertainties in SR-PSU

The processes behind radiation attenuation and heat generation are well understood and the methods to estimate the effects are well established. The main uncertainty is associated with the radionuclide inventory, although it is known to be sufficiently low for heat generation to be negligible.

Adequacy of references supporting the handling in SR-PSU

The supporting reference for neglecting this process (Moreno et al. 2001) is not peer- or factual reviewed, but is based on fundamental physics.

3.1.3 Radiolytic decomposition of organic material

Overview/general description

Nuclear waste is self-irradiated by the ionising radiation emitted from the radionuclide inventory. Irradiation may excite or ionise organic components of the waste either directly, as discussed below, or indirectly, via formation of free radicals from the radiolysis of water molecules (see Section 3.1.4). The primary products of water radiolysis are free electrons, OH-radicals, the hydroperoxyl radical OOH and hydrogen atoms. Free radicals contain an unpaired electron, which makes them highly reactive and able to participate in chain reactions. Therefore the reactions of the OH-radicals with solution components can generate a large variety of organic radicals, as well as stable molecular species such as [2] $ROOR_1$, O_2, H_2O_2, and H_2.

Radiolytic decomposition occurs as a function of radiation intensity (decay energy and frequency of decay), thus the time frame is dependent on the half-lives of the radionuclides present. Therefore, in the shorter term, radiolytic decomposition is dominated by the decay of Co-60 followed by Cs-137 in all repository parts. In the longer term (> 1,000 years), the dominant radionuclides will vary between the repository parts, as follows: the silo, Am-241 and Co-60; BMA and 2BTF, Co-60 and Cs-137; 1BTF, organic and inorganic C-14, and Cs-137; and BLA, Cs-137 and Pu-240 (Moreno et al. 2001).

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[2] The symbol R- is used to denote an arbitrary alkyl group, R-H is an arbitrary alkane.

The yield of a radiolytic decomposition product can be estimated using the G-value, which gives the relationship between the absorbed radiation energy and the amount of product formed. The G-value is commonly expressed in units of number of molecules produced per 100 eV of energy absorbed from ionising radiation. G-values are specific for different products, materials, environmental conditions and type of radiation (alpha, beta and gamma) and should ideally be determined from representative measurements. For mixed wastes, however, such data are rarely available.

Experimental investigations have shown that the hydrogen yield from the irradiation of synthetic wastes can be related to the number of C–H and N–H bonds (η_{x-H}) present per molecule of the organic material (Meisel et al. 1993, Bryan et al. 2000):

$$G(H_2) = 0.031 + 0.013 \cdot \eta_{x-H} \cdot [R\text{–}H]$$

where [R–H] is the molar concentration of the organic component R–H.

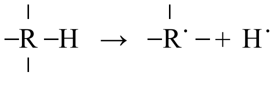
Investigations of the radiolytic generation of hydrogen from Hanford wastes have identified a relationship with the total organic carbon content, TOC (Pederson and Bryan 1996, Bryan et al. 2000):

$$G(H_2) = 0.031 + 0.15 \cdot \mathrm{TOC}\ (\text{wt-\%})$$

The dominant organic materials in SFR include ion exchange resins, bitumen, cellulose, plastics, and the rubber lining of concrete tanks. The radiolytic decomposition of ion exchange resins has been studied in particular, due to the release of functional groups and production of hydrogen gas. Some of the most common types of ion exchange resins used at the Swedish nuclear reactor sites are cation exchangers with sulphonic acid functional groups and anion exchangers with tertiary amine functional groups. During irradiation of sulphonic acid type ion exchange resins, sulphate ions are formed (which may impact the integrity of concrete structures in the repository, see the Barrier process report (SKB 2014a, Section 4.4.5). Irradiation of anion exchange resins with tertiary amine functional groups will produce a mixture of trimethyl amine, dimethyl amine, methyl amine, ammonia and nitrogen. Radiolytic degradation of e.g. cellulose may make the material more accessible to chemical degradation by splitting the carbon chain (SKB 2001b). The radiolytic degradation of cellulose has been reviewed by Humphreys et al. (2010), and they discussed evidence showing that radiolytic processes enhance alkaline cellulose degradation through the generation of end groups amenable to peeling reactions. However, data on the chemical stability of ISA suggest that potentially oxidising conditions created by radiolysis may enhance degradation of ISA.

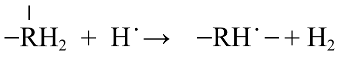
The radiolytic decomposition of bitumen has been studied extensively since it is used to condition waste (e.g. Eschrich 1980, Pettersson and Elert 2001, Sercombe et al. 2004, Valcke et al. 2009). In the absence of oxygen, the primary product of radiolytic decomposition is hydrogen gas, caused by cleavage of the carbon–hydrogen bonds (CEA 2009). The hydrogen gas may cause swelling of the bitumen matrix (CEA 2009). CEA (2009) estimated a hydrogen yield of 1×10^{-3}–1×10^{-2} m^3/year/drum. Investigation of radioactive bitumen stored for 25 years in atmospheric, oxidising conditions showed significant aging to a depth of about 5 cm from the surface. The aged material was hard, very brittle and full of small fissures (Valcke et al. 2009). The conditions may be relevant for the storage of bituminised waste during the operational phase, but not for the post-closure phase.

The radiolytic decomposition of organic materials with a high molecular weight and/or polymeric structure (bitumen, plastics and rubber) may proceed according to the following reaction:



$$-\overset{|}{\underset{|}{R}}-H \rightarrow -\overset{|}{R}^{\cdot}- + H^{\cdot}$$

Therefore two radicals are formed, one within the polymer structure and a hydrogen radical. The hydrogen radical formed is very reactive and the reaction may proceed as follows (Sercombe et al. 2004):



$$-\overset{|}{R}H_2 + H^{\cdot} \rightarrow -RH^{\cdot}- + H_2$$

In the absence of oxygen, the radical formed may react with the polymeric structure of the material resulting in cross-linking. This can be considered an ageing process and may result in a gradual embrittlement of the material (Sercombe et al. 2004).

When oxygen is present, the radical formed (denoted $R^\cdot$) may react as follows (Sercombe et al. 2004):

$R_1^\cdot + O_2 \rightarrow R_1OO^\cdot$

$R_1OO^\cdot + R_2H \rightarrow R_1OOH + R_2^\cdot$

The termination of the chain reactions may occur via different routes (Sercombe et al. 2004):

$R^\cdot + R^\cdot \rightarrow RR$

$ROO^\cdot + R^\cdot \rightarrow ROOR$

$ROO^\cdot + ROO^\cdot \rightarrow ROOR + O_2$

Free radicals can react with oxygen to form highly reactive peroxy radicals, which can cause oxidative chain scission in a polymer that might normally be expected to cross link (Humphreys et al. 2010).

The ageing effects in bitumen exposed to external gamma irradiation have been studied by Rorif et al. (2006). The results show that ionising radiation has a significantly larger impact on the chemical properties of bitumen when oxygen is present.

Aromatic structures in the organic material are fairly stable during irradiation, which is one reason why bitumen is relatively stable (Sercombe et al. 2004).

Dependencies between process and waste form variables

Table 3-3 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Influence by geometry. Yes, a direct influence has been identified. The waste form geometry affects the resultant gamma field inside the waste packages while the overall surface area of the waste is of importance for the beta and alpha fields.

Influence on geometry. No direct influence identified. The yield of hydrogen gas may influence the waste form geometry indirectly by causing swelling of bituminised waste.

Influence by radiation intensity. Yes, a direct influence has been identified. The radiolytic yield inside the waste package is proportional to the dose rate.

Influence on radiation intensity. No direct influence identified. The radiolytic decomposition of organic material cannot affect the radiation intensity since this is defined by the amount and type of radioisotopes.

Influence by temperature. The temperature affects the kinetics of radiolytic reactions and can be accounted for in radiolysis calculations. However, the temperature in the repository will be similar to that of the surrounding geosphere. Therefore, temperature is expected to have a negligible influence on the yield of radiolytic decomposition products from organic materials inside the waste package.

Influence on temperature. No direct influence has been identified.

Influence by hydrological variables. Yes, a direct influence has been identified. The presence of water is a requirement for radiolysis processes and will influence the sequence of reactions that the radicals formed by irradiation of the organic materials will undergo. Therefore, the presence of water will influence the radiolytic decomposition of organic materials.

Influence on hydrological variables. No direct influence has been identified. Indirectly, the production of radiolytic gases affects the pressure inside the waste package and the water flow conditions. The effect on the pressure in the repository is expected to be negligible in comparison to the production of gases by other mechanisms (Moreno et al. 2001).

Table 3-3. Direct dependencies between the process “Radiolytic decomposition of organic material” and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. The geometry affects the amount of energy absorbed in the waste.	Considered in the calculations.	No. Indirectly, the yield of hydrogen gas may cause swelling of bitumen.	Not relevant.
Radiation intensity	Yes. The yield is proportional to the radiation intensity.	Radiation is the source. Input data for the calculations.	No.	Not relevant.
Temperature	Yes. Affects the kinetics of the radical reactions.	Negligible due to insignificant heat generation in the waste.	No.	Not relevant.
Hydrological variables	Yes. The presence of water will influence the radicals formed by irradiation of the organic materials.	Water is assumed present in all calculations.	No. Indirectly, gases formed will influence water flow conditions.	Not relevant.
Mechanical stresses	No.	Not relevant.	No. Indirectly by affecting the swelling properties, see Section 3.5.7.	Not relevant.
Radionuclide inventory	Yes. Different radionuclides yield different radiation doses.	Input data in calculations.	No.	Not relevant.
Material composition	Yes. Different materials have different attenuation properties and stability to irradiation.	Yes. Considered in the calculations of adsorbed doses and radiolytic decomposition.	Yes. Irradiation may cause hardening/ageing of bitumen and affect swelling of ion exchange resins.	Yes. The effects of radiolytic decomposition on the material composition and properties are estimated.
Water composition	Yes. The composition of water, including dissolved gases, influences the yield and reaction of the radiolytic species produced, and thereby the radicals acting on the organic materials.	Included in radiolysis calculations.	Yes. Radiolytic decomposition of ion exchange resins may produce sulphate and amines that will change water composition. Hydrogen peroxide may form, but is likely to decompose rapidly. Radiolytic decomposition of cellulose may produce soluble substances that may affect radionuclide speciation.	Yes. Sulphate is included in the calculations of concrete degradation. The other influences are neglected.
Gas variables	No.	Not relevant.	Yes. Gas components, e.g. H_2 and O_2, are produced by radiolytic decomposition. The gases formed affect the pressure inside the waste package and will influence water flow conditions.	Yes. The amount of gases formed by radiolytic decomposition of organic material is judged to be negligible in comparison with other gas formation processes, see Section 3.5.10.

Influence by mechanical stresses. No direct influence has been identified. Mechanical stresses are not expected to have an impact on the radiolytic decomposition of organic material.

Influence on mechanical stresses. No direct influence has been identified. Indirectly, gases formed by radiolytic decomposition and changes of water uptake properties of e.g. ion exchange resins, may influence the swelling pressure exerted by some waste forms, see Section 3.5.7 for further detail.

Influence by radionuclide inventory. Yes, a direct influence has been identified. The degree of radiolytic decomposition depends on the energy released when a specific radionuclide decays (decay energy) and the inventory of each radionuclide.

Influence on radionuclide inventory. No direct influence has been identified. The degradation of organic materials cannot affect the radionuclide inventory.

Influence by material composition. Yes, a direct influence has been identified. Different materials have different attenuation properties and stabilities to irradiation.

Influence on material composition. Yes, a direct influence has been identified. Irradiation may cause hardening of bitumen matrices. The effect is negligible when the absorbed energy is less than 0.1 MGy (Eschrich 1980). Estimates of the mean radionuclide activities in newly embedded wastes deposited in SFR-1 indicate that the Co-60 content of some waste types corresponds to an absorbed energy exceeding 10^5 Gy (Pettersson and Elert 2001).

Radiolytic decomposition of ion exchange resins may result in the loss of functional groups that affect the swelling properties.

Various polyethylene waste forms containing simulated wastes such as sodium sulphates, borates, incinerator ash and ion exchange resins did not show any significant degradation in compressive strength after exposure to doses as high as 10^6 Gy (Mayberry et al. 1993).

Influence by water composition. Yes, a direct influence has been identified. The water composition influences the yields and reactions of the different radiolytic species produced by radiolysis. It will therefore influence the yield of radicals that interact with organic materials. The different radiolytic reactions in homogeneous solutions are described reliably by kinetic radiolytic modelling. The influence of water composition on the radiolytic decomposition of organic materials is complex but can be estimated using empirical data from experimental investigations.

Influence on water composition. Yes, a direct influence has been identified. Dissolved gases formed by radiolytic decomposition of organic material influence the water composition and may influence the radiolytic reactions.

Radiolytic decomposition of cation exchange resins may form sulphate that could indirectly affect the integrity of concrete via ettringite formation. Radiolytic decomposition of anion exchange resins may form different methyl amines that could act as complexing agents for radionuclides.

Radiolytic decomposition of cellulose may cause chain scission, which may enhance alkaline degradation and produce water soluble substances that could affect the speciation and the release of radionuclides. Oxidants formed by radiolysis may also have an impact on the stability of soluble cellulose degradation products, e.g. ISA.

Influence by gas variables. No direct influence has been identified.

Influence on gas variables. Yes, a direct influence has been identified. Gas components, e.g. H_2 and O_2, are produced. The amount of gas produced in the interior of the waste package is dependent on the type and amount of radionuclides in the waste. The formation of gas affects the pressure inside the waste package and will indirectly influence the flow conditions. The radiolytic decomposition of organic materials generates gases, but in smaller amounts than formed due to metal corrosion (cf. Moreno et al. 2001), see Section 3.5.10.

Boundary conditions

There are no relevant boundary conditions for this process other than the physical boundaries set by the geometries of the components involved.

Model studies/experimental studies

Radiolytic decomposition of water and different waste types have been addressed in a joint EC/NEA status report on gas migration and two-phase flow (Rodwell et al. 1999).

Radiolytic degradation of ion exchange resins and bitumen can release sulphate and oxalate (Van Loon and Hummel 1999a). However, in a previous SFR assessment from 1991, it was judged that degradation products from ion exchange resins and bitumen would only have a small effect on the sorption of tri- and tetravalent radionuclides, under the expected SFR 1 conditions. This view was supported by Savage et al. (2000), in their review of ion exchange resin and bitumen degradation experiments (SKB 2008b).

Pettersson and Elert (2001) have reviewed experiments involving irradiation of bituminised waste. Some of the main results relating to radiolytic decomposition are highlighted briefly in the following paragraphs.

The production of radiolytic gases depends upon the type of bitumen, the dose rate and the absorbed dose (IAEA 1993). Gases formed by radiolytic decomposition consist mainly of hydrogen, along with some carbon monoxide, carbon dioxide, nitrogen oxide and lighter hydrocarbons (IAEA 1993). Duschner et al. (1977) and Kopajtic et al. (1989) concluded that about 95% of the gas produced is hydrogen. Burnay (1987) also found that hydrogen was the dominant product at lower doses but, at doses above about 3 MGy, CO_2 production was comparable to that of H_2. Experiments investigating the effect of external γ-irradiation on a non-radioactive bitumen/salt mixture showed that hydrogen generation is proportional to the exposure dose (Duschner et al. 1977). However, Burnay (1987) showed results where the increase in hydrogen generation was less than proportional to the increase in dose. Distilled bitumen was found to generate slightly more gas than oxidised bitumen in one study (Kopajtic et al. 1989) and slightly less in another (Duschner et al. 1977). However, the difference between the amount of gas generated by the different types of bitumen was small in both studies. At high levels of irradiation, gas generation may lead to bubble formation and therefore swelling and fracturing of the bitumen matrix, see further Section 3.5.7.

Alpha-radiation can cause two to ten times more radiolysis than γ-radiation per unit absorbed energy (Burnay 1987). Measurements made on small scale cans of bituminised waste revealed that at the same dose rate (90 Gy/h), α-loaded samples showed significant swelling, whereas no swelling was observed in γ-loaded samples. However, the α-emitting radionuclide content of bituminised waste is generally low (< 0.2 TBq/m^3) and is therefore of limited importance in terms of swelling (IAEA 1993). Swelling is also dependent on the type of bitumen; while swelling was found to be important for distilled bitumen when gamma doses exceeded 2 MGy, gamma doses up to 200 MGy did not increase the volume of oxidised bitumen (IAEA 1993). Theoretical models have been developed to predict the swelling caused by radiolysis of bituminised waste (Burnay 1987, Phillips et al. 1984), see further Section 3.5.7.

Valcke et al. (1999) found that oxalate was the main degradation product formed during the irradiation of bituminised waste under aerobic conditions, with smaller amounts of formate and (bi) carbonate. This was supported by Kagawa et al. (1999), who also concluded that the total organic carbon (TOC) concentration increases with increasing absorbed dose. The products of α-induced radiolytic degradation of bitumen were not found to influence plutonium solubility under conditions representative of a cement backfilled repository (Greenfield et al. 1997a). Savage et al. (2000) concluded that the organic products of bitumen degradation are insignificant in comparison to those formed by the degradation of cellulose. Experimental results suggested that radiolysis-induced gas generation, swelling, hardening and heating were negligible for absorbed doses of less than 0.1 MGy, although the leach resistance decreased (Eschrich 1980). However, the effect of absorbed doses between 0.1 and 2 MGy suggested that gas generation must be considered when packaging bituminised products, by assuring that the gas can escape and allowing sufficient void volume for swelling. In this absorbed dose range, the changes in leachability and mechanical properties of the product were insignificant. With higher absorbed doses, 2–10 MGy, substantial swelling can take place and the leachability is likely to increase. Kagawa et al. (1999) compared the chemical and radiolytic degradation of pure bitumen and concluded that the dominant degradation pathway of bitumen is oxidation leading to the formation of leachable organic degradation products.

JAEA (2007) report, based on experimental studies by Greenfield et al. (1997a) and Van Loon and Kopajtic (1990), that higher radiation doses do not significantly affect bitumen degradation. Solubility tests on plutonium showed no effect due to the release of bitumen degradation products. Similar bitumen tests using gamma-emmitting showed no significant effect on the chemical form of radionuclides.

Valcke et al. (2009) studied the chemical changes in 25 year old bitumen under irradiation with and without oxygen present using the ATR-FTIR[3] technique. Oxidation of bitumen changes the abundance of C=O and C=C bonds. Comparative studies showed that oxidation was more rapid at a temperature of 130°C than when irradiated with gammarays at low to moderate dose rates in the range of 20–130 Gy/h. It was also found that the effect of radiolysis is highly dependent on the access to oxygen. Oxidation during irradiation occurred near the surface. With low dose rates (< 45 Gy/h), the irradiation dose was found to be limiting, whereas with higher dose rates (> 45 Gy/h), the availability of oxygen was found to be limiting.

Radiolytic degradation of bitumen at high pHs has been shown to produce primarily mono- and dicarboxylic acids and carbonates (Van Loon and Kopajtic 1991a). Of these, oxalate could be a potential complexing agent, but its concentration is deemed to be negligible in a concrete environment due to high calcium content, which would precipitate calcium oxalate (SKB 2008b).

Irradiation of cellulose has been shown to cause chain scission and a gradual decrease in the degree of polymerisation (DP). Compiled results of several experimental investigations revealed a linear relationship between log(DP) and log(Dose) in the range 10^6 to 10^8 rad (Aoki et al. 1977). Humphreys et al. (2010) reviewed the literature and concluded that further experimental investigations are needed, including studies of the impact of radiation doses relevant to the repository conditions. They also stressed that there is currently a lack of detailed information regarding the relationship between radiation and alkaline degradation of cellulose.

Natural analogues/observations from nature

Natural geological occurrences of bitumen (e.g. asphalt lakes) have been targeted as natural analogues of waste bitumen. Natural deposits of bitumen and similar materials result from complex, largely unknown long-term geological processes. The bitumens therefore show wide variation in composition. Bitumen used to solidify radioactive waste is produced industrially under controlled conditions and therefore has well characterised composition and properties. Thus, a direct comparison is difficult and this limits the value of natural analogue studies for bituminised waste. However, natural analogues have been used to obtain qualitative information on the stability of bitumen under a wide range of physical and chemical conditions (see also discussion in Section 3.5.7).

Time perspective

The process decreases in significance with time since the radionuclide inventory and any radiolytical processes are dominated by short-lived radionuclides. The activity in the waste 1,000 years after repository closure will be approximately 2% of the activity at closure. Radiolytic decomposition will generate small amounts of gas and organic compounds, mainly during the first twenty years following repository closure (SKB 2008b).

Handling in the safety assessment SR-PSU

Due to the low radiation levels, radiolysis is not expected to affect the bitumen matrix except in the waste packages receiving the highest absorbed doses, where some swelling of the matrix might occur (Pettersson and Elert 2001). The radiolytic decomposition of bitumen may produce oxalic acid (Valcke et al. 1999). However, under the conditions found in SFR, oxalic acid will form insoluble Ca-oxalate and thus will not affect radionuclide speciation or solubility significantly. No further handling in the safety assessment is performed.

Radiolytic decomposition of sulphonic acid type ion exchange resins may produce sulphate, which may react with concrete to form the sulphate-containing ettringite mineral. The degradation rate is slow (Van Loon and Hummel 1999a), therefore groundwater is the dominant source of sulphate (Savage et al. 2000). No further handling in the safety assessment is performed.

The amount of gas formed due to radiolytic degradation of organic material (bitumen) is estimated see Section 3.5.10.

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[3] Attenuated Total Reflectance Fourier Transform InfraRed Spectroscopy (ATR-FTIR)

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The mechanism by which radiolytic degradation of organic materials occurs is known. The uncertainty in the amount of gas formed due to the process is described in Section 3.5.10.

Clarification of the mechanisms of long term alkaline degradation of cellulose at temperatures and radiation fields relevant to radioactive waste disposal sites has been identified as an area for further research (Humphreys et al. 2010). An improved understanding of these processes will reduce uncertainties associated with the rates of ISA generation and ultimate ISA concentrations employed in PA calculations.

Model simplification uncertainties

The process is accounted for in the gas generation model see Section 3.5.10.

Input data and data uncertainties

The importance of radiolysis is dependent of the radionuclide inventory of the repository. For uncertainties in the radionuclide inventory, see SKB (2013a). The organic material in SFR is not characterised in detail, thus the number of C–H and N–H bonds (η_{x-H}) per molecule of the organic material is not known.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references are published material that has been reviewed by SKB, other competent organisations within the nuclear field and/or by refereed scientific journals.

3.1.4 Water radiolysis

Overview/general description

Water that enters the repository and the waste packages will be affected by the ionising radiation emitted by the waste. This causes the excitation or ionisation of water molecules followed by the breaking of their chemical bonds (*radiolysis*). This process primarily produces free electrons, OH-radicals and hydrogen atoms. Radicals are atoms or molecules resulting from the homolytic cleavage of a chemical bond, and therefore contain an unpaired electron in their valence shell. The unpaired electron makes them highly reactive and able to participate in chain reactions. Reactions with solution components results in the formation of a large variety of radicals, as well as the stable molecular species O_2, H_2O_2, and H_2. The influence of the radicals produced on the organic components of the waste are discussed in Section 3.1.3. Interactions of radiolytic products with inorganic materials, for example cementitious materials, occurs (Bouniol and Bjergbakke 2008) but these are judged to be of minor importance.

In the safety assessment SAFE (SKB 2001a), heat generation in SFR due to corrosion of aluminium and radiolysis of water was calculated, assuming that all radiation enery was absorbed by the waste form (Moreno et al. 2001). The results showed that corrosion of aluminium generates more heat than radiolysis of water in BMA, 1BTF, 2BTF and BLA, while radiolysis of water dominates heat generation in the silo. The highest heat generation calculated was in BLA, where a temperature increase of less than five degrees Celsius as predicted. Heat generation due to radiolysis of water is hence judged to be of negligible importance and does not need to be treated further in the safety assessment.

The amount of gas produced by water radiolysis has been calculated in Moreno et al. (2001). These calculations showed that the amount of gas produced, due to radiolysis of water, is negligible compared to gas produced due to corrosion. The amount of gas produced is a function of radiation dose, and the time during which gas is produced is dependent on the radionuclides' half-lives. In the shorter term, radiolytic gas production is dominated by the decay of Co-60 followed by Cs-137 in all repository parts. In the longer term (> 1,000 years), several radionuclides are of importance. The gas produced in the different repository parts are dominated by: Am-241 and Co-60 in the silo; Co-60 and Cs-137 in BMA and 2BTF; organic and inorganic C-14 and Cs-137 in 1BTF; and Cs-137 and Pu-240 in BLA (Moreno et al. 2001). The gas produced by water radiolysis is negligible as compared to the gas produced by metal corrosion throughout the lifetime of the repository and in all repository parts. Therefore, gas production resulting from the radiolysis of water does not need to be handled further in the safety assessment.

Dependencies between process and waste form variables

Table 3-4 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Table 3-4. Direct dependencies between the process "Water radiolysis" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. The waste form geometry affects the gamma field inside the waste packages, while the overall surface area of the waste affects the beta and alpha fields.	Neglected. Water radiolysis has been shown to be of negligible direct importance in SFR.	No.	Not relevant.
Radiation intensity	Yes. Radiolysis of water inside the waste package is proportional to the dose rate.	Neglected. Water radiolysis has been shown to be of negligible direct importance in SFR.	No.	Not relevant.
Temperature	Yes. Temperature affects the kinetics of the chain reactions initiated by radiolysis and can be accounted for in radiolysis calculations.	Neglected. The temperature variations are expected to be negligible within the waste packages and water radiolysis has been shown to be of negligible direct importance in SFR.	Yes.	Neglected. Shown to be negligible.
Hydrological variables	Yes. The presence of water is prerequisite for water radiolysis.	Neglected. Water radiolysis has been shown to be of negligible direct importance in SFR.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes. Radiolysis occurs as a function of the decay energy, thus the radionuclide inventory.	Different radionuclides produce different amount of gases included in gas generation calculations.	No.	Not relevant.
Material composition	No.	Not relevant.	No.	Not relevant.
Water composition	Yes. The water composition influences the yields and reactions of the different species produced by radiolysis. Dissolved gases have also been shown to affect the products of radiolysis-initiated reactions (see Experimental Studies).	Neglected. Water radiolysis has been shown to be of negligible direct importance in SFR.	Yes. The products of water radiolysis affect the water composition.	Neglected. The radionuclide activity within SFR is low. The effect of water radiolysis on water composition is therefore negligible.
Gas variables	Yes. Gas phase radionuclides contribute to the radiation field.	Neglected. Gas phase radionuclides has a negligible proportion of the total decay energy.	Yes. H_2 and O_2 gases are produced. As a result of water radiolysis.	Neglected. Radiolytic gas generation rates in the different repository parts have been calculated to be negligible in comparison to the rates due to metal corrosion (Moreno et al. 2001).

Boundary conditions

There are no relevant boundary conditions for this process other than the physical boundaries set by the geometries of the components involved.

Model studies/experimental studies

Radiolysis of water has been studied thoroughly in both experiments and models. Low LET (Linear Energy Transfer) radiation, such as gamma, does not produce detectable amounts of the stable species H_2 and H_2O_2 in pure de-aerated water because they react with OH· and H· radicals in a chemical chain reaction to reform H_2O (Allen 1961). In aerated water, virtually all the hydrated electrons and H radicals formed are oxidised by O_2, thus the main products of low LET water radiolysis in an open system are a steady state concentration of H_2O_2 with constant releases of H_2 and O_2 (Spinks and Woods 1990).

Recent experimental and radiolytic modelling studies have shown that oxidant production during gamma radiolysis of water is prevented by relatively small amounts of dissolved H_2 (Pastina et al. 1999, Pastina and LaVerne 2001). In studies of spent fuel corrosion in 5 M NaCl solutions in the presence of metallic iron, no traces of radiolytic oxygen could be detected in the gas phase. Additionally, the iron(II) containing corrosion products magnetite and green rust were identified at the end of the long term experiments (Loida et al. 1996, Grambow et al. 2000). The presence of these corrosion products on iron surfaces indicates an extremely low concentration of radiolytic oxidants in the solution. The absence of radiolytic gas production in 5 M NaCl solutions containing 0.85 mM dissolved hydrogen has also been observed in another study (Kelm and Bohnert 2004).

Experiments and model studies related to the influence of radiolysis and radiolytic products on organic components are discussed in Section 3.1.3. Interactions of radiolytic products with cementitious materials have been modelled for example by Bouniol and Bjergbakke (2008).

Natural analogues/observations from nature

Although not directly applicable to SFR, in the 1990s SKB investigated natural analogues of radiolysis at sites such as Cigar Lake in Canada. This was because difficulties were being encountered with spent fuel radiolysis experiments because of the very slow reaction rates. The modelling results indicated the inadequacy of the existing performance assessment radiolysis models and led to an improved understanding of the long-term processes involved in radiolysis (see Smellie and Karlsson 1996, for details). Overall, the results indicated that our mechanistic understanding of radiolysis processes is adequate enough to model systems such as SFR.

Time perspective

Radiolysis generates small amounts of gas during the first twenty years post closure (SKB 2008b).

Handling in the safety assessment SR-PSU

The amount of gas produced by water radiolysis has been calculated in Moreno et al. (2001). The calculations show that the gas production from water radiolysis is negligible compared to gas formed by corrosion.

Handling of uncertainties in SR-PSU

The processes behind water radiolysis are well understood and the methods to estimate the effects are well established. The main uncertainty is associated with the radionuclide inventory, although it is known to be sufficiently low for water radiolysis to be negligible.

Adequacy of references supporting the handling in SR-PSU

The supporting reference for neglecting this process (Moreno et al. 2001) is not peer- or factual reviewed, but it is based on fundamental physics.

3.2 Thermal processes

3.2.1 Heat transport

Heat transport, or heat transfer, refer to the processes of energy exchange caused by differences in temperature. Generally, heat transport tends to alter the temperature distribution of a system. The temperature may also be changed due to energy dissipation in e.g. chemical reactions or radioactive decay. However, the generated power in dissipative processes in SFR (cement hydration, metal corrosion, radioactive decay of waste etc) in the long-term is too small to significantly influence the temperature evolution. Thus, for SFR conditions, a description of heat transport is equivalent to a description of the temperature evolution of the repository.

The heat transport mechanisms relevant for SFR are conduction and convection. The process of heat conduction tends to level out temperature differences within a body or between bodies in contact with each other, without associated mass transfer. The heat flow is proportional to the temperature gradient (∇T; Fourier's law) and the general governing heat equation (derived from Fourier's law and the law of conservation of energy) for the temperature (T) evolution is

$$\frac{\partial T}{\partial t} = \frac{1}{c_p \cdot \rho} \nabla \cdot (\lambda \nabla T) \qquad \text{Equation 3-1}$$

where c_p is specific heat, ρ is density, and λ is thermal conductivity. Obviously, a general description of heat conduction is a major task in a system composed of many different materials, with different c_p, ρ and λ values, in a complex geometry.

Apart from conduction, heat will also be transferred during mass transport (convection). A general description of this process is also obviously complex, as it e.g. couples to the process of water transport (Section 3.3.2). Convective heat transfer is expected to become more influential with time as the hydraulic conductivity of the waste packages increases due to degradation processes. Furthermore, heat convection in the gas phase will be the dominating heat transfer process during the operational phase of the repository, before closure and subsequent water saturation.

The description of temperature evolution will be modified when phase changes occur, i.e. when water in the repository freezes or thaws. During freezing or thawing, temperature does not change although heat transfer occurs (c_p is infinite at the phase transition temperature). Freezing/thawing is treated as a separate process (Section 3.2.2).

Dependencies between process and waste form variables

Table 3-5 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

The temperature evolution of SFR is completely dictated by its boundary conditions as it does not contain any significant heat sources (the waste is not active enough). Furthermore, this temperature evolution occurs on a very long time scale. Therefore the repository temperature itself is treated as a boundary condition, and the heat transport process is not explicitly taken into account when the various repository compartments are considered. The treatment of the temperature evolution of SFR and its surrounding is found in the Climate report (SKB 2014m).

Boundary conditions

The process itself is treated as a boundary condition – i.e. the repository temperature is given as a function of time. The evaluation of this temperature is treated in the Climate report (SKB 2014m).

Model studies/experimental studies

Heat transfer processes have generally been extensively studied and modelled. See the Climate report (SKB 2014m).

Table 3-5. Direct dependencies between the process "Heat transport" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. The constitution of the system determine how heat flows	The process is not explicitly handled. See justfication in text.	No.	Not relevant.
Radiation intensity	Yes. Radiation produces heat.	The process is not explicitly handled. See justfication in text and Section 3.1.2.	No.	Not relevant.
Temperature	Yes. Temperature differences is an requirement for the process.	The process is not explicitly handled. See justfication in text and Section 3.1.2.	Yes. Heat transport tends to even out temperature differences.	The process is not explicitly handled. See justfication in text.
Hydrological variables	Yes. Water flow may transport heat. Heat capacites may change with saturation state and aggregation state.	The process is not explicitly handled. See justfication in text.	Yes. Through e.g. convection. The influence is however negligible because temperature differences are small.	The process is not explicitly handled. See justfication in text.
Mechanical stresses	Yes. Heat capacites may depend on stress state. The effect is however negligible.	The process is not explicitly handled. See justfication in text.	Yes. Due to thermal expansion/contraction.	The process is not explicitly handled. See justfication in text.
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. Different materials have different thermal conductivities, specific heats etc.	The process is not explicitly handled. See justfication in text.	No.	Not relevant.
Water composition	Yes, in principle as e.g. heat capacites may depend on composition. The effect is however negligible	The process is not explicitly handled. See justfication in text.	No.	Not relevant.
Gas variables	Yes. Gas flow may transport heat.	The process is not explicitly handled. See justfication in text.	Yes. But relevant only during the operational phase when the repository is not water saturated.	The process is not explicitly handled. See justfication in text.

Natural analogues/observations from nature

See the Climate report (SKB 2014m).

Time perspective

The process of heat transport is always active.

Handling in the safety assessment SR-PSU

The temperature evolution of SFR is completely determined by its outer boundary conditions as the heat generation in the waste forms is negligible, see heat generating processes in e.g. Section 3.1.2 (heat generation due to radiation attenuation), Section 3.5.5 (cement hydration), Section 3.5.6 (degradation of organic materials) and Section 3.5.9 (metal corrosion). Furthermore, this temperature evolution occurs on a very long time scale. Therefore, the repository temperature itself is treated as a boundary condition, and the heat transport process is not explicitly taken into account in the SR-PSU safety assessment. The treatment of the temperature evolution of SFR and its surroundings is found in the Climate report (SKB 2014m).

Handling of uncertainties in SR-PSU

Not handled as the process is not treated explicitly.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.2.2 Phase changes/freezing

The SFR repository will experience climate variations during its lifetime, and the possibility of permafrost (ground having a temperature below 0°C for at least two consecutive years) reaching the repository depth must be accounted for. The main scenario for the saftety assessment SR-PSU includes two climate scenarios, global warming and early periglacial Climate report (SKB 2014m). The evolution of the climate-related conditions, for example permafrost depth is shown in Figure 3-1 for the global warming climate case. The early periglacial climate case has an additional periglacial period at about 17,000 years AP. Figure 3-1 shows that permafrost potentially will reach the repository depth (–60 to –120 m) and hence it can not be excluded that water will freeze in all repository components.

Pure bulk water at atmospheric pressure freezes at 0°C. However, there are several factors that affect the freezing point of water or freezing related phenomena at different temperatures;

- Freezing depression due to increased pressure.

  The freezing point of water decreases with increasing pressure. This is a consequence of the higher density of liquid water as compared to ice. The freezing point depression, ΔT_f, as a function of the increased pressure ΔP is quantified by the Clapeyron equation (Atkins and De Paula 2006):

$$\Delta T_f = \frac{\Delta v}{\Delta s}\Delta P \approx -0.075\,°\mathrm{C/MPa} \cdot \Delta P \qquad \text{Equation 3-2}$$

  where Δv and Δs are the difference in molar volume and molar entropy between liquid water and ice, respectively (note that Δv is negative, while Δs is positive). Equation 3-2 shows that very high pressures are required to lower the freezing point significantly. For example, the typical hydrostatic pressure in SFR (50–100 m water column) lowers the freezing point by only tenths of a degree.

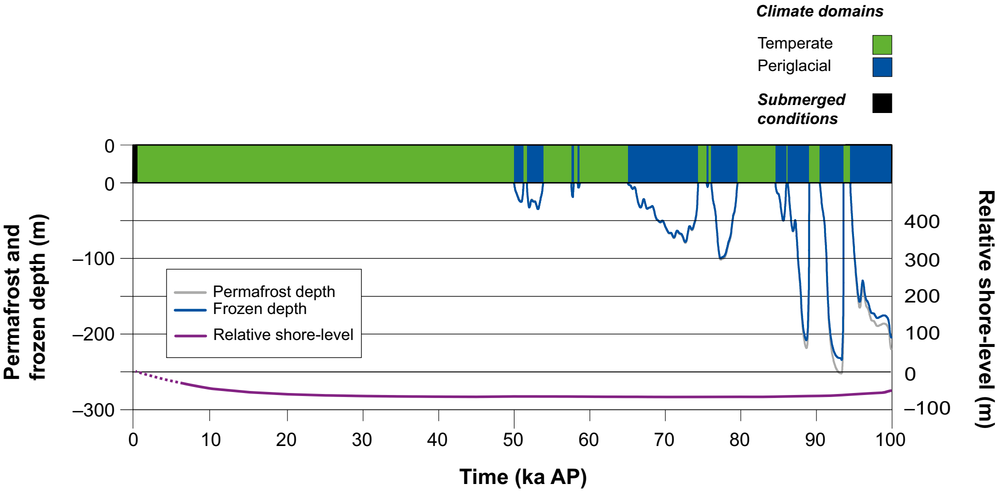

Figure 3-1. Evolution of climate-related conditions at Forsmark as a time series of climate domains and submerged periods for the global warming climate case (Climate report (SKB 2014m, Figure 4-3)).

- Freezing depression due to presence of solutes.

  The presence of solutes in water lowers the freezing point. This is mainly a colligative property, i.e. the freezing point depression depends merely on the concentration of all solutes. A solute of molal concentration c_m (mole/kg) in water lowers the freezing point as (Atkins and De Paula 2006):

  $$\Delta T_f = -1.86\,°\mathrm{C/m} \cdot i \cdot c_m \qquad \text{Equation 3-3}$$

  where i is van't Hoffs factor, which accounts for the dissociation of the dissolved substances (e.g. a NaCl solution of 1 mole/kg will contribute approximately 2 mole/kg because of dissociation into one Cl^- and one Na^+ ion).

  Equation 3-3 shows that the freezing point depression due to solutes can be significant, i.e. in a NaCl solution of 1 mole/kg, the freezing point depression is approximately –3.7°C. Furthermore, as freezing occurs, solute particles are generally expelled from the ice phase which may increase the concentration of the remaining liquid. Thus, ice and liquid solution may co-exist in equilibrium at a range of temperatures, and complete solidification may not necessarily occur at one specific temperature.

- Freezing depression due to small confining volume.

  Several components of SFR can be characterised as porous systems. Water in these systems is confined within pores of a certain size distribution.

  Generally, the (free) energy of an ice crystal of a certain size and shape has a surface contribution, which acts to lower the freezing point. For a bulk sample this contribution is negligible (although it explains the existence of metastable super cooled liquid water) but becomes increasingly influential for confining pores of decreasing size. The mechanism of lowering the freezing point in this manner is known as the Gibbs–Thomson effect (see e.g. Dash et al. 2006).

  For a spherical pore of radius r, the freezing point depression for water is given by (see e.g. Sliwinska-Bartkowiak et al. 1999):

  $$\Delta T_f = -\frac{2 \cdot T_{fb} \cdot \Delta\sigma \cdot \bar{v}}{Lr} \approx -\frac{50\,\mathrm{nm} \cdot °\mathrm{C}}{r} \qquad \text{Equation 3-4}$$

  Where T_{fb} is the freezing point of bulk water measured in absolute temperature, $\Delta\sigma$ is the difference in surface tension between the liquid–pore wall and ice–pore wall interfaces, L is the latent heat of freezing bulk water, and $\bar{v}$ is the specific volume of bulk water. The approximation in Equation 3-4 is achieved by estimating $\Delta\sigma$ from the corresponding values of liquid–vapour and ice–vapour surface tension. It is seen from this formula that, for pores on the sub micro metre scale, the freezing point depression can be substantial, on the order of tens of degrees.

  As the pores are distributed over different sizes, this implies that freezing of the water does not take place at one specific temperature, but occurs gradually in a temperature interval. Within this temperature interval, liquid water and ice occur simultaneously in the porous system.

- Effect of freezing on osmotic pressure/swelling.

  Osmosis is a consequence of a difference in water chemical potential between the system under consideration and its surroundings (separated by a semipermeable barrier). The water chemical potential of ice increases less quickly with decreasing temperature as compared to liquid water. Consequently, osmotic processes change when the surroundings freeze. In general, osmotic pressure decreases with temperature under these conditions, and shrinkage may be induced in osmotically swollen systems.

Consequences of freezing for waste forms in SFR

As water expands when it freezes, stresses and pressures will be induced if water cannot be expelled from the region where freezing occurs, or if the water transport capacity is too limited. These stresses and pressures may cause damage to the waste forms.

Freezing of SFR will always occur in an approximately vertical thermal gradient, with temperature increasing with depth. Under many circumstances, therefore, freezing will not cause increased pressures as water can be expelled downwards. However, because freezing point depression will be different in different components of the repository, situations will also occur where “trapped” water will freeze.

Furthermore, water may also be “trapped” in very transport restricted matrices, e.g. bitumen.

Foremost, the effects of freezing on the waste forms are considered to be secondary to other processes that may induce damage. Freezing processes are coupled to the following other processes:

- Heat transport (energy is released to the surroundings during freezing, and taken from the surroundings during thawing).
- Fracturing (due to increased pressures and stresses).
- Water transport under saturated conditions (due to increased hydrostatic pressure).
- Advection (due to increased hydrostatic pressure).
- Water uptake, swelling (swelling potential diminishes as the external water changes phase to ice).

Dependencies between process and waste form variables

Table 3-6 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Boundary conditions

Temperature in the repository is set by climate evolution. Pore geometries of the components influence the process.

Model studies/experimental studies

The field of freezing in porous systems is well studied both from an engineering and geological perspective owing to its technological and environmental importance (see e.g. Dash et al. 2006, Sliwinska-Bartkowiak et al. 1999).

Natural analogues/observations from nature

Freezing is a common natural process. This has been reviewed e.g. in Dash et al. (2006).

Time perspective

The freezing process is coupled to periods of permafrost and must be considered over the entire repository lifetime. However, the first period of permafrost is not expected until several thousand years after closure.

Table 3-6. Direct dependencies between the process "Phase changes/freezing" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Freezing point influenced by confinement geometry if it is small (sub micron).	Freezing points estimated.	Yes. Pore geometries may be different after freezing. Fractures may have been created or widened.	See Fracturing in Section 3.4.1.
Radiation intensity	No.	Not relevant.	No.	Not relevant.
Temperature	Yes. The freezing point is a certain temperature.	Freezing points estimated.	Yes. Freezing releases energy. Thawing consumes energy.	Influence is considered but not treated quantitatively in modelling for the waste packages. See the **Climate report** (SKB 2014m).
Hydrological variables	Yes. Pressure influences freezing point.	Insignificant, unless very high pressures involved.	Yes. Freezing may cause increased pressure and water flow.	Considered in flow modelling.
Mechanical stresses	No.	Not relevant.	Yes. Freezing may induce stresses and strains.	See Fracturing in Section 3.4.1 .
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. Freezing point is influenced by surface properties.	Freezing points estimated.	No.	Not relevant.
Water composition	Yes. Freezing point is influenced by solutes.	Freezing points estimated.	Yes. Freezing may change composition of remaining unfrozen water.	Influence is considered but not treated quantitatively in modelling for the waste packages.
Gas variables	No.	Not relevant.	No.	Not relevant.

Handling in the safety assessment SR-PSU

Freezing is expected to result in structural deterioration (fracturing) of cement, concrete and bitumen, materials that are present as stabilising matrices in various waste packages. Fractures will alter the hydraulic conductivity in these components, and the effect is handled in the hydrogeological modelling with altered hydraulic conductivities of the repository components.

Comments on specific components

Cement waste matrix: Concrete is a porous system and is expected to be completely water saturated at the time of the first permafrost period (Emborg et al. 2007). Emborg et al. (2007) estimated that a maximum of 5 L/m^3 of water can be frozen in the concrete without damaging it. By considering the pore size distribution of the concrete, they also estimated the amount of water being frozen at –5°C and –10°C to be 17 L/m^3 and 30 L/m^3, respectively. Consequently, fracturing is expected to occur in the concrete during the permafrost period to such an extent that its barrier functions are lost (see further Fracturing in Section 3.4.1). Although the work in Emborg et al. (2007) is related to structural concrete, similar processes are expected in the cement and concrete conditioning. In particular, the barrier functions will be assumed lost after a permafrost period.

Stabilised ion exchange resin: The ion exchange resin takes up water and swells. As the water is "trapped" in the bitumen matrix (diffusion controlled) freezing might cause increased stress and fracturing. This may also occur for resin stabilised in cement.

Evaporated salts solidified in bitumen: Increased stress and fracturing may also occur if "trapped" salt solution freezes in the bitumen pores. If the salt concentration is very high, however (e.g. a $NaNO_3$ solution near saturation) freezing is not expected (freezing point depression much below –10°C).

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The physical mechanisms described here are well studied phenomena.

Model simplification uncertainties

The exact evolution of climate cannot be predicted. Hence, there is an uncertainty in the timing and the extent (in temperature and time) of the permafrost periods.

Input data and data uncertainties

Estimated freezing points depend on various processes and properties. For example, salt concentrations in bitumen depend on the leaching properties of this material as a function of time. Further, the water uptake capacity of exchange resins is connected to its freezing point – if the former changes with ageing, so does the latter.

Adequacy of references supporting the handling in SR-PSU

The supporting references are either work aimed specifically to investigate the specific problem of freezing in engineered barriers in repositories for radioactive waste or are published in international peer-reviewed journals.

3.3 Hydraulic processes

3.3.1 Water uptake and transport during unsaturated conditions

Overview/general description

At the end of the operational period, pumping of groundwater to keep the repository drained will stop. Groundwater will flow through the surrounding rock into the excavated drifts and vaults. The groundwater will gradually saturate the fractures and pores of the rock adjacent to the repository until full saturation is reached. The groundwater will then continue to fill void spaces in drifts and vaults of the repository, gradually saturating the different construction materials and waste packages present in the repository. The processes described here are physical, and therefore do not include the chemical processes involved in water uptake and swelling (Section 3.5.7), or hydration and leaching reactions in cement (Section 3.5.5).

The filling of void spaces in the repository will take place primarily by the gravitational flow of groundwater seeping into the repository, filling up the lower parts first. The time for the voids to fill is determined by the void volume and the rate of groundwater seepage.

For the various porous materials present in the repository (construction materials, backfill materials, concrete packaging and waste form materials), the physical uptake of water is governed by:

- The seepage rate of water into the repository.
- Redistribution of the seepage water between different parts of the repository; inflow may occur preferentially at certain locations due to the heterogeneous flow pattern in the fractured crystalline host rock.
- Any excess (free) water in the waste may be transported by gravitational flow or be redistributed by capillary flow (suction).
- The hydraulic conductivities of the different porous materials including the impact of fractures and other heterogeneities of the porous materials.
- The hydraulic pressure gradients established by the inflow of groundwater.
- Capillary flow processes in the unsaturated pore system of the porous materials.
- The total porosity and degree of water saturation of the porous materials.

- The sequence of materials through which the groundwater will have to penetrate to reach each of the different porous materials, this may include:
  - Shotcrete-coating of the rock walls in vaults and drifts.
  - Plug and sealing materials of access tunnel.
  - Different types of backfill materials in drifts, vaults and around the silo, e.g. crushed rock, sand, sand/bentonite, bentonite.
  - Concrete structures, e.g. concrete wall, bottom and lid, and shaft walls of the silo, concrete containers.
  - Cement grout backfill.
  - Packaging.
  - Waste matrices.
  - Porous waste material.
- The dissipation of gas (air) from the different porous materials. As the wetting proceeds from the outside and inwards, any gas entrapped in the pores will counteract water uptake. The occurrence of any gas generating processes in the waste form will have similar impact on the water uptake. The dissipation of gas may take place by:
  - Pressing out the gas through fractures and larger pores that are dry or where the capillary pressure is sufficiently low (bubble flow).
  - Dissolution of the gas in the inflowing groundwater. If all of the gas can be dissolved, the porous material can reach full water saturation. If only a part of the gas can be dissolved, the dissolved gas must be transported away by means of diffusion through the water saturated pores or by advective flow of the water in order for the saturation process to continue. The entrapped gas will then slowly dissolve at a rate governed by the removal of gases. Eventually, full water saturation is expected in the different porous materials.
  - Consumption of reactive gases, e.g. oxygen, by various processes in the waste form.
- Water may also be transported as a vapour under unsaturated conditions. A prerequisite of this process is that a difference in vapour pressure is maintained between different parts or components present in the repository, e.g. a temperature gradient, or a difference in osmotic pressure caused by different salinities, e.g. in waste packages containing salt concentrates.
- The uptake of water by different chemical processes is described in Section 3.5.7.
- Carbonatisation during the operational phase may affect the hydraulic properties of the concrete materials in the SFR repository to some degree.

Dependencies between process and waste form variables

Table 3-7 shows how the water uptake and transport during unsaturated conditions influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Influence by Geometry. A direct influence has been identified. The dimensions influence the time taken for water to saturate the waste form. The volume of waste form, the voids present and the porosities are used to calculate the resaturation volume. The pore characteristics define the capillary suction and hence the tendency of the material to absorb water during unsaturated conditions. For materials in capillary contact, e.g. a cement waste matrix in direct contact with a concrete packaging material, equilibrium will be gradually established by capillary transport of water. The dimensions also define the transport distances for water during water uptake. The presence of fractures in the waste form may constitute shortcuts for water uptake. The time to reach full water saturation in the waste form is likely to be short and determined by the rate of water penetration of surrounding constructions and/or the rock.

Influence on Geometry. No direct influence has been identified. The geometry can be indirectly influenced by uptake of water in any swelling material or compound present, e.g. salts absorbing waters of crystallisation or ion exchange resins that swell by absorbing water, see Section 3.5.5 and Section 3.5.7. Cement matrices also swell to a small degree in response to resaturation, which reduces the drag force caused by capillary forces (reverse of shrink-drying), see Section 3.5.7.

Table 3-7. Direct dependencies between the process "Water uptake and transport during unsaturated conditions" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Dimensions define the volume of voids to resaturate. Fractures constitute short-cuts for flow. Controlled by geosphere or barrier materials.	Geometry included in the models.	No. Indirectly via swelling, see Section 3.5.5 and Section 3.5.7.	The swelling pressure is calculated, see Section 3.5.7.
Radiation intensity	No. An indirect influence via radiolysis, see Section 3.1.4.	Not relevant.	No. An indirect influence via attenuation, see Section 3.1.2.	Not relevant.
Temperature	Yes. Via viscosity and surface tension of water.	Reflected in the selection of hydraulic conductivities for model calculations. Effects of spatial temperature variability are judged negligible.	Yes. The water uptake redistributes heat. Indirectly the resaturation affects the thermal properties see Section 3.2.1 and Section 3.5.5.	The temperature is calculated.
Hydrological variables	Yes. Pressure is driving force for water uptake.	Included variables in water saturation calculations.	Yes. Water uptake will influence pressure and flow.	The pressure and suction are considered.
Mechanical stresses	No. Indirectly via mechanical stesses affecting the geometry of the poresystem which will influence the water uptake in any compressible waste material.	Not relevant.	No. Indirectly via swelling, see Section 3.5.7.	Not relevant.
Radionuclide inventory	No. Indirect influence via radiolysis, see Section 3.1.4.	Not relevant.	No. Indirectly via transport in water phase, see Section 3.6.2.	Not relevant.
Material composition	Yes. Material properties determine the waterflow and capillary suction.	The material composition is reflected in the selection of material data for calculation of water uptake.	No. Indirectly via mixing/dissolution–precipitation, see Section 3.5.5.	Not relevant.
Water composition	Yes. Salinity will influence density, viscosity and surface tension.	Reflected in the selection of viscosities, densities and surface tension used in water uptake calculations.	No. Indirectly via mixing/dissolution–precipitation, see Section 3.5.5.	Not relevant.
Gas variables	Yes. Gas solubility and reactivity will influence possibility to dissipate entrapped gases.	Concidered in the calculations of water uptake.	Yes. Water uptake will influence the equilibria with gases.	Concidered in the calculations of water uptake.

Influence by Radiation intensity. No direct influence has been identified. The radiation intensity has an indirect influence since radiolysis of water causes gas formation, see Section 3.1.4. Disintegration of water by radiolysis to form gases would counteract water uptake both through the consumption of water and the formation of gases that can be trapped in the waste, see Section 3.5.10. The radiation intensity in the SFR wastes is generally too low for this influence to be of any practical importance.

Influence on Radiation intensity. No direct influence has been identified. Water uptake cannot influence the radiation intensity directly. However, water uptake may have an indirect effect, as water contributes to radiation shielding, see Section 3.1.1.

Influence by Temperature. A direct influence has been identified. Temperature will influence the viscosity of water and hence the hydraulic conductivity controlling the water ingress into the repository and uptake into the waste form. Temperature will also influence the surface tension of water. The viscosity and the surface tension decrease and the hydraulic conductivity increases with increasing temperature. The occurrence of large temperature differences between different components in the repository would increase the driving force for transport of water vapour during the unsaturated initial phase. Temperature differences between different components in the repository are likely to have levelled out during the operational phase, e.g. heat of cement hydration and heat generation due to radioactive decay. Some difference in temperature may exist between groundwater/surrounding rock and the repository structures/waste due to ventilation and climate control of the facility during the operational phase. The overall judgement is that temperature and temperature variability would have insignificant impact on the rate of water uptake.

In the long-term, the occurrence of permafrost and glaciations may introduce major changes in the temperature and the water flow, see Section 3.2.2. However, this is judged irrelevant for water uptake and transport during the unsaturated phase which will take place during the temperate period.

Influence on Temperature. A direct influence has been identified. Physical water uptake will tend to level out temperature differences, as the inflowing water will redistribute heat. Increased water saturation will also increase the overall thermal conductivity of the waste form materials, see Section 3.2.1. Uptake of water may initiate continued hydration of any remaining unhydrated clinker minerals in cement, thereby causing heat production in the waste form, see Section 3.5.5. The overall judgement is that physical water uptake would have insignificant impact on the temperature.

Influence by Hydrological variables. A direct influence has been identified. Groundwater pressure, including capillary pressure, constitutes the driving force for water uptake in the waste form. The initial degree of saturation together with the geometric parameters defines the volume of water required for resaturation. These are included as variables in the calculations of resaturation. The flow pattern of water will define the sequence of water uptake in the waste form in different parts of the repository.

The presence of any excess (free) water in the waste form would locally increase the pressure gradient. It is judged, based on the geometrical dimensions and the hydraulic data for the waste form material, that such an effect would be of short duration and restricted to the operational phase.

In the long-term, the occurrence of permafrost and glaciation may introduce major temperature changes, which will change the aggregation state of water to ice, see Section 3.2.2. However, this is judged irrelevant for water uptake and transport during the unsaturated phase, because saturation will be reached long before any permafrost will develop.

Influence on Hydrological variables. A direct influence has been identified. The uptake of water will gradually change the pressure, degree of saturation and flow due to changes of the capillary pressure (suction), water content and the (relative) hydraulic conductivity.

Influence by Mechanical stresses. No direct influence has been identified. Mechanical stresses will indirectly, via geometry, influence water uptake into any waste form material that is compressible or prone to swelling. For compressible porous materials, an increased mechanical (compressible) stress would reduce the porosity and increase the saturation, thereby influencing the capillary suction. At the same time, the reduced porosity would reduce the hydraulic conductivity. In essence, increased compressive stresses would increase the capillary suction but reduce the hydraulic conductivity and thereby slow down the rate of water uptake.

Influence on Mechanical stresses. No direct influence has been identified. Waste form materials/compounds with swelling properties could increase the mechanical stresses as a result of water uptake.

Influence by Radionuclide inventory. No direct influence has been identified. The uptake of water is not influenced by the radionuclide inventory. The radioactive elements in the SFR repository are in general not abundant enough to form separate chemical compounds or materials, and will be present as trace contaminants in the different waste materials.

Influence on Radionuclide inventory. No direct influence has been identified. The uptake of water does not influence the radionuclide inventory directly, but indirectly via affecting degree of saturation and radionuclide dissolution–precipitation processes. However, indirectly the uptake of water may influence the inventory via changes of the water composition and subsequent transport of radionuclides in water phase, see Section 3.6.2.

Influence by Material composition. A direct influence has been identified. The material composition determines the hydraulic properties of the waste form, e.g. hydraulic conductivities, capillary suction characteristics, surface tension and wetting properties, presence of void spaces and porosities. The presence of any chemical compounds in the waste form that bind or repel water will influence the water uptake. The influence of material composition is reflected in the selection of material data for the model calculations of water uptake.

Influence on Material composition. No direct influence has been identified. Indirectly, the uptake of water may influence the material composition for example by allowing continued hydration of any reactive mineral phases in the waste form; this may create new hydrated mineral surfaces, see Section 3.5.5. Indirectly, uptake of water will also affect the supply of water necessary for sustaining any microbial degradation of organic materials in the waste or waste material, see Section 3.5.8.

Influence by Water composition. A direct influence has been identified. The water composition, such as the salinity, has an influence on the density, viscosity and surface tension of water and may have an influence on the uptake of water. Input data for calculation of water uptake reflect the influence of water composition.

Influence on Water composition. No direct influence has been identified. The water composition can be indirectly influenced by water uptake via dissolution–precipitation, see Section 3.5.5, which may have an impact on the density and viscosity of the pore water and on the surface tension at the pore water – pore gas interface.

Influence by Gas variables. A direct influence has been identified. Different gases have different solubilities in water and some gases can be consumed by biological and chemical reactions, see Section 3.5.8 and Section 3.5.9. Therefore, the gas composition will influence the amount of gas entrapped during water uptake, which in turn influences the rates and processes of gas dissipation (see Section 3.5.10), and thereby the rate of water uptake. The presence of any gas will define the degree of saturation of porous waste form materials.

Influence on Gas variables. A direct influence has been identified. Water uptake will influence the gas composition by establishing equilibria between the water phase and the gas phase according to Henry's law and Raoult law for each of the different gases.

Boundary conditions

The waste is stored in concrete or steel packaging that defines the boundary conditions. These boundary conditions are described in Section 4.2.1 and Section 4.2.2.

Boundary conditions include the pressure and flow of groundwater, temperature, mechanical stresses and the composition of water.

For waste disposed in the silo, water uptake will be governed by the water penetration of the bentonite and concrete barriers of the silo. This may in turn be influenced by the inflow of water through the surrounding rock. These boundary conditions are described in the Barrier process report (SKB 2014a).

For waste stored in BMA, BTF and BLA, water uptake is governed by the inflow of water through the surrounding rock, and when present, through concrete structures and cement grouting. These boundary conditions are described in the Barrier process report (SKB 2014a) and Geosphere process report (SKB 2014e).

Model studies/experimental studies

Specific model studies or experimental studies on water uptake into waste are not generally available owing to the diverse nature of the different wastes. However, some model and experimental studies have been reported for certain waste types with hygroscopic properties. Experiments and model interpretations of water uptake into cemented waste containing soluble salts suggested that some leakage of brine may occur due to condensation of water vapour during storage under moist conditions (Brodersen 1992).

Natural analogues/observations from nature

Although water uptake and transport during unsaturated conditions are well observed and documented in natural materials, water uptake in waste form materials is not, *per se*. However, the seepage of water into the excavated drifts and vaults has been observed and monitored during the construction and operational phases of SFR (SKB 2008b). The rate of inflow has been observed to decrease with time (SKB 2013b).

Time perspective

The inflow of groundwater is expected to fill the void spaces in the drifts and vaults fairly rapidly. The rate of inflow of groundwater is likely to vary over time due to the gradual changes in the groundwater pressure when the repository fills up with water.

Water saturation of the silo will occur by the diffusive inflow of groundwater through bentonite, which will surround the silo (walls, base and lid). Due to the low hydraulic conductivity of the bentonite and the concrete constructions, as well as the entrapment of gases, the water saturation of the silo is expected to be a fairly slow process.

In the other vaults, concrete structures will take up water as groundwater seeps into the repository. Concrete constructions generally have low hydraulic conductivities, which would restrict the ingress of water. However, the concrete walls are fairly thin (apart from the silo), and the presence of fractures observed in some constructions means that the inflow of water and subsequent water saturation can still be expected to occur fairly rapidly.

For the packaging and waste matrices, the uptake of water will start when groundwater penetrates the surrounding structures, such as the silo or other concrete structures. The water uptake and saturation of the packaging and waste matrices (except bitumen, see Section 3.5.7) is expected to be a fairly rapid process. However, for packaging and waste matrices placed in the silo, the rate of water saturation is expected to be determined by the slow inflow of water through the bentonite and the silo concrete constructions (i.e. wall, bottom and lid).

Vapour phase transport of water is expected to be a short-term process and judged to be of minor importance for the safety assessment.

Water uptake will influence the onset of radionuclide transport from the waste matrices. Using a hydrogeological model, Holmén and Stigsson (2001, Chapter 15) have calculated how long it takes to fill and saturate the repository with groundwater. The calculations show that the void (porosity) inside the silo is the last to be filled and that this can take up to 25 years. In a study of how freezing can affect the silo, the time for complete saturation of the bentonite surrounding the concrete silo has been estimated to be of the order of 100 years (Emborg et al. 2007). These two studies indicate the range in the time taken for water saturation of the silo repository. It will only take a few years to fully saturate BMA, BLA and BTF (Holmén and Stigsson 2001, Chapter 15).

Handling in the safety assessment SR-PSU

The water uptake and transport of water during unsaturated conditions is only relevant for a short initial time period. Water uptake defines the time when the release of radionuclides will start. An exception is the release of radioactive gases, which will occur during the unsaturated phase. The time for full saturation of the different parts of the repository has been estimated in Holmén and Stigsson (2001). Due to the relatively short time period when unsaturated conditions prevail, no further handling is judged to be needed in the safety assessment.

Handling of uncertainties in SR-PSU

The effect of the uncertainty in the time to reach full water saturation of the silo repository is treated by analysing different scenarios with numerical models.

The uncertainty in the time estimated to fully saturate BMA, BLA and BTF is judged to have negligible impact on the safety assessment and does not need to be treated further.

Uncertainties in mechanistic understanding

The fundamental processes involved in the uptake and transport of water during unsaturated conditions are well understood.

Model simplification uncertainty

The impacts of model simplifications are transparent and the overall impact on the safety assessment is negligible.

Input data and data uncertainty

Input data are reasonably well known and data uncertainty is documented in the Data report (SKB 2014c).

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.3.2 Water transport under saturated conditions

Overview/general description

This section focuses on water transport under saturated conditions. The water uptake and transport during unsaturated conditions is described separately, see Section 3.3.1.

Once the different structures in the SFR repository have been fully resaturated with water, the hydraulic pressures and gradients will gradually approach a steady-state situation. The groundwater pressure will be determined by the regional/local flow in the rock (see further description in the Geosphere process report (SKB 2014e)), the hydraulic conductivities and the dimensions of the different structures in the repository (see also the Barrier process report (SKB 2014a)).

For each material present in the repository, water transport under saturated conditions is governed by:

- The rate of water flow through the surrounding rock into the repository.
- Distribution of groundwater between different parts of the repository, inflow may occur preferentially at certain locations due to the heterogeneous flow pattern in the fractured crystalline host rock.
- The hydraulic conductivities of the different materials present in the repository.
- The hydraulic pressure gradients established by the regional/local groundwater flow.
- The sequence of materials through which the groundwater will pass on its way through the repository, this may include:
    - Shotcrete-coating of the rock walls in vaults and drifts.
    - Plug and sealing materials of access tunnel.
    - Different types of backfill materials in drifts, vaults and around the silo, e.g. crushed rock, sand, sand/bentonite, bentonite.

  - Concrete structures, e.g. concrete wall, bottom and lid, and shaft walls of the silo, concrete packaging.
  - Cement grout backfill.
  - Packaging.
  - Waste matrices.
  - Porous waste material.
- Buoyancy effects caused by differences in water density. In SFR, two types of density driven buoyancy flow can be envisaged:
  - Re-entrance of saline groundwater into the repository, with the inflow of groundwater with a dissolved salt content corresponding to a chlorinity of up to about 0.5% from the surrounding rock.
  - Formation of saline solutions following water uptake into waste packages containing salt concentrates.

The dissipation of gas formed by any gas generating processes in the waste form (see Section 3.5.10) will have an impact on the water transport under saturated conditions. The dissipation of gas may take place by:

- Pressing the gas out through fractures and larger pores where the capillary pressure is sufficiently low (bubble flow), see Section 3.5.10.
- Dissolution of the gas by the groundwater. If all gas can be dissolved, the porous material will maintain full water saturation and there will not be any impact on the water flow. If only a part of the gas can be dissolved and transported away by means of diffusion or advective flow, locally unsaturated conditions will evolve. The remaining gas will be entrapped and may locally block the water transport, see Section 3.3.1.
- Consumption of reactive gases by various processes in the waste form.

By definition, the presence of gas would mean unsaturated conditions. However, the reappearance of gas after full resaturation affects saturated water flow, and is therefore considered here.

Dependencies between process and waste form variables

Table 3-8 shows how the water transport under saturated conditions influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Influence by Geometry. A direct influence has been identified. The physical dimensions of the waste form have a direct influence on the transport of water under saturated conditions. The flow resistance in the waste form is influenced by the porosity and is proportional to the thickness in the flow direction, and the flow capacity is proportional to the cross sectional area perpendicular to the flow direction. The presence of voids and fractures in the waste form may constitute shortcuts for water transport.

Influence on Geometry. No direct influence has been identified. The waste form geometry can be influenced indirectly by the uptake of water into any swelling material or compound present, e.g. salts absorbing waters of crystallisation or ion exchange resins that absorb water and swell, see Section 3.5.5 and Section 3.5.7. The porosity and hydraulic conductivity of cement matrices may also change to a small degree in response to chemical degradation processes governed by the supply of groundwater species, see Section 3.5.5.

Influence by Radiation intensity. No direct influence has been identified. The radiation intensity has an indirect influence as radiolysis of water can generate gas, see Section 3.1.4. The radiation intensity in the SFR waste is generally too low for this influence to be of any practical importance.

Influence on Radiation intensity. No direct influence has been identified. Although water transport under saturated conditions will not influence the radiation intensity directly, the presence of water may contribute to radiation shielding, see Section 3.1.1. Effects on the shielding are considered in calculations of the attenuation and radiolysis.

Table 3-8. Direct dependencies between the process "Water uptake and transport under saturated conditions" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Water transport is controlled by the geosphere and barrier conditions. The flow resistance is proportional to dimensions. Fractures and voids constitute short-cuts for flow.	Geometry included in the models.	No. Indirect effects arise from the degradation, dissolution or transformation of certain wastes, see Section 3.5.5.	Not relveant.
Radiation intensity	No. Indirect influence via radiolysis, see Section 3.1.4.	Not relevant.	No. Indirect influence via attenuation, see Section 3.1.2.	Not relevant.
Temperature	Yes. Temperature will influence the density and viscosity of water and hence the hydraulic conductivity.	Reflected in the selection of hydraulic conductivities and densities and viscosities of water for use in the calculations.	Yes. Temperature is influenced by the redistribution of heat caused by the water transport, see Section 3.2.1 and Section 3.5.5.	The temperature is set by outer bondary conditions. The redistribution of heat is fast inside the waste form.
Hydrological variables	Yes. The gradient of the hydraulic head, accounting for any density differences caused by differences in salinity or temperature, constitute the driving force for water transport.	Input data in calculations of water transport.	Yes. Transport of water will define the pressure and flow distribution.	The pressure and flow are calculated.
Mechanical stresses	No. Indirectly via geometry, as mechanical stresses will influence the water transport in compressible or swelling materials, reflected in the selection of hydraulic conductivities for calculations.	Not relevant.	No. Indirectly via the swelling pressure, see Section 3.5.7.	Not relevant.
Radionuclide inventory	No. Indirect influence via radiolysis, see Section 3.1.4.	Not relevant.	No. Indirectly via release of radionuclides which will affect inventory, see Section 3.6.2.	Not relevant.
Material composition	Yes. The material composition including density and porosity determines the hydraulic properties.	Relevant material data are selected for the water transport calculations.	No. Indirectly via dissolution–precipitation processes (see Section 3.5.5).	Not relevant.
Water composition	Yes. Water composition, e.g. salinity, influences the viscosity and density of water.	Relevant viscosities and densities are selected for the water transport calculations.	No. Indirectly via mixing/dissolution–precipitation, see Section 3.5.5.	Not relevant.
Gas variables	Yes. Reappearance of a gas phase, e.g. due to corrosion of steel components in the waste influences the water flow.	Effect of gas is considered in water flow calculations.	No. Indirectly water transport will influence the equilibria with gases by changing the water composition. Partitioning of gases according to Henry's and Raoult's laws.	Not relevant.

Influence by Temperature. A direct influence has been identified. Temperature will influence the viscosity of water and hence the hydraulic conductivity controlling water transport in the repository and in the waste form. The viscosity decreases and the hydraulic conductivity increases with increasing temperature. The occurrence of large temperature differences between different components in the repository would cause thermal buoyancy transport of water (convection). Temperature differences between different components in the repository are likely to have levelled out during the operational phase and the resaturation phase, e.g. the heat of cement hydration and the heat generation due to radioactive decay are likely to have diminished to low levels. The overall judgement is that temperature and temperature variability will have an insignificant impact on water transport under saturated conditions.

In the long-term, the occurrence of permafrost and glaciations will change the temperature in the repository, which will introduce major changes in the water flow, see Section 3.2.2.

Influence on Temperature. A direct influence has been identified. Water transport will tend to level out temperature differences by redistributing heat. Transport of water may sustain chemical degradation reactions in waste or cement matrix materials, thereby causing heat production in the waste form, see Section 3.5.5. The overall judgement is that water transport after saturation will have insignificant impact on the temperature.

Influence by Hydrological variables. A direct influence has been identified. The gradient of the hydraulic head, accounting for any density differences caused by differences in salinity or temperature, constitute the driving force for water transport under saturated conditions in the waste form. This is included as a variable in the calculations of water transport.

As a result of prolonged periods of permafrost, the water will freeze, which will inhibit the transport of water. Effects on the local water flow patterns during transition stages need to be considered in climate change scenarios.

Influence on Hydrological variables. A direct influence has been identified. The transport of water will define the pressure and flow distribution in the waste form. These are included as parameters in the water transport calculations.

Influence by Mechanical stresses. No direct influence has been identified. Mechanical stresses will indirectly, via geometry, influence the water transport in any waste form material that is compressible or prone to swelling. For compressible porous materials, an increased mechanical (compressible) stress would reduce the porosity and the hydraulic conductivity, and thereby reduce water transport. Locally increased mechanical stresses may result in the fracturing of waste or waste matrices, which could act as shortcuts for water transport.

Influence on Mechanical stresses. No direct influence has been identified. Water transport will affect the chemical conditions, which may affect the swelling properties of waste form materials/compounds; this may indirectly influence the mechanical stresses, see Section 3.5.7.

Influence by Radionuclide inventory. No direct influence has been identified. The transport of water is not influenced by the radionuclide inventory, only indirect influence via radiolysis, see Section 3.1.4.

Influence on Radionuclide inventory. No direct influence has been identified. The transport of water does not influence the initial radionuclide inventory. However, indirectly the gradual release of radionuclides, transported by diffusion and advection, may redistribute and gradually deplete the inventory over time, see Section 3.6.2.

Influence by Material composition. A direct influence has been identified. The material composition determines the hydraulic properties of the waste form, e.g. hydraulic conductivities and porosities. The influence of material composition is reflected in the selection of material data for the calculations of water transport under saturated conditions.

Influence on Material composition. No direct influence has been identified. The transport of water does not influence the material composition. Indirectly, the material composition may be influenced via dissolution–precipitation processes (see Section 3.5.5) and advection (see Section 3.5.1).

Influence by Water composition. A direct influence has been identified. The water composition, particularly the salinity, has an influence on the density and viscosity of water and may have an influence on the transport of water. Input data for calculation of water transport reflect the influence of water composition.

Influence on Water composition. No direct influence has been identified. The water composition can be influenced by water transport indirectly via dissolution–precipitation, see Section 3.5.5.

Influence by Gas variables. A direct influence has been identified. Any initial presence of a gas phase is treated in Section 3.3.1. The dissipation of dissolved gases is treated in Section 3.5.10. However, the reappearance of a gas phase due to e.g. corrosion of steel components in the waste forming gas will influence the water transport by blocking water conductive pores, and may also cause increased pressure and water flow.

Influence on Gas variables. No direct influence has been identified. Indirectly, water transport will influence the composition of any gas phase present by changes of the water composition, thereby establishing new equilibria between the water phase and the gas phase according to Henry's law and Raoult's law for each of the different gases.

Boundary conditions

The waste is stored in concrete or steel packaging that defines the boundary conditions. These boundary conditions are described in Section 4.2.1 and Section 4.2.2.

Boundary conditions include the pressure and flow of groundwater, temperature, mechanical stresses and the composition of water.

For waste disposed in the silo, the water transport will be governed by the water flow through the bentonite and concrete barriers of the silo. These boundary conditions are described in the Barrier process report (SKB 2014a).

For waste stored in BMA, BTF and BLA the water transport is governed by the flow of water through the surrounding rock, and when present, through concrete structures and cement grouting. These boundary conditions are described in the Barrier process report (SKB 2014a) and Geosphere process report (SKB 2014e).

Model studies/experimental studies

Specific model or experimental studies on water transport in waste are not generally available due to the diverse nature of different wastes.

Natural analogues/observations from nature

Although water transport under saturated conditions is well observed and documented in natural materials, water transport in waste form materials has not been studied or observed in nature *per se*.

Time perspective

The transport of groundwater in drifts and vaults is expected to attain stable flow conditions fairly rapidly. The rate of groundwater transport is likely to vary over time due to the gradual changes in the groundwater pressure after the repository has been resaturated with water.

Water transport through the silo will be restricted by the slow inflow of groundwater through bentonite, which will surround the silo (walls, base and lid). Due to the low hydraulic conductivity of the bentonite and the concrete constructions, as well as the entrapment of gases, the water saturation of the silo is expected to be a fairly slow process.

Water transport in other concrete structures will take place following the resaturation of the repository. Although high quality construction concretes have low hydraulic conductivities, the dimensions (i.e. the wall thickness) of the repository structures are fairly thin (apart from the silo). The presence of fractures observed in some constructions need consideration. The water turn-over time is calculated by numerical models for the different parts of the SFR repository.

For the waste form, the transport of water is dependent on groundwater flow through the surrounding structures, such as the silo or other concrete structures. Water transport in the packaging, and both non-conditioned waste and waste matrices (except bitumen, see Section 3.5.7), is expected to be a fairly rapid process, depending however on the hydraulic gradients. However, for packaging and waste matrices placed in the silo, the turn-over time for water is expected to be determined by the slow diffusive flow of water through the bentonite and the silo bottom and lid.

Handling in the safety assessment SR-PSU

The process of water flow under saturated conditions will be decisive for the safety assessment. The rate of water flow through the waste form is expected to vary with time due to expected changes in hydraulic gradients in the surrounding rock and through successive degradation of the waste and barriers.

Water transport under water saturated conditions is expected to start shortly after repository closure. The time for full saturation of the different parts of the repository has been discussed in Section 3.3.1.

Handling of uncertainties in SR-PSU

The uncertainty in the rate and pattern of water flow in the different parts of the SFR repository under saturated conditions is treated by analysing different scenarios with numerical models.

Uncertainties in mechanistic understanding

The processes involved in the flow of water under saturated conditions are well understood.

Model simplification uncertainty

The impact of model simplifications is transparent and the overall impact on the safety assessment is treated by analysing different scenarios with numerical models.

Input data and data uncertainty

Input data are reasonably well known and data uncertainty is documented in the Data report (SKB 2014c).

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.4 Mechanical processes

3.4.1 Fracturing

Overview/general description

The physical condition of a waste form is determined by the distribution of stresses in the waste and the extent of deformation. Although some fractures may occur during the operating period of SFR, for example due to shrinkage caused by concrete dry out, the majority of fracture-generating processes are expected to occur post-closure. All types of volume change result in changes in the stress distribution, which may lead to the fracturing of the waste form. However, fracture-generating processes and the stress-strain response are somewhat different for cementitous and bituminised matrices.

The cement matrix is an anisotropic, heterogeneous material with internal flaws consisting of interfacial voids between the matrix and the coarse aggregate. However, when the bulk size of the cement exceeds that of the aggregate significantly, it is generally approximated as a uniform material. The internal flaws and fractures that exist prior to loading are usually the starting points for fracturing processes and the fractures are expected to propagate perpendicular to the load when subjected to tension. The cement matrix will exhibit a quasi-brittle response to tensile stress-deformation, i.e. a gradually decreasing stress after the peak load (Shah et al. 1995). The typical stress-strain curve can be divided into three different phases during deformation. The initial linear elastic response is characterised by the initiation and propagation of internal flaws. This stage is followed by a non-linear phase where the internal fractures propagate and localise into major fractures as the load increases. After the peak load has been reached, the fracture continuously propagates and opens, even with a decreasing load. Although, reinforcement has little effect on the initiation of fractures, it provides resistance to the propagation and opening of fractures.

Fractures in a cement matrix can occur either as structural fractures, due to impact from mechanical loads, seismic activity or foundation shifting, or as intrinsic fractures due to various types of dimensional changes. The intrinsic fractures can occur during the initial plastic state through shrinkage and early thermal fracturing. In mature cement, intrinsic fractures can result either from normal mechanisms as creep, thermal expansion/contraction or drying shrinkage or from chemical degradation mechanisms, such as alkali–aggregate reactions or corrosion of reinforcement.

Pure bitumen is elastic, but can be subject to brittle failures at low temperatures (below –10°C) (Portillo and Cebon 2013). The low brittle-to-ductile transition temperature indicates that the material response will be elastic-plastic. A bitumen matrix can be viewed as a fairly continuous phase with no initial internal flaws. In bituminised waste, on the other hand, fracture propagation will occur on a micro-nano scale due to the embedded waste particles. Fractures will also arise due to the swelling of the waste particles as they absorb water. Experiments shows higher water uptake at 3 degrees than at 20 and 30 degrees (Brodén and Wingefors 1992). Interconnected porosity can be expected if bitumen cannot fill the space between the swelling waste particles.

Fractures reduce the structural integrity of both types of waste matrices and increase transport through the waste form. Although the hydraulic and mechanical processes are related in principle, they are often treated separately. Both for the cement and the bitumen matrices, the hydraulic consequences of fractures depend on the size and orientation of individual fractures and the connectivity between individual fractures. Enhanced fluid pressure in a single fracture decreases the effective normal stress across the fracture through fracture widening. The resulting change in hydraulic conductivity is expected to be fully elastic. Although local fracturing within a waste form will not affect the global advection, the fracture pathways through the waste form may enhance the leaching of radionuclides. Additionally, in the case of the cement matrix, the fractures may increase the dissolution rate of cement-specific minerals, which in turn may accelerate the degradation of the waste form and subsequently increase the sensitivity of the system to fractures.

Several mechanisms that could lead to the fracturing of the waste form have been identified

- Formation of ettringite see Section 3.5.5 and Section 4.4.5.
- Shrinkage due to hydration of cement matrix see Section 3.5.5.
- Gaseous pressure see Section 3.5.10.
- Swelling of ion exchange resins and evaporator concentrates see Section 3.5.7.
- Freezing see Section 3.2.2.
- Formation of corrosion products with higher molecular volume than starting material, see Section 3.5.9.
- External load from e.g. rock fallout on waste containers in the BLA (see the Geosphere process report (SKB 2014e)) or earthquakes (see the Geosphere process report (SKB 2014e)).

Dependencies between process and waste form variables

The interactions between the process and the waste form variables defined in Section 2.1.2 are summarised in Table 3-9.

Geometry. Volume changes alter the stress distribution in the waste form, and may lead to fracture formation. The mechanical response of the waste form is also largely governed by the initiation and propagation of the internal fractures and flaws during loading. Thus, the porosity and the pore characteristics of the waste form determine the sensitivity to various fracture-generating processes. Fractures created by fracturing will in turn affect the porosity.

Radiation intensity. The radiation intensity has an indirect influence on the fracturing through gas formation and pressure build-up. Irradiation of bitumen may generate radiolysis gases. At higher radiation intensities, the gases may form bubbles, which could lead to the swelling and fracturing of the bitumen matrix. Cement is not considered to be sensitive to the low radiation intensities prevailing in SFR.

Table 3-9. Direct dependencies between the process "Fracturing" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry changes may result in fractures.	The swelling of bituminised ion exchange resins have been assessed.	Yes. Fracturing will create fractures and thus affect the geometry.	Variations in hydraulic conductivity and diffusivity is accounted for.
Radiation intensity	No. But indirectly via gas variables, since irradiation of bituminised waste can produce gases causing pressure build-up.	Not relevant. Radiation effects judged to be negligible at absorbed doses less than 0.1 MGy. Majority of SFR-waste has long-term doses less than 0.1 MGy.	No.	Not relevant.
Temperature	Yes for bitumen.	Handled as fast release of radionuclides from the bitumen waste form.	No.	Not relevant.
Hydrological variables	Yes.	Freezing is deemed to cause severe damages.	No. Indirectly influenced by geometry, fractures will affect the hydraulic conductivity.	Not relevant.
Mechanical stresses	Yes.	Not specificly handeled gives consequences for hydraulic conductivity and diffusivity.	Yes.	Neglected. Not important compared to other influences.
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes.	Not specificly handeled gives consequences for hydraulic conductivity.	No.	Not relevant.
Water composition	No.	Not relevant.	No.	Not relevant.
Gas variables	No, only indirectly via mechanical stresses.	Not relevant.	No.	Not relevant.

Temperature. Although all chemical processes show a temperature dependency *per se*, these effects are indirect and less important than the effect of freezing in the temperature range expected over the lifetime of the repository.

Hydrological variables. The degree of saturation determines the rate of several degradation processes. Pressure and flow will influence chemical degradation to a lesser degree and indirectly the subsequent chemical-induced fracturing. The extent and connectivity of fractures will influence the flow pattern in the repository. However, flow patterns will only be affected at a late stage when the outer barriers and packaging have failed.

Mechanical stresses. Tensile deformation, due to processes that change the internal volume, and externally applied loads will create mechanical stresses, which may lead to fracture formation.

When the peak load is exceeded, the occurrence of fractures will gradually reduce the mechanical stress.

Radionuclide inventory. The radionuclide inventory is not believed to influence fracturing, and fractures do not influence the radionuclide inventory.

Material composition. The composition of the waste form will determine the fracture evolution from mechanical load. The condition and composition of the ion exchange resin, in terms of residual water, irradiation, additional chemicals etc, indirectly determine the degree of swelling. Although organic material may generate gas, the main process that will lead to gas pressure-induced fracturing is metal corrosion.

Water composition. Water composition has an indirect influence on fracture formation, as it can affect the degradation of the matrix materials, and therefore the material composition and geometry. Sulphate is of particular importance, as it causes the formation of cement minerals that are associated with volume expansion. Conversely, fractures will influence the water composition locally through the accelerated dissolution of certain minerals. Again this is an indirect influence via hydrological variables.

Gas variables. Gas pressure and gas composition can indirectly affect the fracturing via the mechanical stresses of all the waste forms. The presence of carbon dioxide may enhance the formation of carbonate-rich minerals in cement, such as calcite, monocarboaluminate and thaumasite, which may lead to clogging of pores and volume changes of the cementitious waste form. Pre-existing fractures will affect the transport of gases, but not the composition of the gases.

Boundary conditions

The physical boundaries of the waste form are expected to be in contact with water early after repository closure and completely saturated a short time later.

During glaciations, fractures will be subject to changes in mechanical loading, which will affect their hydraulic apertures and lead to increased or decreased transmissivity.

Model studies/experimental studies

The fracturing of bituminised waste following water uptake has been thoroughly assessed in Sercombe et al. (2006) and Gwinner et al. (2006). The diffusion of water, the long-term response of the bitumen matrix and the resultant transport properties for encapsulated radionuclides are well characterised. However, only a few attempts have been made to derive the magnitude of the corresponding swelling pressures, which could result in fracturing of waste containers or barriers in the repository. Recent research focussed on swelling pressures from bituminised waste with embedded salts has been performed in Belgium (Valcke et al. 2010, Mariën et al. 2013). A few studies have been done on pressure build-up from waste containing ion-exchange resins in Finland, Sweden and Japan (Valkiainen and Vuorinen 1985, 1989, Nilsson et al. 1988, Masuda 1992). The consequences of bituminsed ion-exchange resins swelling due to water uptake have been characterised in a simplified model (Pettersson and Elert 2001) using the maximum theoretical volume increase. The maximum swelling data are based on Nilsson et al. (1988) which considers dry resins. The resins in SFR will contain residual water and will not therefore swell to the same degree. However, other studies have emphasised significant variations in swelling, arising from the waste composition, type of bitumen, experimental set-up etc, and also conclude that irradiation may increase the swelling capacity.

A chemical activity gradient and tendency for volume increase will lead to a significant build-up of an osmotic pressure in a completely confined structure, which could result in the containers or barriers of the repository fracturing. However water uptake, which causes the volume increase, and the corresponding swelling pressure are inversely proportional (Nilsson et al. 1988), i.e. in a less confined structure where the exchange resin and the bitumen is allowed a partial volume increase, the maximum swelling pressure will be substantially lower. In Snellman and Valkiainen (1985) the swelling pressure was reported to be reduced by a factor of 5–10, depending on the type of exchange resin and pre-treatment, when the exchange resin was subjected to a volume increase of 10%. For even larger volume increases of 20–30%, the corresponding swelling pressures decreased by a factor of 50–100. Thus, the available void volume will, strongly influence the pressure build up and the formation of fractures. Although no unambiguous conclusions were drawn regarding fracturing due to the swelling in Pettersson and Elert (2001), it was noted that for the waste type F.18, the theoretical volume increase is twice the available void volume in the container. However, since the actual volume increase to fill pre-existing void is almost 40%, the chemical activity gradient, which drives the diffusion of water and the swelling, will have decreased and the remaining swelling pressure is significantly lower and will not necessarily have any detrimental impact. Nevertheless, hitherto there has been no analysis of the structural effects and corresponding fracturing.

Gas production and consequences thereof has been studied in Moreno et al. (2001). For a further discussion see Section 3.5.10. Fracturing due to freezing/thawing has been addressed in Emborg et al. (2007). For a further discussion see Section 3.2.2.

The long-term chemical degradation of the repository and the cement-encapsulated waste has been described using various models (Höglund 2001, Gaucher et al. 2005, Cronstrand 2007). For a further discussion see Section 3.5.5 and Section 4.4.5.

Natural analogues/observation from nature

Natural analogues have been presented for both cement and bituminous marl, but with limited relevance for fracturing processes. The main emphasis in the studies performed has been the long-term chemical stability and the sealing of tectonically reactivated fractures by the precipitation of secondary phases. However, the natural analogue studies have not focussed on to fracture-generating processes relevant to the waste form in the repository, such as freezing, gaseous overpressure, water uptake or ettringite formation.

Time perspective

Fractures will exert an increasing influence on the long-term stability of the repository over its lifetime. However, the first permafrost at repository depth will have such detrimental consequences for all cement-based structures in the repository that further assessment of fracturing processes is not deemed relevant.

Although gas formation is assumed to continue for thousands of years after the repository is completely saturated with water, the maximum pressure build-up associated with expulsion of water will be reached much earlier (Moreno et al. 2001). However, since the pressure build-up will depend on the transmissivity, it is not feasible to assign an exact numerical value to it.

Moreover, a chemically degraded concrete will be more sensitive to mechanical stresses and more likely to fracture. However, according to available studies, the waste matrices and repository walls are predicted to be chemically stable during the period from post-closure to the point where the freezing–thawing will affect the repository.

Handling in the safety assessment SR-PSU

Fracturing is handled by choosing appropriate hydraulic conductivity and diffusivity values in the i.e. hydrogeological, concrete degradation and radionuclide transport modelling.

Handling of uncertainties the safety assessment SR-PSU

Uncertainties in mechanistic understanding

The mechanics of concrete fracture processes is an established field of research; however, the focus has been on stress response due to tensile load, rather than from internal chemical degradation or gas production. Hence, for most processes there is only a weak preliminary understanding of the coupling between stress due to internal volume-changing processes and the occurrence of fractures.

The mechanistic understanding of freezing complies with the requirements of a safety assessment.

The ettrningite mineral occupies a larger molar volume than the initial mineral. However, there is still controversy if ettringite formation causes macroscopic or microscopic expansion (Skalny et al. 2003).

The mechanistic understanding of water uptake of ion exchange resins is sufficient for the purposes of a safety analysis, however the swelling associated with evaporator concentrate has been examined less thoroughly.

Although the production of gas due to corrosion is a well-defined process, the corrosion rates will be strongly influenced by the pH and pore water composition. However, the understanding of the process complies with the requirements of a safety assessment, see Section 3.5.9.

Model simplification uncertainty

The uncertainties regarding freezing/thawing events are covered by conservative assumptions regarding the incompressibility of ice in relation to CSH[4]-gel and the slow pace of the freezing/expansion process.

The models describing the degradation of cement are based on a thermodynamic equilibrium approach and determine global averages in fairly large cells. The degradation mechanisms assume thermodynamic equilibrium and neglect kinetically controlled reactions. The volume changes due to the formation of ettringite are exclusively associated with expansion and simplified by assuming a large molar volume. The formation of expansive minerals is assumed to continue irrespective of the increased pressure or altered conditions for precipitation. An overall uncertainty lies in the approach of estimating the evolution from global averages, rather than from a microscopic understanding.

Although the process by which ion exchange resins re-saturate and swell is fairly well understood, the models are simplified by conservative assumptions in order to address the in-homogenous nature of the waste. A maximum theoretical volume increase derived from non-irradiated dry resins is selected to represent the swelling of an irradiated ion exchange resin containing residual water. The swelling of evaporator concentrate has been estimated from the volume increase when NaNO_3 is dissolved to form a saturated solution. Overall, the swelling of bituminised waste is to a large extent waste and process-specific and has been covered by rather conservative assumptions.

Input data and data uncertainty

Input data and data uncertainty for the generation of fractures through freezing are discussed in Emborg et al. (2007).

Parameter uncertainty in the assessment of expansion due to ettringite formation lies in transport parameters such as diffusivity, molar volume of mineral phases and the consistency of the employed thermodynamic database. Input data and data uncertainty are discussed in Cronstrand (2007).

The swelling due to water uptake by ion exchange resins is estimated from a conservative maximum volume increase (see Model simplification uncertainty).

The corrosion rates for gas production are assumed to be constant over time and the model does not consider their dependence on pH and chloride content.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5 Chemical processes

3.5.1 Advective transport of dissolved species

Overview/general description

There is a range of unconditioned and conditioned waste forms in SFR that possess very different hydraulic properties. Large heterogeneities are also present within the waste forms of a specific type, as they may contain a wide range of different waste materials as well as cement or bitumen conditioning for stabilised wastes. Solutes dissolved in the water can be transported to and from the interior of the waste forms via advection and diffusion. Diffusion is discussed in Section 3.5.2. See also Section 3.6.2 for the handling of radionuclide transport in the waste form.

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[4] Abbreviations commonly used in cement science for the clinker components:
$C = \text{CaO}$, $S = \text{SiO}_2$, $A = \text{Al}_2\text{O}_3$, $F = \text{Fe}_2\text{O}_3$, $H = \text{H}_2\text{O}$, $C\hat{s}H_2 = \text{CaSO}_4\cdot 2\text{H}_2\text{O}$, $N = \text{Na}_2\text{O}$, $K = \text{K}_2\text{O}$

Advective transport of dissolved species

In this section, advection refers to the transport of a dissolved substance by the bulk flow of water. The evolution of the groundwater flow conditions in the waste forms will have a direct impact on the advective transport of dissolved species. The processes of water transport under unsaturated and saturated conditions are further described in Section 3.3.1 and Section 3.3.2, respectively. Groundwater flow is driven by pressure gradients and is affected by the properties of the media, such as the permeability, porosity and presence of fractures, and the fluid properties, such as the density and viscosity.

The relative importance of advection and diffusion for solute transport through a specific waste form is obtained implicitly in the solute transport models used in SR-PSU, which include both mechanisms. It can also be evaluated by means of the dimensionless Péclet number (Equation 3-5), which provides a measure of the ratio between the rates of these two transport mechanisms. Thus, systems with a Péclet number of 1 have equal advective and diffusive transport rates.

$$\mathrm{P_e} = vL/D \qquad \text{Equation 3-5}$$

where $\mathrm{P_e}$ is the Péclet number, v ($\mathrm{m^3/m^2/s}$) is the bulk velocity, L (m) is the distance in the medium and D ($\mathrm{m^2/s}$) is the effective diffusivity in the medium.

Unconditioned waste deposited in BLA is likely to be exposed to advective conditions throughout the lifetime of the repository, with the obvious exception of frozen periglacial conditions (see Section 3.2.2). Transport in conditioned wastes (e.g. all wastes in the BMA and the silo) may be diffusion controlled under initial state conditions. However, these conditioned waste forms may undergo chemical degradation (see Section 3.5.5) and physical changes such as swelling (see Section 3.5.7) over time that affect their pore characteristics and hydraulic properties. Therefore, the extent of both advective and diffusive transport of dissolved solutes is expected to change over time.

After the operational period when pumping ceases, the void spaces in the repository will fill with groundwater primarily via gravitational flow, with the lower parts filled first (see Section 3.3.1 for a description of water uptake during unsaturated conditions). The time for the voids to fill is determined by the void volume and the rate of groundwater seepage. During the resaturation period, the advective transport will be directed inwards from the surrounding rock, and hence dissolved species from the waste form are not expected to be discharged through the barriers to the groundwater system.

Following this initial period, when the vaults, barriers, backfill, and waste packages have become saturated with groundwater, the extent and direction of advective transport of substances is governed by their dissolved concentrations and the water flow.

Changes in the external climate during the first 1,000 years post closure are not expected to affect the temperature of SFR to any significant extent. However, during periods of permafrost and glaciation, temperature in the repository will be so low that the entire repository will freeze and water flow will virtually stop, see Section 3.2.2. The internal freezing may cause penetrating fractures in conditioned waste forms, presumably causing important structural deterioration, see Section 3.4.1. Hence, the waste forms may deteriorate to such a degree that their function as barriers against advective flow is severely compromised.

Hydrodynamic dispersion

The transport of solutes by advection is also affected by hydrodynamic dispersion, which here refers to the net effects of small-scale variations in the flow field, in combination with molecular diffusion and mechanical mixing. Dispersion results in a spread of dissolved substances relative to the advective bulk flow of water, and can occur in the direction of flow or perpendicular to the flow direction. The dispersion effect is caused by processes such as:

- Velocity distribution in single flow channels.
- Mixing of water transported by different flow channels.
- Distributed flow channel sizes (pore sizes) leading to different velocity distributions in different flow channels.
- The presence of materials with different hydraulic conductivities giving rise to distributed flow velocities in different materials.
- The effects of diffusion processes caused by Brownian motion of dissolved substances in the water.

In a single flow channel (or pore), the highest velocity is typically found in the centre of the flow channel and the velocity approaches zero near the channel wall. In materials with distributed channel (or pore) sizes, the velocity distribution in each of the channels will be different, with the highest velocities expected in the largest channels. When materials with different hydraulic conductivities are present and water flow is parallel to the interface between the different material boundaries, the flow will be distributed essentially in proportion to the hydraulic conductivities. For flow perpendicular to the material boundaries, the flow will be essentially equal in the different materials, governed by the least permeable material, and the impact on the dispersion processes will be small.

In solute transport modelling, dispersion effects are often represented mathematically by a dispersion factor, which intends to capture the dispersive effects on scales beneath that modelled explicitly by the flow field. For porous media, dispersion is sometimes represented using a Fickian approach in modelling, assuming diffusion-like behaviour (see Section 3.5.2) with a flux proportional to the gradient in solute concentration. However, this approach is not necessarily accurate because it does not explain the observed scale-dependency of dispersivities. Quantifying dispersion for inclusion in simplified advection–dispersion transport models therefore involves conceptual uncertainties.

Dependencies between process and waste form variables

Table 3-10 shows how the processes influence and are influenced by the waste form variables defined in Section 2.1.2.

Influence by geometry. No direct influence has been identified. Advection will be affected indirectly through water transport (Section 3.3.1 and Section 3.3.2), by the geometric dimensions, porosity and pore characteristics of the waste form and the conditioning matrix, as well as the frequency and size of fractures. The porosity and pore characteristics affect the permeability of the material and thereby the hydraulic conductvity. The thickness of the waste form in the direction of flow affects the flow resistance and thereby the hydraulic head gradient.

Residual metals from e.g. stirring equipment that is used for mixing during conditioning of the waste form, may also affect advection indirectly through water transport, by introducing heterogeneity and increasing the likelihood of a higher porosity in the vicinity of the metal surfaces. Therefore preferential pathways with less flow resistance may be created.

Dynamic changes such as chemical degradation, swelling of the waste form, and corrosion of residual metals will further affect the geometric parameters, which will in turn influence advective transport indirectly through water transport (see further discussion in Section 3.5.5, Section 3.5.7, and Section 3.5.9).

Influence on geometry. No direct influence has been identified. Advection will not have a direct effect on geometry. Indirect effects due to advection-induced changes in the water composition that may influence dissolution, precipitation and recrystallisation reactions and corrosion of residual metals are addressed in Section 3.5.5 and Section 3.5.9 respectively.

Influence by radiation intensity. No direct influence has been identified.

Influence on radiation intensity. No direct influence has been identified.

Influence by temperature. No direct influence has been identified. Temperature may affect water transport (Section 3.3.1 and Section 3.3.2) by thermal convection through changes in the fluid density. This would indirectly influence advective transport. This effect is judged to be negligible due to small temperature variations within the waste forms and between different parts of SFR.

Influence on temperature. No direct influence has been identified. Heat may be redistributed in the waste forms as a result of water transport (Section 3.3.1 and Section 3.3.2), and the mixing of different waters. Heat transport is further considered in Section 3.2.1.

Influence by hydrological variables. Yes, a direct influence has been identified. Advective transport of solutes in the waste forms is controlled by the magnitude, direction and distribution of water flow driven by pressure differences. Other hydrological variables have indirect influences on advection through the process of water transport, a process further described in Section 3.3.1 and Section 3.3.2.

Table 3-10. Direct dependencies between the processes of "Advective transport of dissolved species" and the defined waste form variables and a short note on the handling in SR-PSU.

Parameter	Variable influence on process		Process influence on variable	
	Influence present?	**Handling of influence**	**Influence present?**	**Handling of influence**
Geometry	No. Waste form dimensions, porosity and pore characteristics affect the hydraulic properties (i.e. hydraulic conductivity in stabilised waste forms), which influence advective transport indirectly through water transport.	Not relevant.	No. Indirect effect of advection-induced changes in water chemistry considered in Section 3.5.5 and Section 3.5.9.	Not relevant.
Radiation intensity	No.	Not relevant.	No.	Not relevant.
Temperature	No. Indirectly temperature affects thermal convection of groundwater through changes in density.	Not relevant.	No. Indirectly temperature is influenced by redistribution of heat due to water transport, see Section 3.2.1, 3.3.1 and 3.3.2.	Not relevant.
Hydrological variables	Yes. Magnitude, direction and distribution of water flow have a direct influence on advective transport.	Magnitude, direction and distribution of water flow are included in the transport modelling.	No.	Not relevant.
Mechanical stresses	No. Indirectly mechanical stresses may affect porosity, pore geometry and initiate fracturing, and therefore create preferential paths for water transport.	Not relevant.	No. Indirectly, advection-induced changes in the aqueous speciation may create stress fields through dissolution–precipitation reactions.	Not relevant.
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	No.	Not relevant.	No. Indirect influence on material composition through advection-induced sorption, dissolution and recrystallisation.	Not relevant.
Water composition	Yes. All hydrological parameters being equal, the water composition determines the magnitude of advective transport of solutes. Indirectly, the density and viscosity of water may affect water transport through changes in hydraulic conductivity.	Dissolved concentrations are considered in transport calculations. Indirect influence is handled under water transport in Section 3.3.1 and Section 3.3.2.	Yes. The water composition is influenced by advective transport of dissolved species, colloids and particles, and by mixing of different waters. Indirectly also via dissolution–precipitation, see Section 3.5.5.	Advection-induced changes in water composition is included in transport modelling.
Gas variables	No.	Not relevant.	No.	Not relevant.

These include: the water pressure distribution within the waste forms that is a major control of the extent of water transport; changes in the aggregation state of the water which has an obvious influence on water transport, in that the water flow effectively stops upon freezing, e.g. during periglacial conditions. Water pressure may affect the equilibrium position of dissolution reactions, in particular of gases, thereby altering the dissolved concentrations and indirectly (through the variable water composition) the advective transport of dissolved species in the waste forms.

Influence on hydrological variables. No direct influence has been identified. Advection will not affect hydrological variables directly. Indirect effects due to changes in the water composition that influence the freezing point of water are addressed in Section 3.3.2. Indirect effects due to advection-induced changes in the water composition that result in dissolution or precipitation, which may affect the amount of water and degree of saturation are addressed in Section 3.5.5.

Influence by mechanical stresses. No direct influence has been identified. Mechanical stresses may result in changes in the porosity and pore geometry of the waste form through elastic compression and compaction. The importance of this depends on the strength and compaction of the stabilisation matrix material, the mechanical stress applied, etc, and may indirectly influence advective transport through the process of water transport (Section 3.3.1 and Section 3.3.2). This indirect influence may change over time due to interaction with other processes, such as degradation caused by dissolution, precipitation and recrystallisation (Section 3.5.5) and different external load scenarios, e.g. rock fallout (see the Geosphere process report (SKB 2014e)), and the possible mechanical consequences for the waste forms (see Section 3.4.1).

Influence on mechanical stresses. No direct influence has been identified. Advection will not affect mechanical stresses directly. Indirect effects on mechanical stresses due to advection-induced dissolution, precipitation and recrystallisation reactions are addressed in Section 3.5.5.

Influence by radionuclide inventory. No direct influence has been identified. The radionuclide inventory may influence the extent of advective transport indirectly (via the variable water composition) by affecting the dissolved concentrations of radionuclides in the water in the waste form. The speciation and transport of radionuclides in the water phase is handled as separate processes in Section 3.6.1 and Section 3.6.2, respectively.

Influence on radionuclide inventory. No direct influence has been identified. Advection of radionuclides away from the waste form may influence the evolution of the inventory indirectly by promoting further dissolution.

Influence by material composition. No direct influence has been identified. The material composition of cement stabilised waste forms will influence the porosity and pore geometry of the waste form significantly, which affect the extent of water transport (Section 3.3.1 and Section 3.3.2), and therefore has an indirect influence on advection. Residual metals from e.g. stirring equipment that is used for mixing during conditioning of the waste form may further affect advection indirectly through porosity changes upon corrosion of the metal (Section 3.5.9). Material composition may also affect the extent of advection indirectly as a result of sorption/uptake (Section 3.5.3), dissolution, precipitation and recrystallisation reactions (Section 3.5.5) and the influence of these processes on the aqueous concentration gradients.

Influence on material composition. No direct influence has been identified. Advection will affect material composition indirectly due to sorption (Section 3.5.3), dissolution, precipitation and recrystallisation reactions (Section 3.5.5) resulting from indirect advection-induced changes in the water composition.

Influence by water composition. Yes, a direct influence has been identified. The water composition is a major control of the extent of advective transport of dissolved species through the waste forms. The density and viscosity of the solution may furthermore influence advective transport indirectly, through water transport (Section 3.3.1 and Section 3.3.2), by affecting the hydraulic conductivity.

Influence on water composition. Yes, a direct influence has been identified. Advection affects the water composition through the movement of dissolved chemical species, colloids, particles and dissolved gases. Indirectly, advective transport of dissolved species may induce dissolution, precipitation and recrystallisation reactions (Section 3.5.5) which may influence the water composition.

Influence by gas variables. No direct influence has been identified. The presence of gas in the pores of the stabilised waste forms will influence advection indirectly, through the process of water transport (Section 3.3.1 and Section 3.3.2), by creating locally unsaturated conditions, changing the water flow pattern, displacing pore water, and limiting the accessible pore volume for advection of dissolved species (see Section 3.3.1 for water transport during unsaturated conditions). The occurrence of any connected gas-filled porosity in the waste forms would allow for transport of compounds in gas phase which is described in Section 3.5.10 and Section 3.6.3.

Influence on gas variables. No direct influence has been identified. The advection of dissolved gases away from the source will influence the gas composition and pressure indirectly by promoting further gas dissolution.

Boundary conditions

The boundary conditions for the processes of advective transport of dissolved species in the waste forms are the groundwater composition and the extent and direction of water flow at the physical boundaries to the surrounding packaging, and the solid/water interface within the waste form over which exchange of mass and heat occur.

Model studies/experimental studies

According to the best of our knowledge there are no experimental studies investigating advective transport and solute dispersion through the waste forms at SFR. There are however experimental studies on permeability in unfractured and fractured cement (e.g. Langton and Kosson 2009, NEA 2012b, and references therein) that may be of some relevance for evaluating advective transport in the waste form and waste packaging materials. Concrete plugs are present in the Äspö HRL, and have been examined with respect to water flow (SKB 2010a).

There are several modelling studies evaluating the role of advection and dispersion processes within the waste in SFR. These include radionuclide transport modelling (e.g. Lindgren et al. 2001, Thomson et al. 2008a, see further Section 3.6.2), models for solute transport involved in concrete degradation (e.g. Cronstrand 2007, Höglund 2001, see also Section 3.5.5), and modelling of the redox evolution (e.g. Duro et al. 2012c, see also metal corrosion in Section 3.5.9). The advective transport models rely on assumed or modelled water flow rates. Underlying hydrogeological modelling studies are further described in Section 3.3.1 and Section 3.3.2.

Natural analogues/observations from nature

Natural analogues of advection and dispersion and observations of these processes in nature are common but are not considered here due to the detailed theoretical understanding of the process of advection and the cautiously chosen handling of dispersion.

Time perspective

Advective transport by flowing groundwater will occur within some parts of SFR, at least, over its lifetime. Dynamic changes in hydraulic properties are expected, particularly from freeze damage (resulting in e.g. fracturing) during periglacial permafrost. Solute transport in the pores of stabilised waste forms, which is initially diffusion-controlled, may therefore become advection-dominated as a result of dissolution reactions and freezing. Solute transport in advective flow paths may also become diffusion-controlled as a result of precipitation of secondary mineral phases, in particular downstream in alkaline discharge waters.

Handling in the safety assessment

Advective transport is a core consideration in the safety assessment of solute transport in all SFR compartments, including the waste forms. The process is incorporated in the governing equations used for radionuclide transport modelling. A coarsely discretised compartment approach is applied in modelling, which implies a conservative estimate of dispersion. The numerical dispersion introduced by the relatively coarse discretisation of the waste form is greater than the expected physical dispersion.

Solute advective transport is considered in concrete degradation (e.g. Cronstrand 2007, and redox evolution (e.g. Duro et al. 2012c) modelling.

Handling of uncertainties

Uncertainties in mechanistic understanding

The process of advection can be considered mature science and the conceptual uncertainties are small.

Model simplifications uncertainties

The model simplifications relate to the model representation of the complex geometries of the waste forms and the inherent heterogeneities introduced by variations in material composition, the presence of residual metal equipment, joints between construction elements, occurrence of fractures and fractures and the uncertainties related to the prediction of change of material properties in response to ongoing degradation processes over time. The assignment of boundary conditions to reflect the changes of groundwater chemical composition over time may introduce additional uncertainties.

These model simplification uncertainties may be handled by choosing pessimistic hydraulic gradients and conductivities for the waste forms in the transport modelling. In SR-SPU a more pessimistic handling is chosen, by applying a mixed tank compartment model approach.

Input data and data uncertainties

Uncertainties in the transport properties of the different types of waste forms are significant, e.g. due to heterogeneities in the waste form and the presence of residual metal equipment. The uncertainties in input data and data uncertainties are handled by assigning pessimistic values in modelling. The sensitivity to input data is checked by parameter variations and scenario analysis.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.2 Diffusive transport of dissolved species

Overview/general description

A wide range of unconditioned and conditioned waste forms are present in SFR, and these possess very different diffusive properties. There is also large heterogeneity within individual packaging when they contain a variety of waste materials and conditioning. Transport in conditioned wastes in e.g. the BMA and the silo is likely diffusion controlled under the initial state conditions. However, the conditioned waste forms may undergo chemical degradation (see Section 3.5.5) and physical changes such as swelling (see Section 3.5.7), which may affect the pore characteristics of the conditioning and result in altered properties that influence both diffusive and advective transport of dissolved solutes. Unconditioned waste deposited in BLA is likely to be exposed to advective conditions throughout the lifetime of the repository with the obvious exception of frozen periglacial conditions (see Section 3.2.2). Determining whether transport in a specific type of waste form is or will be dominated by diffusion is therefore difficult and requires careful consideration of these transient effects as well as the initial presence and frequency of heterogeneities and preferential flow paths.

Diffusion of uncharged molecules

Concentration gradients of uncharged molecules in solution result in the diffusion of the molecules from higher to lower concentration regions. This process is driven by the Brownian motion of the molecules and is described well by Fick's laws for dilute single phase systems. The process of diffusion is species specific, and can therefore transport different species in different directions simultaneously, according to their concentration gradients. In one spatial dimension, the molecular flux (J; mole/m^2/s) can be expressed in terms of the diffusivity (D; m^2/s) and the concentration gradient ($\mathrm{d}c/\mathrm{d}x$; mole/m^3/m) by Fick's first law:

$$J = -D\,\mathrm{d}c/\mathrm{d}x \qquad \text{Equation 3-6}$$

Fick's first and second laws describe diffusion in a homogeneous medium, such as a liquid. In heterogeneous porous media such as the cement conditioned waste forms, the diffusion path is longer than for free diffusion in a solution. The actual path length in relation to the geometrical distance in the porous medium is referred to as the tortuosity (τ). The rate of diffusive transport is also affected by changes in the pore size or "bottle necks" along the diffusion path, represented by the constrictivity factor (δ_D). The diffusive flux through the pores in a porous medium is therefore less than that in a free solution. This is accounted for in the pore diffusivity (D_p; m^2/s), which is less than the free diffusivity (D_0; m^2/s) for the same species:

$$D_p = D_0 \delta_D / \tau^2 \qquad \text{Equation 3-7}$$

The term δ_D/τ^2 is commonly referred to as the formation factor and is derived experimentally as one entity (Höglund 2001).

Furthermore, the presence of a solid phase restricts molecular movement to the saturated pore space (i.e. excludes the solid volume). This is accounted for in the effective diffusivity (D_e; m^2/s) which also takes the transport porosity (ϕ_m; m^3/m^3) of the medium into account. The effective diffusivity in the porous medium is therefore less than the pore diffusivity and can be written:

$$D_e = D_p \phi_m \qquad \text{Equation 3-8}$$

In cement stabilised wastes, the total porosity of the cement will be the sum of the capillary, gel and contraction pores, which may each be present at a few percent of the total volume (Höglund 2001). Gel pores are the smallest, and typically fall into the size range 0.5–10 nm, while capillary pores are in the range 0.01–10 µm. Contraction pores are larger than capillary pores and are effectively voids initially filled with trapped air (Brandt 2009). The effective diffusivity of chemical species will depend on the types of pores present, with the greatest diffusivity expected in the capillary and contraction pores. Granite or silica ballast in cement offers a negligible diffusion pathway. Although not always used as a component of the cement conditioning, some types of waste forms contain ballast material. The influence of ballast material may furthermore be significant for diffusive transport in concrete packaging (Höglund 2001), which is described in Section 4.4.2. The effect of ballast material on diffusion in the waste form and packaging is handled by selecting appropriate effective diffusivities of the material. In the preparation of the waste forms containing ion-exchange resins, metal stirring equipment is used. This equipment remains in the waste form after disposal and the cement around these stirrers may be of lower density than the bulk cement, as a consequence of water separation during early hydration. Different thermal expansion coefficients in cement and steel may further create inhomogeneities at the interface between the materials during early heat generation and subsequent cooling, possibly creating pathways of increased diffusive or advective transport. Furthermore, corrosion of these and other metals in the wastes (see Section 3.5.9) may eventually create void space that provides pathways for diffusive or advective transport.

Transport by diffusion is of particular importance in systems with negligible advective transport. The relative importance of advective and diffusive transport can be evaluated by means of the dimensionless Péclet number (see Section 3.5.1) which provides a measure of the ratio between the rates of these two transport mechanisms. Information on which of the processes of advection and diffusion dominates solute transport in a specific waste form (i.e. the Péclet number) is obtained implicitly in the transport models used in SR-PSU, which include both mechanisms.

Diffusion of ions

In real world systems, many chemical species are ionic in nature, meaning that diffusion will be affected by electrostatic interactions between dissolved ions (e.g. Galíndez and Molinero 2010). Divergent diffusion of different ions, due to differences in their concentration gradients and diffusion coefficients in the given medium, induces an electric potential and constrains further diffusion. This can be described as the condition of electroneutrality. Therefore, ion diffusion is not predicted accurately using Fick's laws, and the more complicated Poisson–Nernst–Planck equations that take ionic effects into account may be more appropriate (Galíndez and Molinero 2010). Diffusion is also constrained by the condition of electroneutrality when diffusive gradients exist counter to one another, for example in a system with an input of KCl at one end and NaCl at the other. Here, the diffusion of each cation is influenced by the diffusion of the other, generating an inter-diffusion coefficient for the cation pair. Where there is a significant difference in the concentrations of the two cations in the system, the inter-diffusion coefficient tends towards the diffusion coefficient of the cation with the lower concentration (Lerman 1988). The Onsager reciprocal relationship allows for more complex inter-diffusion systems to be described (for further details, see e.g. Lerman 1988).

In addition to ion–ion effects, surface–ion interactions can affect diffusion through porous matrices. These are documented well in bentonite clay (e.g. Ochs et al. 2001, SKB 2010a), and to a lesser extent in cement or concrete (e.g. Zhang and Buenfeld 1997, Chatterji 2004). Surface-ion effects occur in small pores with negatively charged surfaces, as found in highly alkaline cement. The first effect, anion exclusion, occurs when the pore size is so small that the electric double layers (EDL) generated by the negatively charged pore surfaces overlap. The EDL is dominated by counter ions, i.e. cations, thus EDL overlap creates a solution phase barrier to anionic species (SKB 2010a). The converse of anion exclusion is enhanced cation diffusion, resulting from the relatively high dissolved cation concentrations generated in the EDL. The high concentration generates a greater diffusion gradient running parallel to the pore surface, enhancing diffusion relative to the bulk solution. Electrical double layers contract with increased ionic strength, thus the ionic strength of the conditioned waste form porewater will influence the extent of both anion exclusion and enhanced cation diffusion.

Chemical impacts of diffusion

All species that undergo Brownian motion, from simple ions to complexes and colloids, undergo diffusion. The geochemical conditions of the waste forms are therefore affected by diffusion, with gradients in pH and Eh resulting in the diffusion of protons, hydroxyl ions, pH-altered species, electron-rich (chemically reduced), and electron-poor (chemically oxidised) species, respectively. These are all chemically labile and their diffusion is distinctly coupled with further chemical reactions as they reach lower concentration zones. Moreover, the diffusion of species arising from the waste form itself, the packaging, barriers and geosphere change the composition of the waste form porewater, which can lead to sorption, precipitation and recrystallisation reactions (see Section 3.5.3 and Section 3.5.5). Diffusion will also disperse elevated concentrations of chemical species originating from the waste, allowing further dissolution to occur (see Section 3.5.5). Diffusion may therefore control the porosity and integrity of the solid phases, which in turn affect the effective diffusivity of species within the system. Depending on the mineralogical changes in the waste form, the effective diffusivity can decrease as well as increase. Despite the dynamic chemical processes within cement and the possibility of the precipitiation of fracture-filling materials such as calcite during interactions with groundwater, the fully hydrated waste form does not have an intrinsic capacity to self-heal. Therefore the possibility of formation of fractures and fractures during degradation of cement waste form matrices cannot be discarded.

Fracture formation

Fractures and fractures have a higher porosity than the bulk material, and therefore introduce paths with a higher effective diffusivity (Equation 3-8) and possibly advective conditions. The extent of fracture formation dictates the importance of these transport paths; fracture density and/or effective diffusivity need to be significantly larger than in the bulk material to have a notable effect on the overall diffusion through the waste form.

Future periglacial periods will cause the waste forms as well as other constructions in SFR to freeze, resulting in possibly widespread penetrating microfracture formation. This may lower the diffusive barrier function of the conditioned waste forms significantly (SKB 2008b).

Dependencies between process and waste form variables

The following table (Table 3-11) shows how the process influences and is influenced by the waste form variables defined in Section 2.1.2.

Table 3-11. Direct dependencies between the process “Diffusive transport of dissolved species” and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Diffusion is proportional to waste form dimensions and is significantly affected by heterogeneities and pore geometry.	Included in the transport modelling.	No.	Not relevant.
Radiation intensity	No.	Not relevant.	No.	Not relevant.
Temperature	Yes. Affects diffusivity. At high temperature gradients even Soret effects may occur.	Not considered due to the largely isothermal conditions in SFR.	No.	Not relevant.
Hydrological variables	Yes. The aggregation state of water directly influences the extent of diffusion.	Changes in effective diffusivity due to water freezing will be included in the transport modelling.	No.	Not relevant.
Mechanical stresses	No. Indirectly mechanical stresses affect porosity and pore geometry, and therefore indirectly the effective diffusivity of species.	Not relevant.	No.	Not relevant.
Radionuclide inventory	No. Indirectly the diffusion of radionuclides is directly influenced by the dissolved concentration which, in turn, is affected by the inventory.	Not relevant.	No. Indirectly diffusion of dissolved radionuclides promotes further dissolution which affects the evolution of the inventory.	Not relevant.
Material composition	No. Indirectly material composition determines the porosity and the pore geometry in the stabilised waste forms.	Not relevant.	No.	Not relevant.
Water composition	Yes. A major control of diffusion in the waste forms.	Included in the transport models	Yes. Affects the water composition through the movement of dissolved chemical species, colloids, particles and dissolved gases in stagnant systems.	Included in the transport models.
Gas variables	No. Indirectly diffusion is directly influenced by the dissolved concentration which, in turn, is affected by the gas variables within the waste form.	Not relevant.	No. Indirectly diffusion of dissolved gases will influence their aqueous concentration which, in turn, affects the gas composition.	Not relevant.

Influence by geometry. Yes, a direct influence has been identified. Diffusion will be affected significantly by the geometric dimensions, porosity and pore characteristics of the waste form and the conditioning matrix, as well as the frequency and size of fractures. The cross-sectional area affects the extent of diffusion, while the thickness of the waste form influences the diffusion path length, and the porosity affects constrictivity and tortuosity of the path, thus the effective diffusivity of species. Narrow pores may also lead to surface-ion effects, i.e. anion exclusion and enhanced cation diffusion.

Residual metals from e.g. stirring equipment that is used for mixing during conditioning of the waste form may affect diffusion directly due to heterogeneities with possible increased porosity in the vicinity of the metal surfaces creating pathways with increased diffusivities.

Dynamic changes such as chemical degradation, swelling of the waste form, and corrosion of residual metals will influence the geometric parameters, which will in turn influence diffusion (see further discussion in Section 3.5.5, Section 3.5.7, and Section 3.5.9).

Influence on geometry. No direct influence has been identified. Diffusion will not have a direct effect on geometry. Indirect effects due to diffusion-induced changes in the water composition that may influence dissolution, precipitation and recrystallisation reactions and corrosion of residual metals are addressed in Section 3.5.5 and Section 3.5.9 respectively.

Influence by radiation intensity. No direct influence has been identified.

Influence on radiation intensity. No direct influence has been identified.

Influence by temperature. Yes, a direct influence has been identified. Temperature will affect the rate of diffusion, with higher temperatures increasing the rate of diffusion due to increased Brownian motion. The Stokes–Einstein relationship explains how the diffusion coefficient varies with temperature and viscosity. This shows that the product of the diffusion coefficient and viscosity of the solution divided by the temperature is constant. However, this simple relationship does not hold true for ionic species. At low concentrations of ionic species, the diffusivity increases by approximately a factor of two between 0 and 25°C (Lerman 1988).

Temperature gradients may also induce changes in chemical potential, creating diffusional gradients (Lerman 1988). This is known as thermal diffusion or the Soret effect. The buffer, backfill and closure process report for SR-Site (SKB 2010a) suggests that a change from ambient temperature to 50–60°C doubles the effective diffusivity of species. This sensitivity to temperature was considered to be too small to be included in the model. The impact of thermal diffusion is judged to be negligible due to the practically isothermal conditions in the SFR repository, at any given time.

Influence on temperature. No direct influence has been identified. Diffusion of dissolved species will not have any direct effect on temperature.

Influence by hydrological variables. Yes, a direct influence has been identified. Diffusion is dependent on the concentration gradient and the pore characteristics of the waste forms, thus hydrological variables directly affect diffusion when there is a change in aggregation state. The freezing of water during glaciation periods will clearly slow the rate of diffusion. Other hydrological variables have indirect influences on diffusion. The total diffusive transport through the solution phase will be affected by the amount of water and degree of saturation, when dissolution is solubility-controlled. Lower amounts of water lead to dissolution of less solid material and therefore diffusion of a smaller amount of dissolved species. Water pressure may affect the equilibrium position of dissolution reactions, in particular of gases, thereby altering the concentration gradients in the waste forms. If large amounts of water flow through the repository, e.g. during post glacial ice melting, the relative importance of diffusion may decrease as advective transport becomes more prominent, an effect that may be quantified using the Péclet number. Therefore, the relative importance of diffusion is dependent on the magnitude, direction and distribution of water flow.

Influence on hydrological variables. No direct influence has been identified. Diffusion will not affect hydrological variables directly. Indirect effects due to changes in the water composition that influence the freezing point of water are addressed in Section 3.2.2. Indirect effects due to diffusion-induced changes in the water composition that result in dissolution or precipitation, which may affect the amount of water and degree of saturation, are addressed in Section 3.5.5.

Influence by mechanical stresses. No direct influence has been identified. Mechanical stresses may influence diffusion indirectly through changes in the porosity and pore geometry of the waste form resulting from elastic compression and compaction. The degree of this impact depends on the strength and compaction of the stabilisation matrix material, the mechanical stress applied, etc. This may change over time due to interactions with other processes, such as degradation caused by dissolution, precipitation and recrystallisation (Section 3.5.5) and different external load scenarios, e.g. rock fallout (see the Geosphere process report (SKB 2014e)) and the possible mechanical consequences for the waste forms (see Section 3.4.1). Except for extreme conditions, which are handled by scenario analyses, the impact of mechanical stresses on diffusion is judged negligible.

Influence on mechanical stresses. No direct influence has been identified. Diffusion will not affect mechanical stresses directly. Indirect effects on mechanical stresses due to diffusion-induced dissolution, precipitation and recrystallisation reaction are addressed in Section 3.5.5.

Influence by radionuclide inventory. No direct influence has been identified. The radionuclide inventory may influence the rate of diffusive transport indirectly by affecting the dissolved concentrations of radionuclides in the water at the source. The speciation of radionuclides is handled in Section 3.6.1.

Influence on radionuclide inventory. No direct influence has been identified. Diffusion of radionuclides away from the source may influence the evolution of the inventory indirectly by promoting further dissolution.

Influence by material composition. No direct influence has been identified. The material composition in cement stabilised waste will significantly influence the porosity and pore geometry of the waste form and therefore has an indirect influence on diffusion. Residual metals from e.g. stirring equipment that is used for mixing during conditioning of the waste form may further affect diffusion indirectly through porosity changes upon corrosion of the metal (Section 3.5.9). Material composition may also indirectly affect the extent of diffusion as a result of sorption (Section 3.5.3), dissolution, precipitation and recrystallisation reactions (Section 3.5.5) and the influence of these processes on the aqueous concentration gradients.

Influence on material composition. No direct influence has been identified. Diffusion will only affect material composition indirectly due to sorption (Section 3.5.3), dissolution, precipitation and recrystallisation reactions (Section 3.5.5) resulting from diffusion-induced changes in the water composition.

Influence by water composition. Yes, a direct influence has been identified. The water composition is a major control of diffusive transport in the waste forms. Diffusion will occur simultaneously in different directions for different dissolved chemical species, colloids, particles, and dissolved gases, according to the individual concentration gradients. Spatial variations in pH and Eh will determine the diffusion of protons, hydroxyl ions, and pH and Eh-sensitive chemical species. The water composition will also influence the diffusivity of individual ionic species due to the constraints of electroneutrality and interdiffusion between the diffusing species. Diffusivity is also related to the viscosity of the solution, which in turn is controlled to a significant extent by the water composition.

Influence on water composition. Yes, a direct influence has been identified. Diffusion affects the water composition through the movement of dissolved chemical species, colloids, particles and dissolved gases in stagnant systems. It also influences the pH, redox conditions, water density and viscosity along their respective gradients. Under advective conditions, determined by the local Péclet number, the influence by diffusion may be less or negligible.

Influence by gas variables. No direct influence has been identified. The presence of gas in the pores of the stabilised waste forms will indirectly influence diffusion by limiting the accessible pore volume for diffusion of dissolved species. The occurrence of any connected gas-filled porosity in the waste forms would allow for diffusive or advective transport of gaseous compounds, which is described in Section 3.5.10 and Section 3.6.3.

The amount, composition, volume and pressure degree of saturation of gases in different parts of the waste forms may indirectly influence diffusion by gas dissolving into the aqueous phase creating concentration gradients of dissolved species. The magnitude, direction and distribution of gas flow will affect the extent to which dissolved gas concentrations vary within the waste form.

Influence on gas variables. No direct influence has been identified. The diffusion of dissolved gases away from the source will influence gas composition and pressure indirectly by promoting further gas dissolution.

Boundary conditions

The boundaries of this process are the surrounding packaging and the solid/water interface within the waste form over which exchange of mass and heat occur.

Model studies/experimental studies

A recent modelling study has highlighted that predictions of concrete evolution are sensitive to the equations used to define diffusion (Galíndez and Molinero 2010). The inclusion of ion–ion interactions, through Poisson–Nernst–Planck equations, alters the predicted concentrations of ions in the concrete porewater as a function of depth and time, compared to the predictions using Fick's laws. This affects when the porewater is predicted to be over-saturated with respect to different solid phases and thus, the patterns of predicted mineral precipitation. Galíndez and Molinero (2010) found that Fick's laws predicted lower sulphate and Ca^{2+} concentrations in cement porewater as a result of lower sodium sulphate diffusion into concrete than predicted by Poisson–Nernst–Planck equations. This meant that while gypsum ($CaSO_4$) precipitation was predicted using Poisson–Nernst–Planck equations, it was not predicted using Fick's laws. The results of the modelling were not verified directly by experimental data, but through acceptable agreement with the output of a different model, STADIUM, involving the same ion–ion interactions (Marchand et al. 2002) that has been validated by experimental data (e.g. Maltais et al. 2004).

Numerous modelling efforts of solute transport have been carried out specifically for SFR safety assessment purposes, evaluating the importance of diffusion and how the process is affected by various parameters. Gaucher et al. (2005) modelled the chemical evolution of the silo near-field by means of reactive transport simulations with the code PHAST. They considered only diffusive transport of radionuclides and performed sensitivity studies considering different diffusion coefficients and their influence on the chemical and hydrological evolution of the silo barriers.

The degradation of cementitious materials in SFR, and the consequences on diffusive properties were also modelled by Höglund (2001) and with respect to climate changes (in particular permafrost) by Cronstrand (2007). The results showed a high degree of leaching in the more exposed parts of the cement whereas the inner parts of the barriers were only significantly affected when the initial concrete was assumed to be fractured.

Pettersson and Elert (2001) studied the long term behaviour of bituminised waste in SFR and indicated that the rate determining step for the release of radionuclide from a bitumen waste matrix is water uptake and establishment of a connected porosity rather than the diffusion of radionuclides.

Radionuclide transport from the waste in SFR has been evaluated in several earlier safety assessments, most recently in the SAFE (Lindgren et al. 2001) and SAR-08 (Thomson et al. 2008a) assessments. Thomson et al. (2008a) presented an AMBER model of the near field of each type of repository and for different scenarios (silo, BMA, 1BTF, 2BTF and BLA). Both advection and diffusion within the waste and from the waste through the repository to the geosphere were considered in the calculations.

Time perspective

Diffusion is anticipated to be a dominant transport mechanism in stabilised waste forms prior to major fracturing events, that for example may result as a consequence of freezing during future periglacial permafrost. The diffusivity of species within the waste form will change with time as the stabilising material evolves, altering the porosity and pore characteristics as well as the gradients of dissolved chemical species against the dynamic ambient groundwater conditions.

Natural analogues/observations from nature

Diffusion is difficult to evaluate quantitatively in natural analogue studies because key factors such as the original inputs and conditions are not well defined. There are several natural analogue studies focussed on the migration of radionuclides. Aspects of diffusion have been studied in the geosphere (matrix diffusion specially), and in clays that may be considered as analogues of bentonite.

Such natural analogues include Cigar Lake (Cramer and Smellie 1994), Poços de Caldas (Chapman et al. 1991), El Berrocal (Rivas et al. 1997), Maqarin (Smellie 1998), among others. However, the published natural analogue studies at these sites are of limited relevance in quantifying the process of diffusion in the engineered cement or bitumen waste matrices at SFR. A recent but not yet published JAEA study of iodine migration in cement at Maqarin may provide additional knowledge and understanding of the process of diffusive transport in alkaline cementitious materials. See further Section 3.6.2 on radionuclide transport in the water phase.

Handling in the safety assessment SR-PSU

Diffusive transport is a core consideration in the safety assessment for solute transport in all compartments in SFR, including the waste forms. The process is incorporated in the governing equations used for radionuclide transport modelling.

Solute diffusive transport is included in concrete degradation (e.g. Cronstrand 2007), and redox evolution, (e.g. Duro et al. 2012c) modelling.

Handling of uncertainties

Uncertainties in mechanistic understanding

Diffusion processes can be considered to be a mature science and the conceptual uncertainties are small.

Model simplifications uncertainties

The model simplifications relate to the model representation of the complex geometries of the waste forms and the inherent heterogeneities introduced by variations in material composition, the presence of residual metal equipment, joints between construction elements, occurrence of fractures and fractures and the uncertainties related to the prediction of change of material properties in response to ongoing degradation processes over time. The assignment of boundary conditions to reflect the changes of groundwater chemical composition over time may introduce additional uncertainties.

The conceptual model that Fick's laws entails is not entirely reliable when the movement of ionic species is involved. Unlike uncharged molecules, ionic species are subjected to various electrical forces which are not accounted for in Fick's laws. The charged nature of the ionic particles is at the origin of various interactions between the drifting particles (ion/ion and ion/solvent interactions). These so-called activity effects become important as the concentration of the various ions in solution increases. The electrical charge of the particles may also contribute to generate specific ion/solid interactions. Despite the relative importance of activity effects and ion/solid interaction phenomena, the most relevant feature which distinguishes ion diffusion from molecular diffusion involves the electrical coupling of the various ionic fluxes. During the diffusion process, the different ionic species tend to drift at divergent speeds (in response to their respective concentration gradients and diffusion coefficients in the medium where the movement takes place) thus inducing electrical imbalances which conspire against the local electroneutrality of the system. Any local excess charge transferred by the ions movement generates an electrical field (referred to as diffusion potential) which tends to restore the electroneutrality by harmonically altering the diffusion rate of all the species involved.

The diffusion transport of ionic species is therefore constrained by the electroneutrality requirement, which should hold at any point of the liquid phase. Electroneutrality is evaluated by lumping the electric contribution of all the species present in solution. This requirement is taken into account by the well known Nernst–Planck equation. Galíndez and Molinero (2010) have demonstrated that neglecting electrochemical diffusion may lead to errors in modelling diffusive reactive transport in cement pastes.

These model simplification uncertainties are handled in the selection of effective diffusivities for the waste forms in the transport modelling.

Input data and data uncertainties

Uncertainties in transport properties of the different types of waste forms are significant, e.g. due to heterogeneities in the waste form and the presence of residual metal equipment. The uncertainties in input data and data uncertainties are handled in the selection of values in modelling. The sensitivity to input data is checked by parameter variations and scenario analysis.

One of the important uncertainty concerns is the quantification of the initial state. Also, experimental values of effective diffusion coefficients are not available for the various waste matrices at SFR. They must be estimated from diffusion coefficient values in free water, and porosity and formation factors of the waste matrices or from generic experimental diffusion data in cement and bitumen (see e.g. CEA 2009, Karlsson and Isacsson 2003, Mattigod et al. 2011, Tuutti 1982).

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.3 Sorption/uptake

Overview/general description

There are many different materials in the SFR repository that can potentially act as sorbents or sinks for radionuclides. The most abundant are cement and different types of steel. These materials are found both in the waste and as packaging materials. The sorption/uptake in bitumen, if any, is negligible compared to concrete and steel see Section 3.5.4.

Corrosion of iron-based materials present in the repository, such as steel, creates new surfaces with high sorption capacity for radionuclides. Sorption onto the corrosion products of the scrap metals present in the wastes could result in a slower release of radionuclides from the wastes. However, in the safety assessment no credit is given for the sorption of radionuclides on corrosion products.

Accordingly, this section focuses on the sorption/uptake of radionuclides and the main relevant chemical elements and species present in cement systems (such as Ca, Mg, sulphate, etc) to hardened cement paste/cement (waste form) and concrete. Since hydrated cement is the most important component of concrete in terms of sorption/uptake, both systems (cement and concrete) are treated together here. The influence of organic complexing agents on radionuclide sorption/uptake is also discussed.

The term ‘sorption’ is often used to describe surface adsorption, i.e. an essentially two-dimensional process, which distinguishes it from three-dimensional uptake processes such as incorporation or diffusion into the solid structure. Surface adsorption is typical for clay or oxide minerals, where solute-surface interactions can be described by the relatively well-defined processes of ion exchange and surface complexation (cf. SKB 2010a, Section 3.5).

Due to the complex nature of hydrated cement paste (HCP), the range of interactions involving dissolved species and solid phases is much broader than in case of clay or oxide minerals. As explained in more detail below, this section is therefore not restricted to surface adsorption, but also encompasses a number of other uptake processes, including three-dimensional incorporation.

Hydrated cement paste (HCP) has several unique features that provide a framework for considering sorption/uptake processes. These are summarised briefly in the following, while a general description of the properties of hydrated cement paste is given in Section 3.5.5:

- HCP is a mixture of several mineral phases with markedly different sorption/uptake properties. An overview of the relevant HCP mineral phases is given in the next sub-section.
- The majority of these minerals are not well crystallised and have a high bulk reactivity. These minerals are subject to continuous compositional changes and related structural rearrangements.
- A distinctive feature of hydrated cement is therefore its evolution with time (or more specifically, its degradation as a function of the amount of percolating water). Typically, this evolution can be described in terms of degradation stages (which are discussed in more detail in Section 3.5.5). Therefore, the overall reactivity and the sorption/uptake properties of HCP are not constant.

Mineral phases

As pointed out above, HCP comprises a range of different minerals, which have different characteristics with respect to the sorption/uptake of dissolved constituents. The major cement solid phases (by mass) are quasi- amorphous CSH phases (Calcium-Silicate-Hydrates) and crystalline portlandite ($Ca(OH)_2$). Minor phases include ettringite (aluminoferrite trisulphate, AF_t), monosulphate (aluminoferrite monosulphate, AF_m), hydrogarnet and hydrotalcite, which are also crystalline. Calcite may form during HCP evolution.

In concrete or mortar, the aggregate material provides additional minerals, such as calcite, quartz, feldspars, mica. The degree to which the surface of these minerals is exposed to the surrounding solution will depend on the type of aggregate and the state of degradation. To a first approximation, it can be assumed that the main phases responsible for the various sorption/uptake processes in concrete and mortar are associated with HCP (possible exceptions for specific radionuclides are discussed in the sections below).

In general, HCP has a high specific surface area; typically > 50 m^2/g. This arises mainly from the CSH phases, which are reported to have a specific surface area of about 150–450 m^2/g (Taylor 1990, Glasser 1993, Tits et al. 2006a). In comparison, the crystalline phases have a much lower specific surface area (e.g. about 6 m^2/g for portlandite).

In terms of sorption/uptake processes, the main minerals in HCP are the quasi-amorphous CSH phases and the crystalline aluminates:

- **CSH phases.** These are the main hydration products of cement clinker and possess a very low crystallinity (gel-like, nearly X-ray amorphous) and a high sorption/uptake capacity. The low crystallinity and imperfect structure of CSH give rise to a high density of reactive sites (Glasser 1993) and do not allow differentiation between surface adsorption and other uptake (bulk-incorporation) processes.
- CSH phases vary in composition and the Ca/Si molar ratio (C/S) changes from about 1.6 to 0.83 during the portlandite leaching phase of cement degradation. The amount and distribution of reactive sites (internal and external), and therefore the sorption/uptake properties of cement are dependent on the C/S ratio. Importantly, the C/S ratio influences the surface charge (zeta potential) of CSH phases during the portlandite leaching stage of cement degradation. At C/S > 1.2, there is a positive zeta potential, while on-going leaching of Ca to C/S < 1.2 removes Ca from silicate binding sites and results in a negative zeta potential. Note that at pH > 13, which precedes portlandite leaching, the low solubility of Ca in the system means that many silicate binding sites are unoccupied and the cement has a negative zeta potential (Pointeau et al. 2006a).
- Sorption on/uptake by CSH can occur through a number of processes, although only a few have been elucidated. Surface sorption can take place by surface complexation on Si–OH groups and/or ion exchange (replacing Ca). Other uptake processes including incorporation into the solid phases are also relevant.
- **Aluminosulphates.** The aluminosulphates ettringite (AF_t) and monosulphate (AF_m) may form during the hardening and subsequent evolution of cement paste, depending on the availability of sulphate and the temperature (cf. Taylor 1990). Ettringite is more common and forms at ambient temperature when sufficient sulphate is available. Structurally, it consists of Ca-aluminate columns with sulphate located in the channels between the columns. Sorption/uptake typically occurs by the displacement of sulphate by other anions and also by the displacement of Ca and Al in the columns.
- Monosulphate formation is favoured by sulphate-limiting conditions and elevated temperatures. It has a similar composition to ettringite but a different structure, with Ca-aluminate platelets and sulphate located in the interlayers. As with ettringite, monosulphate favours crystallochemical substitution reactions.
- **Hydrogarnet** and **hydrotalcite** are Ca- and Mg-aluminates, respectively, and are minor components of HCP. Sorption/uptake is most likely to occur via crystallochemical substitution reactions in both cases.

- **Portlandite** ($Ca(OH)_2$) is an important constituent of fresh (unleached) HCP. In highly degraded HCP, **brucite** ($Mg(OH)_2$) may be relevant. Both minerals are thought to play a minor role for sorption/uptake processes.
- **Calcite** may form during HCP evolution or be present as part of the aggregate material. Sorption/uptake typically takes place through substitution reactions (cf. Curti 1997).

Sorption/uptake of chemical elements and species

Sorption/uptake of aqueous elements and species to HCP occurs via a variety of mechanisms (see e.g. the recent overview by Wang et al. (2013) and the underlying detailed reports by Wang et al. (2009) and Ochs et al. (2011)). In some cases, uptake involves more than one mechanism while, in others, the uptake mechanism is very specific. Some mechanisms are only relevant for a particular group of species and, for some elements, not all uptake processes have yet been identified.

The current knowledge regarding specific uptake processes also varies significantly. When a mechanism is understood, it is generally based on the uptake of a specific element. Similarly, competitive effects typically have to be inferred from experiments with single elements. However, a systematic understanding (e.g. of changes in the magnitude of uptake as a function of pH) exists for many elements even when the actual uptake process is not known. It is therefore difficult and not very meaningful to treat sorption/uptake processes in a generalised way. Accordingly, a brief overview of sorption/uptake processes is given below and element specific uptake processes are discussed in the model studies/experimental studies section.

In general:

- Processes involving the incorporation of species into amorphous CSH phases are of major importance. These resemble the formation of solid solutions but are not necessarily stoichiometric, due to the poorly structured nature of CSH and its resultant flexibility in terms of incorporating hydroxides between the silicate layers. Co-precipitation of dissolved radionuclides and major elements with CSH phases may also occur in the course of alteration of CSH phases.
- Classical solid-solution phases also form from the more crystalline aluminate minerals and calcite, where mineral constituents are replaced stoichiometrically by trace elements.
- The CSH phases also give rise to classical sorption reactions, including ion exchange with the Ca^{2+} ions of the CaOH layers and surface complexation with exposed Si- and O-atoms in the silicate sheets.
- As some trace elements interact with HCP, new mineral phases form. As these solubility-limiting solids only form in the presence of certain hydrated cement minerals and not from homogeneous solution, this process can be considered within the definition of uptake applied here.
- Within concrete or mortar, ions may sorb to the aggregate material (mainly relevant for radionuclides involved in ion exchange, i.e. alkali metals and alkaline earth metals), as well as to the HCP.

In addition to these sorption/uptake processes (in the wider sense), the mechanism for the retention of some radionuclides will be isotopic exchange (e.g. exchange with the corresponding stable isotope within the cement mineral phase). In this context, it is important to note that HCP contains a wide range of trace elements, some at concentrations that are at or near the respective solubility limits. Some of these solubility limits are well constrained by experimental and thermodynamic data, while others are only determined empirically.

The process description of the inter-dependencies between sorption/uptake and waste form variables will be restricted to the effect of sorption/uptake on the fate of the radionuclides and other elements. The effect of the processes on the properties of the cement phases themselves is discussed in a separate process, see Section 3.5.5.

Influence of organic substances

The above descriptions are relevant to most external water conditions that may be experienced, due to the relatively narrow range of pH and dissolved concentrations of carbonate, sulphate etc established by the various hydrated cement minerals. However, the waste, and in some cases the concrete or grout itself, is a source of a range of soluble organic substances. Depending on their concentrations, these substances may have a significant effect on radionuclide sorption/uptake. Work carried out within the disposal programme of SKB (Fanger et al. 2001, Dario et al. 2004a, Keith-Roach et al. 2014) shows that relevant organics include a range of compounds with the ability to form complexes of varying stability with most metal ions. Specifically:

- A number of well-defined complexing agents containing carboxylate functional groups, which stem mainly from decontamination processes at nuclear power plants.
- Degradation products of cellulose and of a polyacrylonitrile filter aid ("UP2").
- Concrete admixtures and their degradation products.

The complexing agents concerned are all well-defined compounds with high water solubility and strong complexing properties towards most metal ions. This group comprises the following carboxylic acids, which will be present as the respective carboxylate anions/conjugate bases, considering the high pH in cement-equilibrated solutions:

- The polyamino carboxylic acids EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid), which are strong chelating agents for hard and soft metal ions due to the presence of O- and N-functional groups.
- Hydroxo carboxylic acids (citric, gluconic, oxalic acid), which are also good complexing agents especially for hard metal ions.
- ISA (isosaccharinate), a degradation product of cellulose in alkaline solutions (Bradbury and Van Loon 1998), is also a hydroxy-carboxylic acid. Two diastereomeric forms (α-ISA, β-ISA) are produced during cellulose degradation. As the complexation power of β-ISA is about two orders of magnitude lower in comparison to the α-form (Van Loon and Glaus 1998), α-ISA is more relevant with respect to radionuclide complexation.
- Degradation products of a polyacrylonitrile filter aid (UP2, cf. Dario et al. 2004a) are also of relevance. UP2 will be bituminised prior to disposal (in F.17 type wastes), which is likely to delay the onset of alkaline degradation for some time. Therefore, degradation is expected to take place under portlandite buffered conditions (pH 12.5) and the available evidence (Duro et al. 2012a) suggests that the conditions will limit the extent of degradation. Duro et al. (2012a) investigated the effect of UP2 degradation products on the sorption/uptake of Eu-152 to cement. The degradation products obtained at pH 12.5 (buffered by $Ca(OH)_2$) and room temperature, which are the most relevant to SFR, did not affect Eu sorption/uptake significantly. The maximum degradation product concentration in this experiment was approximately 8 mg/dm^3 of DOC and was the maximum, plateau concentration obtained in the degradation experiments. The degradation experiments used an initial UP2 fibre concentration of 25 g/dm^3, which is equivalent to the highest UP2 fibre concentration currently disposed in BMA (in compartment 6). Therefore, the data are very relevant to SFR and indicate that radionuclide mobility will not be affected significantly by UP2 degradation.
- Cement admixtures, such as plasticisers/superplasticisers, or their degradation products may also be of some relevance. Most of these are polymeric substances featuring mainly carboxylic or sulphonic acid functional groups. Typical examples are naphthalene or melamine formaldehyde condensates or polycarboxylates such as the product Glenium. All these substances are introduced during the preparation of the concrete or grout and are thus mostly incorporated in the hardened material. The available evidence (Andersson et al. 2008, Glaus and Van Loon 2004b, Dario et al. 2004a) suggests that the actual admixtures are not mobilised from the solid after hardening, but shorter-chain compounds (monomers–oligomers) can be leached. These compounds may be present as impurities in the original formulations or may be created in the process of mixing and hardening.

- In terms of influencing the sorption/uptake of radionuclides and main elements, the properties of the different groups of organic substances can be summarised as follows:
  - In general, the substances introduced above have the potential to reduce sorption/uptake by forming dissolved aqueous species with radionuclides (i.e. by competing with the solid surfaces for the available amount of dissolved radionuclides according to the law of mass-action). This mode of action can be identified as the most relevant process for radionuclide sorption/uptake in the presence of organic complexing agents.
  - Since most of the relevant organic substances have several functional groups (are multi-dentate), they may also modify sorption/uptake processes by forming ternary surface species with certain radionuclides or possibly by sorbing on the surface (thereby modifying it).
  - It can be expected that the dissolved concentrations of the organic molecules will be partly controlled by the sorption of the substances themselves.
  - Whether a measurable influence on the sorption/uptake of radionuclides will take place depends very much on the concentration of the organic compounds. Typical concentration ranges that may be expected are discussed in the "Concentrations" sub-section. It is important in this context that many of the relevant radionuclides tend to hydrolyse and that the concentration of OH^- (which is also a strong ligand) is always very high (≈0.1 M) in cement systems.
  - Most potentially relevant compounds are carboxylic or hydroxo-carboxylic acids. It can be expected that these substances will be able to form weak to fairly stable dissolved complexes with practically all cationic elements, which may lead to a decrease of their sorption/uptake. EDTA and NTA contain nitrogen groups which increase their ability to form complexes with soft metal ions.
  - A few degradation products of concrete admixtures possess only sulphonate functional groups. In comparison to the carboxylates, these show much weaker complexation properties and can therefore also be expected to have a less important effect on uptake.

Concentrations

As mentioned above, the potential effect of organic complexing agents on sorption/uptake depends strongly on their aqueous concentrations. Keith-Roach et al. (2014) estimated concentrations in SFR. For ISA, the estimated concentration is in the range of about 4×10^{-6} M to 1×10^{-2} M, considering cellulose degradation to ISA with a rate constant from Glaus and Van Loon (2008) and sorption of ISA to HCP solids according to Van Loon and Glaus (1998). Estimations using a higher yield or neglecting sorption would give higher concentrations, but are judged as highly conservative.

While ISA is not fully stable in all HCP solutions, independent studies (Glaus and Van Loon 2009, Greenfield et al. 1995) determined that the chemical degradation of α-ISA requires the presence of oxygen (or possibly other oxidising agents). Thus, chemical degradation may not occur under reducing conditions typical for an underground repository. On the other hand, it cannot always be excluded that degradation, rather than sorption, may be responsible for the loss of ISA from solution in aerobic laboratory experiments.

The following approximate concentrations of carboxylic acids have been estimated to be present in SFR by Keith-Roach et al. (2014):

EDTA	7×10^{-7} M to 1×10^{-5} M
NTA	2×10^{-4} M to 2×10^{-3} M
citrate	4×10^{-5} M to 9×10^{-4} M
oxalate	1×10^{-5} M (6×10^{-5} M to 1×10^{-4} M)
gluconate	3×10^{-10} M to 8×10^{-9} M

In the presence of calcium ions, some of these compounds may form solids that may limit their solubility. Bradbury and Van Loon (1998) report maximum ISA solubilities in cement porewater of 11 mM at pH 12.5 and 43 mM at pH 13.3, controlled by the precipitation of $Ca(ISA)_2$. Oxalate concentration is solubility limited by formation of Ca-oxalate at 1×10^{-5} M.

Note that these concentration estimates are rather general in nature. For actual safety evaluations, the concentrations in each repository compartment would have to be evaluated in more detail as done in Keith-Roach et al. (2014).

Trends in the impact of complexing agents on radionuclide sorption/uptake as a function of cement degradation

The influence of organic complexing agents on radionuclide sorption/uptake has not been investigated directly as a function of the cement degradation state. However, a few general trends can be postulated based on the information discussed above and in the later section on model/experimental studies:

- The main process involving organic complexing agents (complexation of radionuclides in solution by dissolved organics) will always take place against the competition of radionuclide-hydrolysis. This competition can be expected to decrease with cement degradation, due to the decreasing pH and OH^- concentration.
- The total dissolved concentration of organic complexing agents as well as their availability for the complexation of radionuclides may be influenced by several degradation-dependent processes:
  - Sorption of carboxylic acids and similar compounds on mineral surfaces typically decreases with increasing pH (due to the increased competition by OH^-, (Stumm and Morgan 1996)).
  - The speciation of most organic complexing agents is likely to be strongly influenced by Ca complexation in solution. While most actinides/lanthanides as well as transition metals will form more stable complexes with the organic compounds of concern, Ca concentrations in cement-equilibrated solutions are high (in the mM range) and can therefore compete effectively with radionuclides for the organic complexing agents. As will be discussed further below, in many systems radionuclide sorption/uptake starts to decrease once the concentration of the organic compounds starts to exceed the dissolved Ca concentration.
  - Several of the relevant organics (ISA, oxalate) may form Ca-solids of limited solubility (with Ca-oxalate having a lower solubility limit). Formation of such solids will depend on the dissolved Ca concentration, which is controlled by the state of cement degradation.
- Overall, it appears that the total dissolved concentration of organic compounds is a critical factor with regard to radionuclide uptake. In all likelihood, the influence of the cement degradation state will be less important.

Dependencies between process and waste form variables

In this section the dependencies between sorption/uptake onto cement and system components are described.

The interactions between the process sorption/uptake on cement and the waste form variables defined in Section 2.1.2 are summarised in Table 3-12.

Cementitious waste form geometry. Uptake (incorporation) of major elements or ions on the HCP structure can indirectly lead to mineral expansion and fracturing. This is expected to result mostly from processes that involve relatively high concentrations of chloride, sulphate and carbonate (see also Section 3.4.1).

Radiation intensity. Radiolysis may affect the speciation of certain radionuclides, but is not expected to have a notable direct influence on the actual sorption/uptake processes. Indirect effects through mineral and water composition may be possible. Alteration of the HCP solids by radiolysis will not be relevant in comparison with chemical degradation/alteration due to the relatively low radiation fields. Radiation may also affect the composition and complexing properties of organic substances through various radiolysis effects see Section 3.1.3. Therefore, the degree to which sorption/uptake is influenced by organic substances may indirectly be affected by radiation.

Table 3-12. Direct dependencies between the process "Sorption/uptake" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No. Sorption/uptake is a molecular-level chemical process that is not influenced by macroscopic geometry.	Not relevant.	No. However, sorption/uptake of certain ions (e.g. sulphate) can lead to mineral alteration, which could create fractures.	Not relevant.
Radiation intensity	No.	Not relevant.	Yes. Possible minor redistribution of radionuclides due to sorption/uptake.	Not concidered relevant.
Temperature	Yes. Temperature will effect sorption/uptake equlibrium. Indirectly, temperature will have an effect on the solids involved in sorption/uptake processes.	Neglected. Expected to be of minor relevance due to the expected small variability of temperature in SFR, or, at least, the uncertainty on the effect of temperature will be lower than the uncertainty in other parameters.	No.	Not relevant.
Hydrological variables	Yes. The contact time between solid and solution can be affected (quasi-equilibrium is often only established after contact times of several weeks or more). Indirectly through water and solid phase composition.	Yes. Indirectly included by careful selection of K_d values.	No. There is an indirect effect since incorporation of major ions in HCP may cause mineral expansion and alter flowpaths.	Not relevant.
Mechanical stresses	No.	Not relevant.	No. See hydrological variables.	Not relevant.
Radionuclide inventory	No. The inventory will influence the water composition (see water composition).	Not relevant.	No.	Not relevant.
Material composition	Yes. The composition of the material influences its sorption/uptake properties.	Included in K_d where relevant	Yes. Incorporation of major ions in HCP may cause mineral alteration.	Considered in the context of cement degradation.
Water composition	Yes. Water composition can affect sorption/uptake.	Included in K_d where relevant.	Yes. Sorption/uptake on HCP influences dissolved concentration.	Included in K_d where relevant.
Gas variables	No. CO_2 can influence mineralogy. Gas composition can influence sorption/uptake indirectly through water composition and aqueous speciation.	Not relevant.	No. However, there is an indirect effect through the influence on dissolved concentrations.	Not relevant.

Temperature will influence sorption/uptake processes in several ways. First, it is known that temperature can have an effect on sorption/uptake processes such as ion exchange, surface complexation, and solid solution formation. Second, the aqueous speciation of radionuclides and major elements will change as a function of temperature. While this effect can be predicted with reasonable certainty, the influence of temperature on sorption/uptake in the complex HCP system is not known. Similarly, a possible indirect influence via temperature-induced changes in mineralogy is difficult to estimate. Based on the (overall) low crystallinity and high reactivity of HCP, as well as the narrow temperature range expected for SFR, it is assumed that chemical effects will dominate.

Hydrological variables. Waterflow can change the concentration of dissolved species and hence the equilibrium, which will have an indirect influence on sorption/uptake. An indirect influence via flow-induced changes in porewater composition is not likely, as the porewater composition is well buffered. Changes in pressure of CO_2 can be expected to alter the solid phase composition (carbonation), because the dissolved carbonate concentration is controlled by calcite or other solids. Incorporation of major ions (including carbonate) present at relatively high concentrations in HCP minerals (and precipitation from homogeneous solution) may lead to an increase in volume and pore clogging, thus decreasing flow (and diffusion).

Mechanical stresses. Flowpaths may be influenced, see hydrological variables.

Material composition. Sorption/uptake is dependent on the composition of HCP and possibly on the aggregate composition. The composition of HCP is determined by the clinker composition, grout/concrete formulation, and degradation through contact with groundwater.

Water composition can have an important direct influence on sorption/uptake. In some cases, the dissolved concentration of radionuclides can influence the type and magnitude of sorption/uptake processes (see discussion of individual radionuclides further below). Elevated concentrations of ions such as (stable) chloride or sulphate in the wastes will lead to elevated concentrations in the pore solution, although the pore solution in HCP is well buffered with respect to pH and the concentration of some typical groundwater constituents. The same is true for organic complexing agents such as EDTA. Whether this will have a significant effect on sorption/uptake depends on the process involved and needs to be evaluated for each element (or group of elements). Additionally, the water composition has an indirect influence on sorption/uptake by affecting cement degradation and the resulting mineral composition of HCP. Uptake can also influence the composition of incoming groundwater by incorporation of major ions into HCP. Most of the solid–liquid equilibria important for determining the water composition can be understood by using thermodynamic solubility products.

Gas variables. Certain gases can influence the mineralogy of HCP, which could affect sorption/uptake properties. No major effect is expected, however, in comparison to the mineral alteration by degradation through contact with water. Indirectly, the gas composition can influence sorption/uptake through aqueous speciation (e.g. by changing the oxidation state of radionuclides).

Boundary conditions

The boundary conditions for sorption/uptake within the cementitious waste forms are:

- Those of the transport processes that control the exchange of solutes between the surrounding water and the cementitious waste forms compartments, i.e. those of the processes diffusion and advection/dispersion.
- All boundary conditions relevant for assessing cement/concrete degradation, as this process will partly determine the sorption/uptake properties of the solid.
- Further boundary conditions include the radionuclide concentration and distribution in the waste, as well as the temperature.

Model studies/experimental studies (including time perspective)

As mentioned in the introduction, sorption/uptake processes in HCP can vary significantly among different groups of elements/radionuclides. Similarly, process understanding is often closely related to a specific element or group of elements. Below, the various processes are therefore discussed directly in the context of the uptake of relevant radionuclides or major elements. Where appropriate, radionuclides are grouped according to similar behaviour.

It should be noted that the literature is not covered comprehensively. The focus is placed on publications that provide information about the processes involved, and especially on those that allow the evaluation of sorption/uptake as a function of degradation state. For example, studies reporting single-point sorption/uptake measurements or referring to blended cement-based binders not relevant to SFR are typically not taken into account. Similarly, a large amount of literature exists on the leaching behaviour of radionuclides, heavy metals, etc from specific cement-based solidification matrices, but the information is normally not relevant to SFR conditions.

In general, the following sections are based on data and interpretations given in the original literature; where relevant, the recent reviews and compilations by Wang et al. (2009, 2013), Ochs et al. (2011), Evans (2008) and Wieland and Van Loon (2002) are also considered. The literature used to derive K_d values for quantifying the magnitude of radionuclide sorption/uptake is discussed in the Data report (SKB 2014c).

It should be noted that chemical sorption/uptake processes are identical for all (stable or radioactive) isotopes of a given element. Most of the elements/radionuclides discussed are only present at trace concentrations in cement systems. In these cases, there is no difference in the overall sorption/uptake processes of the different isotopes. On the other hand, from a PA point of view, there are some cases of interest where the trace radioisotope is present alongside large amounts of the respective element in the form of stable isotopes. Examples are the PA-relevant isotopes of hydrogen (H-3) and carbon (C-14). The respective partitioning processes for these are also addressed below.

The relevance of organics in terms of influencing sorption/uptake processes differs among the various classes of organic compounds as well as among the different groups of radioelements. At the same time, the effects of organic substances are generally understood only for a limited number of systems of interest. Therefore, the influence of organics on sorption/uptake processes is mostly described directly in the context of the uptake of specific radionuclides or main elements, rather than in a general fashion. While little to no direct information (such as spectroscopic evidence) is available regarding the mechanisms by which organic compounds influence radionuclide uptake, it can generally be expected that the formation of aqueous radionuclide–organic complexes will compete with radionuclide uptake, based on mass-action laws. Accordingly, the evidence discussed in the following rests mainly on comparisons of radionuclide uptake in the presence vs. absence of organic compounds.

Sorption/uptake data from a number of experimental studies are available for comparison. Data from studies in which radionuclide sorption/uptake has only been measured in the presence of organics are not included, due to the difficulties in comparing the values with the radionuclide data from a different experimental system.

As far as possible, on the basis of the information available to date, sorption/uptake processes are discussed for different states of cement degradation. These states are distinguished by solution chemistry, see Section 3.5.5. Briefly, the following states are considered for the discussion of sorption/uptake processes (pH values refer to 25°C):

State I: Corresponding to fresh hydrated cement paste (HCP). Alkali metals are still present, pH is around 13.2 or above. Ca:Si ratio (C/S) of the CSH phases is high (≥ 1.5).

State II: Alkali metals are largely removed from the system, and pH is buffered by portlandite at a value of 12.5.

State III: Portlandite is exhausted and the pH is buffered by the (incongruent) dissolution of CSH phases. In this phase, pH will decrease from 12.5 to about 10.5 as CSH phases lose Ca^{2+}. The C/S will decrease.

State IV: CSH phases are still present and are dissolving congruently. C/S is in the range 0.8–1, and pH is < 10.5 to about 10. Ettringite and other aluminosulphates have disappeared.

States I–III are also considered in Cronstrand (2007); state IV is added to address uptake under conditions where C/S is low and aluminosulphates are absent. This is only relevant for those radionuclides that are taken up mainly by aluminosulphates.

Tritium (H-3 or T)

Tritium sorption/uptake by HCP depends on its chemical speciation:

- When tritium is in the form of tritiated water (HTO), sorption/uptake can be assumed to be negligible. Further, the system will be saturated with the chemically identical H_2O. In terms of overall retention, the following processes may also be operative:
  - It is very likely that tritium will be retained through isotopic exchange, with exchange of T for H. This is especially important for fresh material, where the original clinker phases are still undergoing hydration reactions, a smaller fraction of tritium may also be bound during later stages in the resulting hydrated cement minerals.
  - Under diffusive transport conditions, some type of physical retention (e.g. by diffusion into dead-end pores) of diffusing water/HTO may also be possible.
- The situation would be quite different for other forms of tritium, such as tritiated organic compounds. In this case, the degree of sorption/uptake and the processes involved would depend on the specific compound(s).

Influence of organic complexing agents

No effect is expected for tritium in the form of tritiated water (HTO). In case of tritiated organic compounds, any effect would depend on the type of compounds and on the possibility of tritium being exchanged among the different organic compounds.

Carbon-14 (C-14)

As with tritium, C-14 is a radioisotope of an element that is present in HCP in large amounts as its stable isotopes (mainly C-12, very minor amounts of C-13). Sorption/uptake is dependent on the form of C-14 and on the concentration of carbon in the cement system. The main forms of C-14 can be inorganic or organic:

- In case of inorganic carbon, it can be assumed that it exists mainly in the form of carbonate. This will be discussed further below.
- If C-14 is present in an organic form, sorption/uptake processes will depend on the nature of the respective compounds.
  - Using the cellulose degradation product iso-saccarinic acid (ISA), as an example for a low-molecular weight organic acid, sorption on HCP can be significant and kinetically fast (Bradbury and Van Loon 1998). This suggests that surface adsorption processes take place. However, ISA shows a notable affinity for HCP and may not be representative of other organics.
  - On the other hand, it may be more likely that C-14 is incorporated into volatile hydrocarbons, in which case negligible sorption would be expected (Wieland and Van Loon 2002).

For C-14 present as carbonate, sorption/uptake or isotopic dilution of C-14 may take place, depending on the amount of stable carbonate present in the system:

- In typical cement systems, the concentration of Ca ions will be high enough to control the solubility of dissolved carbonate through the equilibrium with calcite (Taylor 1990). In such a case, any potential sorption site for carbonate will already be saturated, and the main sink for radioactive carbonate would be isotopic dilution with stable carbonate in calcite (Bradbury and Sarott 1995). The calculation of a partition coefficient for radioactive carbonate therefore requires an estimate of the accessibility of calcite for isotopic exchange.
- Under conditions where the dissolved carbonate concentration is well below the solubility limit with respect to calcite, sorption/uptake processes of carbonate may include incorporation in ettringite and anion exchange or electrostatic sorption to positively charged CSH (Pointeau et al. 2008).

Influence of organic complexing agents

The presence of organic ligands is not expected to influence isotopic exchange of inorganic C-14. Sorption/uptake of organic C-14 could be affected if C-14 exchanges between the different organic compounds; this is in turn dependent on the type of C-14-containing compounds and organic complexing agents.

Halides: chlorine (Cl), iodine (I)

These elements are expected to be present exclusively as simple anions (chloride and iodide, respectively). Both anions are highly soluble and sorb relatively weakly to HCP. Chloride is known to form the highly soluble Friedel's salt (a Ca-Al-oxychloride) and possibly Ca-oxychlorides when dissolved concentrations reach millimolar levels (Glasser et al. 2008). Iodide analogues of these compounds seem possible (Brown and Grutzeck 1985), but total iodide concentrations are presumably never high enough in HCP for this to be relevant.

In case of chloride, it appears that sorption/uptake processes depend on the total chloride concentration, which will be determined by stable chloride (Wang et al. 2009). When dissolved concentrations of chloride are high enough, chloride is expected to be incorporated in HCP by the formation of Friedel's salt and possibly the formation of solid solutions with AF_m or AF_t phases (Glasser et al. 2008). It can be debated whether these processes should be viewed as uptake or whether they are better represented by a (apparent) solubility limit.

At lower concentrations, chloride sorbs to HCP by a process that shows characteristics of anion exchange/electrostatic interaction. Pointeau et al. (2008) showed that the sorption/uptake of chloride (as well as iodide, see below) is highest at state II of cement degradation, which coincides with a maximum in the dissolved Ca concentration and a corresponding maximum in the positive surface charge on HCP. This is consistent with the zeta-potential measurements by Pointeau et al. (2006a). Based on experiments with different HCP minerals, Aggarwal et al. (2000) report that the aluminate phases in HCP are most important for chloride sorption/uptake. At the same time, they observed lower sorption/uptake of chloride with increasing sulphate concentration, pointing to competition by different anions for the same positive-charge sites. Iodide behaviour generally seems to follow the same trends (Pointeau et al. 2008, Aggarwal et al. 2000).

In the context of SFR, it needs to be kept in mind that HCP typically contains concentrations of chloride that can lead to nearly millimolar dissolved concentrations (Glasser et al. 2008). This may be important in two ways:

- For Cl-36, isotopic exchange may contribute to sorption/uptake, and this is often difficult to separate from other processes.
- Considering the similarity between chloride and iodide, high chloride concentrations could influence iodide sorption/uptake. According to Atkins and Glasser (1992), no significant effect is expected for HCP (only small effects were observed for pure CSH).

Because chloride and iodide are relatively mobile, information on sorption/uptake can be derived from diffusion experiments (Sarott et al. 1992, Jakob et al. 1999). While chloride showed an approximately consistent degree of sorption/uptake in batch and diffusion experiments, iodide sorption/uptake appeared to be an order of magnitude lower in a diffusion test compared to a disperse batch experiment (Wieland and Van Loon 2002). This could indicate a strong dependence on the solid/liquid ratio (S/L). No explanations for this are available to date.

Trends associated with chloride sorption/uptake

When chloride concentrations are less than millimolar, chloride appears to sorb on HCP mainly as a function of the dissolved Ca concentration and the concentration of competing anions. Following the Ca concentration as a function of cement degradation, chloride uptake should increase from state I to state II and then decrease in the transition into state III. In the case of higher total chloride concentrations, incorporation into (or solubility limitation by) Friedel's salts and similar compounds can be expected to be approximately constant for all degradation states, as long as sufficient Ca and Al are present. This process will not presumably be relevant in highly degraded material. Overall, sorption/uptake is expected to be higher when the total chloride concentrations are low.

Trends associated with iodide sorption/uptake

The trends described above for chloride are expected to be relevant for iodide. In addition, iodide uptake seems to decrease significantly with increasing S/L ratio. While this trend has not been clearly explained to date, it is compatible with the low iodide uptake observed in diffusion experiments (Wieland and Van Loon 2002, Wang et al. 2009).

Influence of organic complexing agents

No information was found in the literature on the influence of organic complexing agents on halide sorption/uptake. Considering the properties of the organic compounds considered here, no interaction with chloride and iodide (in particular, no formation of aqueous complexes) is expected. It cannot be excluded that organic acid anions may interfere with sorption/uptake processes of chloride/iodide that are driven by electrostatic interactions, but this is considered insignificant in view of the much higher concentrations of OH^- and stable chloride.

Alkali metals: caesium (Cs)

The sorption/uptake of Cs by HCP and concrete/mortar samples has been studied extensively, as well as on individual HCP mineral phases, especially CSH (e.g. Andersson et al. 1983, Hietanen et al. 1984, Allard et al. 1984, Faucon et al. 1998b, Aggarwal et al. 2000, Pointeau et al. 2000, Ochs et al. 2006). As Cs has a very low tendency to form complexes and exists mainly as Cs^+ ion in solution, even in the highly alkaline pH-range, it generally sorbs via cation exchange. This has been studied particularly well in clays (SKB 2010a). Since components of many potential concrete aggregate materials have a high cation exchange capacity (clays, micas), additional sorption/uptake processes for Cs may be relevant for concrete:

- In HCP, sorption/uptake of Cs occurs mainly on CSH phases, this is discussed below.
- In concrete, sorption/uptake will also take place on HCP, but a significant sorption capacity may also be offered by the aggregate material, depending on its composition (especially content of clay or mica minerals). For example, Andersson et al. (1983) and Hietanen et al. (1984) observed higher Cs sorption/uptake in crushed concrete than in crushed HCP. The typical ion exchange reactions on these minerals are discussed in the buffer and backfill process report (SKB 2010a) The potential contribution of aggregates to sorption/uptake is also a question of their accessibility; this is not known conclusively for degraded (rather than crushed) concrete.
- It can be noted that the concrete aggregate material will continue to contribute to sorption/uptake after HCP has degraded completely.
- The aggregates used for mortar (quartz sand or finely ground limestone) have only low concentrations of sorption sites and no ion exchange properties. In comparison to HCP, their contribution to sorption/uptake can typically be neglected.

While the sorption/uptake mechanism is not known in detail, the following general features have been established on the basis of these studies:

- CSH are the main sorption/uptake-relevant phases (Aggarwal et al. 2000, Ochs et al. 2006).
- Cs exchanges with other alkali and alkaline earth metal ions (mainly Ca) associated with the deprotonated Si–OH groups of CSH. It appears that these groups (or exchange positions) are located on both the exterior as well as interior surfaces of CSH.

It has to be pointed out that this type of exchange may differ from the classical ion exchange (cf. clay minerals) in several aspects:

- While there is obviously a competition between Cs and other cations, it has not been established clearly that the exchange is exactly stoichiometric. The degree to which different cations compete with Cs for sorption sites or exchange positions also depends on the concentrations of such sites (which is a function of the C/S ratio, see above).
- Cs sorbs to CSH over a wide range of C/S ratios. Since CSH phases undergo a change in surface charge at C/S ≈ 1.2 (see the chloride sub section above), it appears that sorption/uptake can take place against the surface charge (i.e. positively charged Cs ions can sorb onto positively charged CSH minerals), which implies a chemical contribution.

Based on the information available to date, the understanding of sorption/uptake processes for Cs at a macroscopic level can be summarised as follows (Wang et al. 2009):

- It is well established that the extent of Cs sorption/uptake is mainly related to the C/S ratio, with sorption/uptake increasing as C/S decreases. This has been observed for both HCP and pure CSH phases and is related to surface charge and dissolved Ca concentration (Pointeau et al. 2000, Ochs et al. 2006, Wang et al. 2009):
  - In the case of CSH, the dissolved Ca concentration decreases roughly with decreasing C/S. This results in a change from positive to negative overall surface charge as well as a decreased competition by Ca ions as C/S decreases. Both effects results in higher sorption/uptake of Cs.
  - The concentration of surface/internal sites of CSH available for cation sorption also seems to increase with decreasing C/S ratio.
- As pointed out above, Cs sorption is an exchange-type reaction and therefore decreases in the presence of other alkali and earth-alkali ions. In whole HCP or concrete systems, the dissolved concentrations of Ca and especially Na and K ions are determined by several solids and generally decrease with increasing degradation.
- Similarly, Cs sorption/uptake will be influenced by the presence of groundwater with high salinity, for example.

Trends associated with Cs sorption/uptake

Based on the processes identified above, it can be expected that Cs sorption/uptake will increase as a function of HCP degradation, following the evolution of CSH. It can further be expected that the increase from state I to II may be less pronounced than the increase from state II to III:

- Ca solubility is lower in state I than in state II due to the high pH in state I. At the same time, high concentration of Na and K are present in state I, which lowers sorption/uptake of Cs.
- The transition from state II to state III coincides with the loss of portlandite. All factors (decreasing C/S and Ca concentration) favour Cs sorption/uptake in state III.

Influence of organic complexing agents

The sorption/uptake processes discussed above and the weak tendency of Cs^+ to form complexes suggest that the sorption/uptake of Cs will not be reduced in the presence of organic complexing agents. No significant complexation is expected by the organic substances considered here. On the other hand, stronger organic complexation is expected for ions (mainly Ca^{2+}) that compete with Cs for sorption/uptake on HCP. This could be relevant in the later stages of cement degradation, when the dissolved Ca concentration is no longer controlled by portlandite.

Available data for gluconate and ISA on fresh hydrated cement (Bradbury and Van Loon 1998, Holgersson et al. 1998) indicate that the sorption/uptake of Cs is not affected by the presence of organics under realistic conditions.

Alkali-earth elements: radium (Ra) and strontium (Sr)

The sorption/uptake of Ra and Sr to HCP and concrete mimics the behaviour of Ca very closely (Tits et al. 2006a, b, Wieland et al. 2008). For Sr, there is direct spectroscopic evidence (XAFS) that Sr sorbs to the CSH phases of HCP (Wieland et al. 2008). In comparison to CSH, calcite does not play an important role for Sr and Ra sorption/uptake (Wang et al. 2009). Thus, the processes and trends discussed above for Cs are also expected to be relevant for Ra and Sr. However, the following differences are noteworthy:

- It appears that Sr and Ra sorption is more reversible than that of Cs, and their ion exchange reactions with Ca are more clearly stoichiometric.
- In terms of competing ions that affect Sr and Ra sorption/uptake, Ca appears to be more important than alkali metal ions. Accordingly, the magnitude of Sr and Ra sorption/uptake is related more directly to the dissolved Ca concentration.

Trends associated with Sr and Ra sorption/uptake

The importance of dissolved Ca concentrations suggests that sorption/uptake will decrease during cement degradation from state I to state II, in line with the increasing dissolved Ca concentration. From state II to state III, sorption/uptake of Sr and Ra is expected to increase again, most likely to a greater degree than in state I.

Influence of organic compounds

Since most of the organic compounds considered here are known to form fairly stable aqueous complexes with Ca ions, similar interactions can be expected for Sr and Ra. Wieland et al. (2000) observed no measurable effect on Sr sorption/uptake in the presence of ISA at equilibrium concentrations up to 1 mM. At higher ISA concentrations, Sr sorption/uptake seemed to increase slightly and only started to decrease at ISA concentrations > 10 mM.

Silver (Ag)

Silver will only be present in the monovalent form. It only hydrolyses weakly, thus the Ag^+ ion may be the dominant species up to pH ≈ 12 (Baes and Mesmer 1976). Silver is known to form strong chloride complexes.

No data on sorption/uptake or other information of direct relevance for HCP are available. In terms of basic chemical properties, the charge/M-O bond distance ratio and hydrolysis behaviour of Ag seems to be similar to that of alkali elements (Baes and Mesmer 1976). As a first approximation, this would point to a sorption/uptake behaviour similar to that of Cs or Sr.

With regard to sorption on the aggregate materials, Legoux et al. (1992) observed that Ag sorption on a silica-rich soil was of the same magnitude as Cs and Ra sorption under similar conditions (pH ≈ 6).

Influence of organic complexing agents

The evidence from Baes and Mesmer (1976) can be taken to indicate that (hydroxo-) carboxylates would not significantly influence the behaviour of Ag in high-pH solutions. However, N-containing ligands such as EDTA and NTA can form stable complexes with the soft Ag^+ ion (Hart 2005), indicating a potentially important influence on sorption/uptake. However, no quantitative information could be found in the literature.

Cadmium (Cd)

Cadmium exists as the divalent ion in aqueous solutions. It does not hydrolyse very strongly (similarly to nickel ions), and has a relatively soft metal character (Baes and Mesmer 1976).

Very little information is available regarding sorption/uptake of Cd by HCP. Pomiès et al. (2001) studied the interaction of Cd with CSH phases by synthesising CSH in the presence of Cd and by reacting synthetic CSH with (oversaturated) Cd-solutions. Based on spectroscopic evidence, they concluded that Cd was taken up to a significant extent, exchanging with Ca in the CSH structure. A similar replacement of Ca with Cd was also shown for portlandite. In a study that was not directly aimed at elucidating uptake, Polettini et al. (2002) also found that Cd was taken up by CSH.

In the absence of direct information on Cd sorption/uptake by HCP, Pb or Zn may be used as analogues to make a first estimate of the magnitude of Cd uptake. This would indicate some uptake by HCP for all degradation states involving CSH phases (Andra 2005), which is consistent with the above observations.

Cadmium can also be expected to sorb to aggregate material. The typical ion exchange and surface complexation reactions on these minerals are discussed in the buffer and backfill process report (SKB 2010a).

Influence of organic complexing agents

Not enough information is available on the sorption/uptake processes of Cd to assess the influence of organics. However, there is no clear reason why the main process of interaction (formation of aqueous metal–organic complexes) should not be relevant. Considering the soft chemical character of Cd, EDTA and NTA could be of particular importance.

Palladium (Pd)

The only relevant oxidation state of aqueous palladium is Pd(II) (Hummel et al. 2002). While Pd(II) as a typical B-metal ion forms strong complexes with soft ligands such as chloride, it also hydrolyses very strongly (with a tendency to form polynuclear/colloidal species).

No data for the sorption/uptake of Pd by HCP have been found. Similarly, no data are available for any of the other platinum group metals, which could serve as chemical analogues. Again, Pb may be used for a first estimate of Pd sorption/uptake. This would indicate some sorption/uptake by HCP for all degradation states involving CSH phases (Andra 2005).

Information relating to Pd sorption on clays and similar minerals is also unavailable or of limited quality, but nickel or lead may serve as reasonable analogues for clay-type minerals and calcite (Bradbury and Baeyens 1997, Ochs and Talerico 2004).

Influence of organic complexing agents

Not enough information is available to evaluate the influence of organics. The main process of interaction (formation of aqueous metal–organic complexes) can again be expected to be relevant. Due to the soft chemical character of Pd, EDTA and NTA can be expected to be of particular relevance.

Cobalt (Co)

In aqueous solutions, Co(II) is the only relevant oxidation state. The aqueous chemistry of Co is therefore expected to be similar to that of Ni (Baes and Mesmer 1976). However, in Co-doped HCP, Co(III) forms when hardening takes place in the presence of oxygen (Vespa et al. 2007). In the absence of oxygen, no oxidation to Co(III) is observed. For SFR (sorption/uptake by already hardened HCP, aqueous environment), only Co(II) is considered relevant.

In several experiments using reducing slag-concrete and grouts, Kaplan and co-workers (see e.g. Kaplan and Coates 2007) observed substantial uptake of Co (similar order of magnitude as for various actinides)). They observed much slower release than uptake, as for all RN studied. Based on studies addressing the synthesis of metal-substituted layered double hydroxide (LDH)-minerals (Johnson and Glasser 2003) and Co/Ni-exchanged crystalline CSH minerals (Komarneni et al. 1988) as a first approximation, it is expected that Co behaviour will be analogous to Ni or possibly Zn.

On the other hand, Wieland and Van Loon (2002) observed Co behaviour in HCP suspensions as a function of solid/liquid ratio that corresponds to a solubility-limiting rather than a sorption/uptake-type process. This would mean that the partitioning of radioactive Co isotopes would follow an isotopic exchange process, rather than some type of chemical uptake (see also the section on Ni below). The Co-phases discussed by Vespa et al. (2007) could be seen as potentially solubility-limiting solids.

Influence of organic complexing agents

Very little direct information is available. In a recent study, Holgersson et al. (2011) found no influence of EDTA, citrate or ISA on Co sorption/uptake by fresh and leached (phase II) hydrated cement. This would be consistent with isotopic exchange rather than chemical interactions.

Nickel (Ni): radioactive isotopes

Nickel only exists in the +II oxidation state in aqueous solutions. Ni(II) has only a moderate tendency to hydrolyse, with the Ni^{2+} aquo ion being the dominant species up to pH ≈ 9 (Hummel et al. 2002).

The total Ni concentration in cementitious systems is typically dominated by the background Ni content of HCP, stemming from the original clinker used for cement production (cf. Wang et al. 2009). Note that this is not specific to SFR but is a typical feature of clinker material. This background concentration of Ni is sufficient to reach the solubility limit of Ni in the porewater of hydrated cement (Andra 2005, Ochs and Talerico 2006). The dissolved Ni concentration in cement systems is limited by the solubility of a Ni-bearing layered double hydroxide (LDH) phase (Scheidegger et al. 2000, Vespa et al. 2006).

Given the presence of a dissolved Ni concentration corresponding to the solubility limit of a solid Ni-phase, any chemical sink for Ni in the system is saturated. The partitioning of any added radioactive Ni isotope will then follow isotopic exchange with the main mass of Ni in the system (Wieland et al. 2006) i.e. no chemical sorption/uptake process is expected to take place.

These findings were corroborated by the studies of Wieland et al. (2000, 2006). Wieland and Van Loon (2002) also showed that the apparent sorption/uptake of Ni-63 on a variety of HCP samples systematically decreased with the S/L ratio, which would not be expected for a sorption process, but can be explained by solubility limitation.

The calculation of a partition coefficient for radioactive nickel would therefore ideally be based on estimates of the solubility limits of the Ni-LDH phase for the different degradation states and the accessibility of this phase with regard to isotopic exchange. In the absence of such information, sorption/uptake can be estimated using data from similar systems (such as Wieland and Van Loon 2002, Andra 2005).

Influence of organic complexing agents

Following the above discussion, the influence of organic complexing agents on the partitioning of radioactive Ni should be limited to the influence on the solubility (or accessibility) of Ni-LDH phases. However, these data are not available and so the following discussion is based on experiments involving comparison of Ni sorption/uptake by HCP in the presence and absence of organic complexing agents.

Glaus and Van Loon (2004b) noted that various organic compounds had a much weaker influence on Ni^{2+} sorption/uptake in comparison to Eu^{3+} and Th^{4+}. Further, compounds with additional N-functional groups did not appear to affect Ni more strongly than those without, which contrasts with the general rule for the formation of stable Ni complexes. Additionally, inconclusive results were obtained in experiments examining the effect of 0.2–2 weight/volume % initial gluconate concentrations on Ni-63 sorption/uptake. Wieland et al. (2000) reported that ISA had no influence on Ni sorption/uptake up to a concentration of about 1 mM. At higher ISA concentrations, their results were not conclusive (enhancing or reducing Ni sorption/uptake, depending on concentration). Holgersson et al. (1998) reported that 5 mM ISA had no influence on Ni sorption/uptake by HCP. These observations are more consistent with the hypothesis of Ni partitioning via isotopic exchange rather than a chemical sorption/uptake process.

However, some valuable information can be extracted from experiments in which Ni sorption/uptake was studied on solids that were presumably Ni-free (i.e. where partitioning of Ni was dominated by chemical processes). Bradbury and Van Loon (1998) showed that gluconate does not influence Ni sorption/uptake on CSH-phases at gluconate concentrations below 10^{-4} M. Van Loon and Glaus (1998) compared Ni sorption on feldspar in the absence and presence of ISA. Feldspar was chosen because ISA does not sorb to it, allowing the effect of $NiISA_2$ aqueous complex formation to be determined. Ni sorption was only significantly reduced with dissolved ISA concentrations > 0.01 M (some experiments indicated increased sorption in the presence of lower ISA concentrations).

Trivalent actinides and lanthanides

This group of species includes the actinides americium (Am), curium (Cm) and reduced plutonium Pu(III) as well as the lanthanide elements europium (Eu), holmium (Ho) and samarium (Sm). The chemical behaviour of these species is generally very similar, but Hummel et al. (2002) noted that Eu undergoes stronger hydrolysis than Am. The available information on sorption/uptake processes in cement systems provides no compelling reason to distinguish between these elements.

Sorption/uptake of trivalent actinides and lanthanides by HCP and HCP mineral phases is very strong in general (Wieland and Van Loon 2002, Wang et al. 2009). The available information suggests that a two step process occurs: with surface adsorption followed by some type of incorporation. The first process is fast, with linear sorption behaviour (Wieland et al. 1998, Tits et al. 2003), while the subsequent incorporation appears to bind the species irreversibly (accordingly, radionuclide release is typically very slow). Spectroscopic evidence obtained using Cm and Eu suggests that the incorporation step involves an exchange with Ca (Wieland et al. 1998, Tits et al. 2003, Pointeau et al. 2001, Stumpf et al. 2004). Pointeau et al. (2004) report a similar fixation into CSH for Am.

Various studies have also observed some type of surface precipitation of trivalent actinides/lanthanides with Ca and Si (e.g. Pointeau et al. 2001). However, the evidence for this process appears to be less robust. It is also not clear whether this only occurs at the relatively high tracer concentrations needed for the experiments.

Relatively little information is available regarding possible changes in sorption/uptake processes as a function of HCP degradation. Pointeau et al. (2001) found no change in Am sorption/uptake by CSH as a function of C/S ratio, but only a limited C/S range was studied.

In addition to the typical HCP mineral phases, trivalent actinides/lanthanides are also taken up strongly into calcite via incorporation into the lattice. Calcite may form as a result of cement degradation or be present in the aggregate. Stumpf et al. (2004) also observed surface sorption of Cm on portlandite.

A decrease in sorption/uptake with increasing solid/liquid ratio (S/L) has been reported by Wieland and Van Loon (2002) in experiments with Eu, but the underlying mechanism is not understood. This could be relevant when data from disperse batch systems (with crushed HCP) are applied to intact materials with a much higher solid/liquid ratio. However, in view of the experimental uncertainties, Wieland and Van Loon (2002) do not consider the trend observed for Eu significant.

Trends associated with trivalent actinide and lanthanide sorption/uptake

The available evidence points to CSH as the most relevant HCP mineral for sorption/uptake of these elements in SFR. However, similarly strong sorption/uptake has been observed on CSH and HCP. None of the evidence suggests a change in sorption/uptake as a function of C/S. Therefore, constant (strong) sorption/uptake can be expected for all degradation states.

Influence of organic complexing agents

In broad terms, the sorption/uptake of trivalent actinides and lanthanides is likely to be affected by organic complexing agents, due to the typically strong aqueous complexes formed. Therefore, more pertinent studies are available than for most other groups of elements:

- The effect of ISA on Eu sorption/uptake was investigated by Van Loon and Glaus (1998) and Wieland et al. (1998). Both studies indicated that ISA concentrations below 1 mM do not have a significant influence on Eu sorption/uptake. This is broadly consistent with more recent measurements (Dario et al. 2004a).
- Dario et al. (2004a) studied the effect of a range of organic compounds used as complexing agents. To investigate the role of dissolved Ca, they used TiO_2 as a model solid as well as HCP.
  - In the presence of EDTA alone (no Ca added), Eu sorption on TiO_2 started to decrease with μM concentrations of EDTA. When 2 mM Ca was added to resemble cement systems, Eu sorption decreased when the EDTA concentration exceeded about 1 mM. This was consistent with the results from the cement system and demonstrated competition between Ca and Eu

  ions for EDTA. In both systems with Ca, Eu sorption started to decrease once the concentration of EDTA started to exceed the dissolved Ca concentration. A nearly identical picture was observed with NTA.
  - Their experiments indicated that Ca is less important in the case of citric acid, but Eu sorption on HCP also decreased with around 1 mM citrate. Oxalic acid showed no effect at concentrations up to 10 mM and may have precipitated as Ca-oxalate.

- Dario et al. (2004a, b) also studied the effect of cement additives.
  - The polycarboxylate Glenium 51 appears to lead to a reduction of Eu sorption at a concentration of about 0.01% of the liquid phase.
  - Gluconate is reported to lead to a reduction of Eu sorption at fairly low concentrations (≈10 µM). This is in contrast with the information given in Bradbury and Van Loon (1998), which indicates rather weak effects of gluconate plus substantial sorption of gluconate to HCP. The reason for this difference is not clear at the moment.

- The degradation of the UP2 filter aid and the effect of the degradation products on Eu sorption were also studied by Dario et al. (2004a, c). In the presence of Ca and at high pH, as well as a slightly elevated temperature (60°C), UP2 degraded quite readily, leading to almost 0.1 M DOC concentrations after 100 days (corresponding to 15% of the initial UP2 material). A clear reduction in Eu sorption was evident at a DOC concentration of about 1 mM; this effect seemed to be independent of the Ca concentration. A later study (Duro et al. 2012a) showed that under more SFR relevant conditions the effect upon sorption/uptake is not as drastic and could be neglected.

Tetravalent actinides

This group includes thorium (Th) as well as the reduced (IV) forms of plutonium (Pu), uranium (U) and neptunium (Np). The chemical behaviour and in particular the hydrolysis of these species is very similar. Within the pH range considered here, only the $An(OH)_4^0$ complexes are relevant. With the exception of Th, all other actinides in this group can access other oxidation states.

The following discussion of sorption/uptake processes is based on research carried out using Th. For the other actinides, very few studies and data are available. In addition, the results are more difficult to interpret due to the problems of maintaining oxidation state IV in the laboratory. It is assumed that the same sorption/uptake processes are important for all tetravalent actinides, which is consistent with the available information.

Sorption/uptake of Th by cementitious materials (including CSH minerals) is very strong under all conditions, as shown by a large range of studies (e.g. Allard et al. 1984, Heath et al. 1996, Wierczinski et al. 1998, Wieland et al. 1998, 2002, Wieland and Van Loon 2002, Tits et al. 2010).

The studies by Allard et al. (1984) and Heath et al. (1996) showed that the cement/concrete formulation has a negligible influence on Th sorption/uptake. This was corroborated by Tits et al. (2010), who performed a systematic investigation of the influence of C/S ratio of CSH phases on Th sorption/uptake, and observed no effect. However, Wierczinski et al. (1998) and Cowper et al. (2006) found an increase in sorption/uptake with an increase in HCP degradation. It was not clear, however, whether this was related to the change in the C/S ratio or to the relative increase (in mass-fraction) of CSH phases in comparison to other HCP minerals.

The sorption/uptake processes of tetravalent actinides on HCP are not known, which is partly due to experimental difficulties. In the case of HCP and CSH minerals corresponding to state I, Wieland et al. (2008) and Tits et al. (2010) found that Th sorption/uptake was fast, with equilibrium reached within one day. Further, for CSH phases, desorption values were found to be the same as sorption/uptake values (within the expected uncertainty), which indicates reversible sorption. This evidence suggests that Th sorbs to CSH by some type of surface adsorption. This is consistent with the strong hydrolysis of Th and its tendency to sorb strongly to any surface-OH groups.

Wieland and Van Loon (2002) observed that Th sorption/uptake was dependent on the S/L ratio, with sorption/uptake decreasing with an increase in S/L. However, the authors noted the practical limitations of the experimental S/L ratios used, due to the low solubility and very strong sorption/uptake of Th in combination with a relatively high analytical detection limit. Thus, their observation is only valid for a small range of S/L ratios. The concept of a reversible (surface) adsorption process would be more consistent with K_d values that are independent of S/L ratio. Overall, the present data situation is not conclusive with respect to a possible effect of solid/liquid ratio on the magnitude of sorption/uptake.

Finally it can be pointed out that Th also sorbs very strongly on calcite (Tits et al. 2002) and on clay- and oxide-type minerals (Bradbury and Baeyens 2005).

Trends associated with tetravalent actinide sorption/uptake

Based on the available data, the magnitude of sorption/uptake can be expected to be similar regardless of cement degradation state (states I–III). This is consistent with the hydrolysis behaviour of tetravalent actinides. As a first approximation, it may be assumed that sorption could be equally high on crystalline and calcareous aggregate material.

Influence of organic complexing agents

Of all radionuclides, tetravalent actinides appear to be most affected by the presence of organic complexing agents (Bradbury and Van Loon 1998, Greenfield et al. 1992). As in the case of most radionuclides, the available evidence focuses on the effect of ISA.

Sorption/uptake studies of Th by Holgersson et al. (1998) and Wieland et al. (1998, 2002) on different HCP samples in the absence and presence of ISA give the following picture (note that there is some uncertainty in the ISA concentrations as the actual equilibrium solution-phase concentration is not always known precisely; the numbers below should be total concentrations present).

- At a concentration of less than 0.1 mM up to approximately 1 mM, ISA has no influence on the sorption/uptake of Th. The exact onset of a measurable effect is not entirely consistent between the studies. While Wieland et al. (1998, 2002) noted a decrease of Th sorption/uptake at ISA concentrations of about 0.5 mM, Holgersson et al. (1998) saw no effect at 3 mM. Greenfield et al. (1997a) observed a significant reduction of U(IV) sorption/uptake (roughly an order of magnitude in terms of K_d) at an estimated ISA concentration of about 1 mM.
- Once ISA concentrations exceed these levels, it seems that an order of magnitude increase in ISA concentration leads to a decrease of Th sorption/uptake (expressed as a K_d value) by two orders of magnitude.
- At least in the case of intermediate ISA concentrations, it appears that the effect of ISA (reduction of sorption/uptake) is time-dependent and is lessened with long equilibration times.

Similar results were obtained by Van Loon and Glaus (1998) for the sorption of Th on feldspar at high pH in the presence/absence of ISA (feldspar was chosen to avoid sorption of ISA).

Zirconium (Zr)

Zr(IV) is the only oxidation state of zirconium in aqueous solutions. Like the tetravalent actinide Th, Zr hydrolyses strongly (Hummel et al. 2002).

To date, mainly one systematic data set for Zr sorption/uptake on cementitious materials exists. Pointeau et al. (2004) investigated the sorption/uptake of Zr by degraded HCP (from CEM I and CEM V cements) and on CSH phases with C/S ratios of 0.7, 0.9, 1.0, 1.3, in the pH range of pH ≈ 10–12. While the sorption/uptake mechanisms were not identified, this dataset showed that

- Zr sorbs strongly under all conditions, which is consistent with the strong hydrolysis of this element.
- Sorption/uptake generally increases as the C/S ratio decreases.
- The magnitude of sorption/uptake as well as the trend vs. C/S is similar for all solid substrates investigated.

Therefore, it appears that CSH-phases are mainly responsible for Zr sorption/uptake by HCP. It can only be speculated whether the increase in sorption/uptake with decreasing pH is related to the speciation of Zr or to changes in the (surface) properties of the solids, but the latter may be more probable considering the relatively constant speciation of Zr in the pH-range investigated.

The important role of CSH phases is confirmed by the data of Baston et al. (2010), who observed strong uptake by unaltered as well as leached Nirex Reference Vault Backfill. Due to the uncertainty in the data, they observed no clear trend of uptake as a function of alteration, however.

Trends associated with zirconium sorption/uptake

In terms of the cement degradation state, all the materials investigated by Pointeau et al. (2004) were in state III and therefore offered no insight into Zr sorption/uptake at higher pH (less degraded HCP). Nevertheless, it can be assumed as a first approximation, that Zr sorption/uptake is generally very strong and that it is likely to increase as a function of cement degradation.

Influence of organic complexing agents

Brownsword et al. (2002) studied the effect of cellulose degradation products on the sorption/uptake of Zr. It must be assumed that other degradation products were present as well as ISA, and the results of the experiments were not conclusive (Zr sorption/uptake decreased or increased, depending on the cellulose loading). In the absence of better data, it can be assumed that Zr is affected in a similar way to Th.

Tin (Sn)

While tin may exist in two oxidation states in aqueous solutions, Sn(II) and Sn(IV), only the +IV state is relevant for environments with medium to high pH. Like tetravalent actinides and Zr, Sn(IV) hydrolyses very strongly (Hummel et al. 2002).

Based on a number of studies available involving different HCP and individual minerals (CSH, aluminates) (e.g. Bayliss et al. 1989, Baker et al. 1994, Heath et al. 1996, Wieland and Van Loon 2002, Bonhoure et al. 2003, Andra 2005, Ochs and Talerico 2006), the sorption/uptake of Sn(IV) on HCP is strong under all conditions. This is consistent with:

- The strong tendency of Sn(IV) to hydrolyse (see also Zr and tetravalent actinides).
- The affinity of the hydrolytic Sn-species dominant at high pH towards Ca (and presumably other divalent ions), leading to the formation of sparingly soluble Ca-stannates (Lothenbach et al. 2000).

It appears that sorption/uptake is higher on CSH phases than on calcite, hydrogarnet and hydrotalcite (Andra 2005, Ochs and Talerico 2006). However, the C/S ratio appears to have no significant influence on Sn sorption/uptake by to CSH. The S/L ratio does not seem to affect uptake either. Bonhoure et al. (2003) and Ochs and Talerico (2004) determined isotherm data on HCP and CSH minerals, respectively, showing that Sn sorption/uptake by cementitious materials is linear and sorption/uptake by both HCP and CSH can be interpreted using a single K_d value.

While the mechanisms of Sn(IV) sorption/uptake by HCP are not well understood, Bonhoure et al. (2003) provided spectroscopic information on the structural environment of sorbed Sn:

- When Sn(IV) was introduced to CSH phases, inner-sphere complex formation was observed.
- Sn seemed to form a different type of inner-sphere complex when it interacted with HCP. Despite the apparently weaker sorption/uptake of Sn by ettringite than by CSH, the structural environment of Sn in HCP points towards ettringite as a possible host phase for Sn(IV).

Therefore, the available information cannot identify the mineral phase dominating sorption/uptake or distinguish between surface sorption and incorporation conclusively.

Trends associated with tin(IV) sorption/uptake

The sorption/uptake processes for Sn(IV) are not well understood, and the available information does not indicate a clear trend in Sn(IV) sorption/uptake as a function of cement degradation. However, the available evidence (strong sorption/uptake on HCP, CSH, aluminates; apparently little influence of pH and C/S) indicates that uptake of Sn(IV) could be approximately similar for all degradation states (given the presence of CSH).

Influence of organic complexing agents

No relevant information is available. As a first approximation, similar effects as for Th may be assumed.

Technetium (Tc)

Technetium is present as Tc(IV) under reducing conditions and Tc(VII) (pertechnetate, TcO_4^-) under oxidising conditions (Hummel et al. 2002). Sorption/uptake of pertechnetate is discussed in the section on oxo-anions.

Tc(IV) hydrolyses very strongly, but forms different hydrolytic species than the tetravalent actinides. Tc(VII) exists as the pertechnetate anion across the entire pH range. An important aspect of Tc chemistry is the sensitivity of Tc(IV) towards oxidation, which makes it very difficult to avoid the presence of traces of Tc(VII) in experiments. Since traces of the highly soluble and weakly sorbing Tc(VII) can influence the measured K_d values, for Tc these can be difficult to evaluate accurately. Further, sulphides present in certain cement types may precipitate Tc-sulphides, which would lead to artefacts in sorption/uptake experiments (Baker et al. 2004).

Accordingly, little reliable information on the sorption/uptake of Tc(IV) by cementitious materials is available. A systematic set of sorption/uptake data for CSH and HCP obtained under defined, reducing conditions is provided in Andra (2005). These data show strong sorption/uptake of Tc(IV) on both CSH and HCP, indicating that CSH may be responsible for Tc(IV) sorption/uptake. Further, degradation appears to have no clear influence. However, no information on the sorption/uptake processes is available to date.

Trends associated with technetium(IV) sorption/uptake

The limited information available indicates strong sorption/uptake of Tc(IV), with no clear influence of degradation state (given that CSH are still present).

Influence of organic complexing agents on Tc(IV)

No relevant information is available. As a first approximation, similar effects as for Th may be assumed.

Niobium (Nb)

The only relevant oxidation state is +V, but the aqueous speciation of Nb in alkaline solutions is not well known. Similar to Sn (see above), hydrolytic Nb species appear to form sparingly soluble solids with Ca ions, and the closest chemical analogue in terms of hydrolysis and affinity of species for Ca may be Sn(IV) (Talerico et al. 2004, Andra 2005)

Even less is known about the possible sorption/uptake processes of Nb on HCP. Some measurements are available for different HCP samples by Pilkington and Stone (1990) and for HCP and CSH samples with different C/S ratios (Andra 2005). The latter experiments were reportedly conducted in solutions that were initially oversaturated, but sorption/uptake and desorption values were similar, and the magnitude of sorption/uptake is roughly compatible with the values observed by Pilkington and Stone (1990), which was interpreted by Wang et al. (2009) to indicate some type of reversible process.

The few available data indicate roughly constant, high sorption/uptake in states I and II. Data available for sorption/uptake in state III are lower, but their relevance is questionable as they correspond to pH values < 10.

Trends associated with niobium (V) sorption/uptake

Considering the above, as well as an at least approximate analogy with Sn(IV), no strong sorption/uptake trends are expected as a function of degradation within the pH range > 13 to ≈ 10.5.

Influence of organic compounds

It is not clear how the organics considered here would interact with Nb. Given that Nb behaves more like a hydrolysed cation than like an oxo-anion at high pH, the formation of aqueous Nb–organic complexes could be expected. If so, a reduction of sorption/uptake similar to tri- and tetravalent actinides could be assumed conservatively.

Oxo-anions of selenium (Se), molybdenum (Mo) and technetium (Tc)

The following oxidation states are considered here:

- Selenium can exist in aqueous solutions in the oxidation states –II (selenide, HSe^-), +IV (selenite, SeO_3^{2-}) and +VI (selenate, SeO_4^{2-}). No information is available for the uptake of selenide, information for selenite and selenate is discussed below.
- The only relevant oxidation state for molybdenum is +VI (molybdate, MoO_4^{2-}).
- Technetium may exist in two oxidation states under the relevant conditions, +IV and +VII (pertechnetate, TcO_4^-). Below, only Tc(VII) is discussed; for an overall discussion on Tc, see above.

It is known that ettringite, in which sulphate is located in channels of a Ca-aluminate framework, is able to accommodate various oxo-anions (such as selenate, chromate) instead of sulphate (Kumarathasan et al. 1990). The importance of ettringite (and monosulphate) for the sorption/uptake of selenate on HCP has been confirmed in several studies (Ochs et al. 2002, Baur and Johnson 2003, Ochs and Talerico 2006).

Selenate has been shown to sorb relatively weakly on CSH, but strongly on ettringite and monosulphate. Sorption/uptake on HCP is also limited, which is consistent with the small fraction of aluminosulphate minerals in HCP. Ochs et al. (2002) determined selenate and chromate sorption/uptake in ettringite as a function of selenate or chromate and sulphate concentrations. They developed a solid-solution model that could explain the sorption/uptake of several oxo-anions (selenate, chromate, as well as perrhenate) on ettringite and fresh/degraded HCP for a range of solid and solution compositions. The main process was the substitution of oxo-anions with sulphate in ettringite, therefore dissolved sulphate competes with the other oxo-anions.

Molybdate is very similar to selenate in terms of its behaviour in aqueous systems, because they are isostructural and isoelectric. It can therefore be expected that molybdate and selenate replace sulphate in the aluminate phases to a similar extent. Therefore, nearly identical sorption/uptake processes can be expected. This is confirmed by the only dataset available for the sorption/uptake of molybdate on HCP (Kato et al. 2002), which shows very close agreement with data for Se(VI).

No suitable data for Tc(VII) were found. Using perrhenate as analogue for pertechnetate, Ochs et al. (2002) measured very low sorption/uptake. However, they showed that the solid-solution model for selenate and chromate could explain the sorption/uptake of perrhenate.

The uptake of selenite appears to be more complex than that of selenate. While selenite sorption/uptake on ettringite is weaker than that of Se(VI), selenite has been shown to sorb appreciably on nearly all HCP minerals investigated as well as on HCP (Sugiyama and Fujita 1999, Ochs et al. 2002, Baur and Johnson 2003, Ochs and Talerico 2006, Pointeau et al. 2006b, Macé et al. 2007). This suggests a more generic uptake mechanism (such as surface uptake/ligand exchange, incorporation in CSH) in addition to the possible ion-specific replacement of sulphate in aluminosulphates. Macé et al. (2007) observed initially fast uptake kinetics, followed by a slower process, which could be diffusion into the solid. They also observed a reduction of Se(IV) uptake on HCP when the temperature was increased from 20°C to 70°C, which was presumably due to the disappearance of ettringite and an increase in the crystallinity of CSH (i.e. a decrease in specific surface area).

Trends associated with Se(VI), Mo(VI) and Tc(VII) uptake

As the main uptake process involves substituting for sulphate in ettringite (or monosulphate), it can be expected that uptake on HCP is directly related to

- The amount of ettringite and/or monosulphate present, with uptake tending to very low values in the absence of these minerals.
- The dissolved concentration of sulphate, with high sulphate concentrations leading to lower uptake of other oxo-anions.

Trends associated with Se(IV) uptake

The sorption/uptake mechanisms are not known in detail, but sorption/uptake appears to take place on all HCP minerals and to be fairly uniform throughout states I–III of cement degradation. Notably, this should hold as long as CSH are present (and are not thermally altered).

Influence of organic compounds

Pointeau et al. (2006b) investigated the effect of three organic complexing agents (EDTA, ISA, gluconic acid) on the sorption/uptake of selenite (Se(IV)) on fresh and degraded HCP. EDTA and ISA had a particularly strong impact on Se sorption/uptake, but the magnitude of the effects depended on the order of addition (i.e. whether the organic complexing agent was pre-equilibrated with HCP or not). With EDTA and ISA concentrations of 2×10^{-3} M, sorption/uptake decreased by roughly a factor 2–3 without pre-equilibration, and by one to two orders of magnitude with pre-equilibration. Pointeau et al. (2006b) proposed that sorption of the organic acid anions competes with the sorption/uptake of the selenite anion. This is consistent with i) simple mass law considerations and ii) the reasonable assumption of similar uptake mechanisms of these anions, considering their similar behaviour in terms of Ca^{2+} complexation.

The oxo-anions of higher oxidation states (selenate, molybdate, pertechnetate) are presumably less influenced by competitive effects, since they are taken up by a more unique process (replacement of sulphate in ettringite and monosulphate).

Natural analogues/observations from nature

Analogue studies are available that characterise cement degradation, including attack by specific ions (as for example chloride, cf. Lagerblad and Trägårdh 1995, Smellie 1998). A number of studies on trace element mineralogy at Maqarin provided qualitative evidence for the association of relevant elements with HCP mineral phases (Milodowski et al. 1998).

Handling in the safety assessment in PSU

After saturation, radionuclide sorption/uptake on cement is included in the modelling of radionuclide transport (see handling of processes in Section 3.6.2 and Section 4.5.2). Sorption/uptake is quantified using element/oxidation state-specific K_d values. Sorption/uptake on bitumen, waste materials and corrosion products is neglected.

Handling of uncertainties in PSU

Uncertainties in mechanistic understanding

As mentioned in the introduction, the level of understanding of sorption/uptake varies vary much between different radionuclides. Therefore, uncertainties are discussed together with sorption/uptake processes for specific elements (or groups of elements) in the section on model studies/experimental studies.

Model simplifications uncertainties

Quantification of sorption/uptake is based on the simple concept of constant K_d. It is important to note that the distribution coefficient K_d simply represents a measure quantifying the distribution of a solute between the solution phase and some sorbing solid phase; K_d provides no information regarding the nature of the underlying processes that resulted in the respective distribution. Also, K_d is not applicable to the description of a solubility limitation of a given solute according to some solubility product (i.e. is not applicable to oversaturated systems). As a simple distribution coefficient, K_d is a highly conditional parameter, which is strictly only valid for the specific set of conditions used to derive it. The uncertainties of a K_d for a given set of conditions can be estimated. Because hydrated cement systems are well buffered, it should be also possible to sufficiently constrain the conditions. At the same time, the simple K_d concept is based on reversibility of sorption/uptake. While reversibility has been shown in some cases (see e.g. the section on Th above), reversibility cannot be assumed *a priori* in view of the various incorporation processes relevant for uptake by HCP. In the long run, the continuous changes that the solid HCP is undergoing may also lead to an apparent non-reversibility, which has to be separated from actual sorption/uptake processes. More details are given in the Data report (SKB 2014c).

Input data and data uncertainties

For the most part, input data are K_d values that can be used directly in consequence calculations. Uncertainties of these K_d values can be estimated for a given set of conditions and degradation states. These details are given in the Data report (SKB 2014c).

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or similar reviews by other competent organisations within the nuclear field, or have been published by refereed scientific journals.

3.5.4 Colloid formation and transport

Overview/general description

Colloids, Brownian particles in the 1 nm to 1 μm size range (operationally, the cut off size for colloids is 0.45 μm), are characterised by their large specific surface area, on which contaminants may be sorbed. Mobile colloids may therefore enhance the transport of contaminants that would otherwise be sorbed onto immobile surfaces. The role of Colloid-Facilitated Transport (CFT) is often overlooked in solute transport because of the relatively low concentration of colloids. However, CFT may be crucial for chemicals that are hazardous at very low concentrations and is therefore of concern for nuclear waste management.

Colloid-Facilitated Transport of contaminants must be considered in safety assessment modelling if four criteria are met (Ryan and Elimelech 1996): colloids must be (i) present (ii) stable (iii) mobile, and (iv) contaminants must interact with colloids strongly enough to compete with sorption onto immobile solid surfaces.

Further to this, in a more elaborate decision tree, Swanton et al. (2010) introduced criterias for radionuclide-colloidal interactions. The first two criterias deal with colloid formation and stability. The third criterion focuses on the transport of colloids and on their interactions with immobile solid surfaces. The last criterion considers the relative affinities of contaminants for sorption onto surfaces in the colloid–water–solid system.

(i) Presence of colloids at SFR:

Colloids are meta-stable particles that thrive in biogeochemical and interfacial gradients. The nature and diversity of the containment barriers and the waste contained in SFR would give sufficiently high gradients to stimulate colloid generation when granitic groundwater gets in contact with the containment and the waste.

Considering the composition of the waste form, four types of colloids are expected: organic colloids, cementitious colloids, iron oxyhydroxide colloids resulting from steel corrosion and radionuclide intrinsic colloids. In addition, the chemical and microbial degradation of organic materials, e.g. degradation of cellulose will affect the water composition and thence the formation of colloids. Bitumen is a colloidal material in itself and may potentially generate particles as a result of its chemical and/or biological degradation.

Ramsay et al. (1988) describe the generation of near-field colloids from cementitious material as a sequence of processes. The first step involves the initial dissolution of cement material, leading to the supersaturation of the cement pore water (CPW) with respect to solubility-controlling phases and, finally, nucleation and growth of colloids. According to Ramsay et al. (1991), the generation of near-field colloids and their concentration in CPW critically depends on the silica content of the cementitious material.

Colloids may be generated in the near-field of a repository by similar mechanisms to those occurring in groundwater systems. They may be generated by the physical disintegration (spalling) of the cement matrices in contact with water (e.g. Swanton et al. 2000) and the corrosion of metallic constituents of the wastes (e.g. steels, Magnox, zircaloy, aluminium), waste containers and other metal structures within the repository. Ramsay (1988), recognising that cement is essentially a colloid-based material, highlighted the potential formation of colloids from the cementitious backfill and waste encapsulation grouts by the dissolution and reprecipitation of cement phases. Colloids may also grow by aggregation processes or may break-up to form smaller particles by disaggregation (peptisation). The rate of colloid aggregation or peptisation depends on the interaction forces that control colloid stability during collision.

More recently Wieland and Spieler (2001) have performed a very careful characterisation of colloidal content and particle size distribution in CPW corresponding to evolved cement in equilibrium with $Ca(OH)_2(s)$. The total colloid concentration was in the 1×10^{12} to 5×10^{14} particles per liter. The predominant particle size range was under 50 nm. The estimated colloidal mass concentrations were relatively small, less than 0.1 ppm. The relatively low colloidal mass concentrations were explained by the destabilisation effect of the Ca^{2+} concentration in equilibrium with portlandite that are larger than millimolar in these initial cement degradation stages (see next Section on Colloidal Stability). In a later work Fujita et al. (2003) found similar colloidal population numbers (10^{11} to 10^{12} particles/dm^3 in leachates from High Flyash and Silica fume-content Cement, (HFSC, low alkalinity cement) with an inverse correlation with Solid/Liquid ratio in the range 1:5 to 1:100 and also an inverse correlation with temperature in the range 25–60°C. They also investigated the composition and mechanism of generation and they concluded that the particles were basically Si, Ca, Al aggregates that have been detached from the cement.

However, Alexander and Möri (2003) indicated a much larger spread in population numbers for near-field colloids, ranging some 10 orders of magnitude.

Bitumen is a colloidal system by itself and its stability has been studied in relation to its rheological properties and the constructive applications. There are no specific investigations related to colloidal generation in bituminised waste, but the work by Rodriguez-Valverde et al. (2003) indicates that bitumens become polydispersed in high pH water solutions but high ionic strength destabilises the dispersions.

Iron oxyhydroxide colloids may be generated during the corrosion of steel by the oxygen remaining in the system after the operational period. This process is discussed in the Metal Corrosion Section 3.5.9.

Organic compounds have a tendency to build colloidal suspensions in aquatic media. In a recent review performed by NDA on the colloidal behaviour of the near field of a cementitious repository (Swanton et al. 2010), the authors concluded that there is no information regarding colloidal generation and stability of organic materials in the near field.

Intrinsic radionuclide colloids result from the aggregation of hydrolysed radionuclides, particularly the highly charged actinides released from the waste (Neck et al. 2002, Walther et al. 2009). Although the actinide content is relatively low in the SFR inventory the process should be handled accordingly.

Microbes are additional potential carriers of radionuclides but are discussed within the Microbial Processes section (3.5.8) and will not be discussed further here.

(ii) Stability of colloids:

Electrostatic forces are involved in the stabilisation of colloids, thus colloids stability depends upon the colloid composition, the ionic strength of the surrounding solution and the pH. Colloids are often characterised by their pH_{pzc} (pH at which colloid surface charge is zero). The alkaline pH within CPW is propitious to colloid formation, as it results in negatively charged surfaces, enhancing colloid stability. However, high ionic strength solutions favour colloid coagulation as they reduce the thickness of the electrical double layer surrounding the colloids and, hence, intercolloid repulsion. Colloids are dispersed in solutions of moderate ionic strength.

Since mineral surfaces are generally negatively charged, cation concentrations have a particular influence on colloid stability. Alkaline earth cations such as Ca^{2+} and Mg^{2+} are important because concentrations higher than 10^{-4} mole/dm^3 promote colloid coagulation (Laaksoharju et al. 1995). Both Ca^{2+} and Mg^{2+} are expected to be present at significant concentrations in Forsmark groundwaters over most of a glacial cycle. Their influence in the near-field is deemed to be limited due to the presence of cementitious materials that ensure high alkaline earth divalent cation concentrations over the entire climatic evolution of the system. The range of Ca^{2+} concentrations during cement degradation (10^{-2} to 10^{-4} mole/dm^3) would in principle promote colloid coagulation in the relevant pH range (11 to 13), see Figure 3-2, where Ca^{2+} concentrations have been reported as a function of pH for a number of cement flow-through experiments (Borkel et al. 2011).

On the other hand, bitumen colloids are quite stable at alkaline pH-values and their stability is not much affected by the presence of Ca^{2+} concentrations in the millimolar range (Liu et al. 2002).

By and large, there are two sets of conditions in SFR: most of the vaults are under cementitious conditions, with high alkalinities and relatively high Ca^{2+} concentrations, while BLA contains bituminised waste that is not surrounded by cement. In these conditions and according to Bruno et al. (2013) it is clear that bitumen colloidal suspensions are stable at high pH due to their negative surface charge. Hence they would preferentially mobilise radionuclides that are positively or neutrally charged under SFR conditions.

However, Van Loon and Kopajtic (1991b, c, d) studied the sorption behaviour of radionuclides on bitumen, their results indicate that sorption of radionuclides on bitumen suspensions is low and consequently the resulting radionuclide transport will be limited.

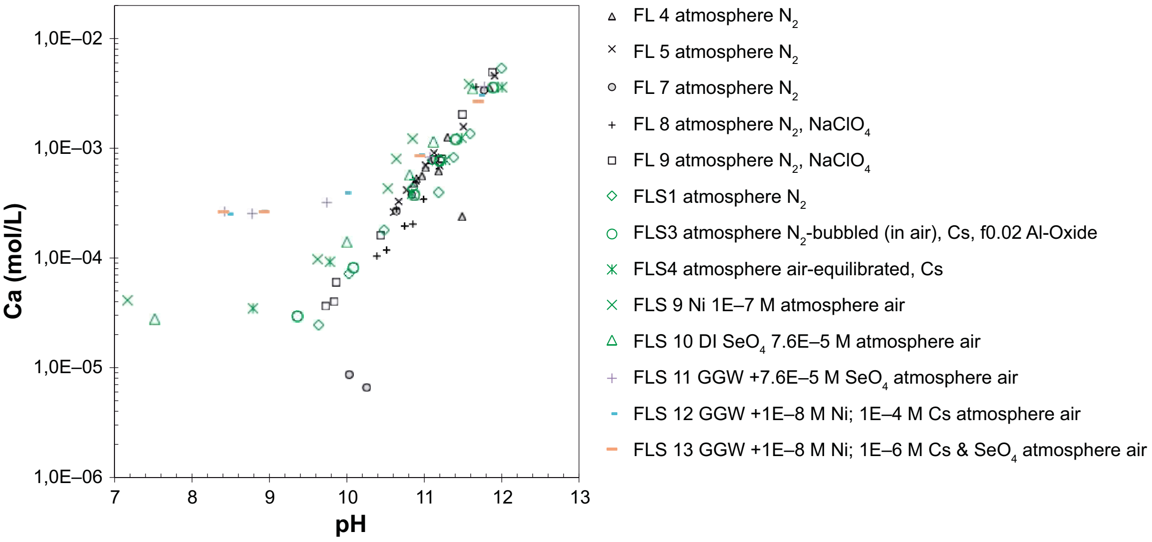

Figure 3-2. *Ca^{2+} concentrations as a function of pH for a number of cement flow-through experiments (Borkel et al. 2011).*

The concentration of colloids in the waste forms deposited in the silo and in the BMA and BTF vaults is, in principle, assumed to be negligible. The main reason is that the surrounding concrete barriers and cement packaging will supply calcium ions, which will destabilise colloidal suspensions. Furthermore, the calcium content of the intruding groundwater should prevent extensive colloid formation in BLA, which is lined with shotcrete but has no concrete barriers. However, due to the less extensive cementitious source for cations, colloids may be of potential concern in BLA, and in those parts of the system where organic waste and bitumen are abundant. This is particularly true in the case when dilute glacial groundwaters reach the BLA, promoting stability. This possibility is accounted for in specific calculations of the limiting colloidal concentrations that may be attained if and when the Ca^{2+} content in the shotcrete is washed away by the intruding dilute groundwaters. The initial calculations indicate that this will happen in some hundreds of years (Molinero et al. 2013).

(iii) Mobility of colloids:

Several physical and geochemical factors influence the stability of colloids, and as a consequence, their transport. A number of chemically or/and physically controlled filtration processes such as straining, ripening, attachment, and settling are involved in colloid removal. Attachment depends mainly on solution and surface chemistry, whereas the other removal mechanisms depend on size and density of colloids, pore structure, and flow velocity. The gradient of water velocities, the size distribution of pores, the rugosity and tortuosity of the medium surfaces and pores influence the mechanical filtration of colloids by the medium (Ryan and Elimenech 1996). Hence, colloid filtration can occur through either mechanical or electrostatic processes.

The concentration and size of pores/fractures in the waste form will affect the filtration of colloids and thus the concentration of colloids in the porewater of the waste form and surrounding system components. Filtering of colloids can take place in the various cement or bitumen stabilised waste forms themselves, and also in the surrounding packaging including steel drums and concrete moulds, and within the engineered barriers such as the concrete backfill, concrete structures, and the bentonite backfill in the silo.

Stagnant hydraulic conditions in these locations are expected, based on the initial state specifications of these components, which are unfavourable for the transport of colloids.

(iv) Colloid–water–solid system stability and transport:

Colloid populations have a polydispersed size distribution, making it more difficult to characterise their behaviour accurately. For example, small colloids may diffuse into the matrix or coagulate, whereas larger colloids may settle or be retained by the porous media. Intermediate colloids are usually the most mobile as they may travel through the fastest pathways and are often prevented from entering the smallest pores of the medium.

Heterogeneities such as fractures in cement waste matrices, and unevenly distributed porosities in bituminised wastes, may reduce the structural integrity of the waste form resulting in increased transport.

Transport of colloids attached to the surface of gas bubbles could affect the concentration of colloids in the different components of the repository system and this will be handled in the Gas Transport section (Section 3.5.10 and Section 3.6.3).

Dependencies between process and waste form variables

Interactions between the process and the waste form variables defined in Section 2.1.2 are summarised in Table 3-13.

Geometry. The presence of connected voids and fractures, especially in the cement and bitumen waste forms, will affect colloid transport and filtration. Volume expansion of ion-exchange resins in cement could cause fracturing of the cement waste matrix and surrounding containers, and generate colloids. Colloidal transport and filtering may influence the geometry through ripening and/or clogging of the conductive pores. However, the effect may be safely neglected due to the low concentrations of colloids expected in most parts of the system.

Table 3-13. Direct dependencies between the process "Colloid formation and transport" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. The pore and fracture geometry will affect transport and filtration.	Influence neglected because of the low colloid concentration expected in most parts of the repository. The possible effect on bitumen filtration and transport neglected due to the negligible impact on RN transport by bitumen colloids.	Yes. Through ripening/clogging of pores.	Influence neglected because of the low colloid concentration expected in most parts of the repository. The possible positive effect by clogging of pores by bitumen colloids are not accounted for.
Radiation intensity	No. But there is an indirect effect through decomposition of bitumen with possible generation of organic colloids.	Not relevant.	No.	Not relevant.
Temperature	Yes. Affects colloid stability.	Influence neglected. Not relevant in the range of temperatures expected.	No.	Not relevant.
Hydrological variables	Yes. Increased flow through the waste form may mobilise filtered colloids and generate colloids by erosion.	Colloids are neglected based on stability criteria. The effect on bitumen colloids neglected due to negligible impact on radionuclide transport.	No. Indirectly there is an effect via geometry.	Not relevant.
Mechanical stresses	No. Indirectly there is an effect when the cement waste matrix fractures.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes. Due to generation of eigencolloids from hydrolysed Pu(IV, III) and Am(III) species.	Neglected due to the low amounts of these nuclides in the inventory.	No. An indirect effect through water composition since dissolved radionuclides can sorb on colloids and be transported.	Not relevant.
Material composition	Yes. Cement and bitumen may generate and filter colloids.	Colloids are neglected based on stability criteria. Effects on bitumen colloids neglected due to negligible impact on RN transport.	No.	Not relevant.
Water composition	Yes. The pH and ionic strength will be particularly important for determining colloid stability.	Colloids are neglected based on stability criteria. Bitumen colloids are deemed present but neglected due to negligible impact on radionuclide transport.	Yes.Transport of colloids could influence the total dissolved solid content and the concentration of species prone to sorption onto these colloids.	Neglected influence due to low amounts of colloids based on stability criteria. Bitumen colloids neglected due to negligible impact on RN transport.
Gas variables	Yes. Hydrophobic attachement of colloids to gas bubbles might occur.	Neglected due to the expected low amounts of colloids. Effects due to existence of bitumen colloids neglected due to the low impact for radionuclides.	No.	Not relevant.

Radiation intensity. No direct influence has been identified, but there is an indirect effect through radiolytic decomposition of organic material (e.g. bitumen), with possible generation of organic colloids (see Section 3.1.3). This indirect influence is neglected because of the relatively moderate radionuclide inventory in most parts of SFR.

Temperature. An increase in temperature may thermodynamically favour the aggregation of colloids. Inorganic particles may evolve towards more stable phases. However, some repulsive forces increase with temperature in emulsions (fluid interfaces) due to molecular-scale fluctuations caused by thermal fluctuation interactions (Petkov et al. 1998). The complex temperature dependence of the electrostatic repulsion has also been studied in García-García et al. (2010). The temperature gradient in SFR is however too small to have any significant effect and the influence is therefore neglected.

Hydrological variables. Increased groundwater flow leads to colloid mobilisation (McKay et al. 2000). Both the abundance of colloids and the size of mobilised colloids increase with a rising flow rate, as expected from hydrodynamic detachment theory (Ryan and Elimenech 1996). Colloid formation could also affect flow properties indirectly via Geometry, by clogging smaller pore spaces in the waste matrices.

Mechanical stresses. Fracturing of a cement waste matrix, can potentially favour the formation of colloids. The same applies for bituminised waste matrices, where fracturing and spallation could enhance colloidal generation. This is an indirect influence of mechanical stresses via the process of fracturing (see Section 3.4.1).

Radionuclide inventory. The release of hydrolysed species from the waste may aggregate and form intrinsic radionuclide colloids. Only the limited Pu and Am inventory is of concern for this issue.

Material composition. The composition of the waste form materials determines their surface charge, which may influence the filtration of dispersed colloids, through electrostatic interaction.

There is also an indirect influence via Geometry whereby recrystallisation/mineralisation of the cement hydration products in the waste matrix may change the internal physical structure of the cement (pore size and pore connectivity), which could affect the filter function of the cement waste matrix. Furthermore, this could potentially favour the formation of colloids, although the presence of calcium-rich cement pore waters will inhibit the stability of the colloidal dispersions.

Water composition. Surface charge is dependent on the pH of the solution. Thus, the surface charge of a colloid depends on its mineralogy and the pH of the solution. If colloids and the surfaces of the porous medium have the same charge, repulsive forces help maintain colloid stability. Conversely, attractive or neutral forces favour colloid coagulation and deposition. Since variations in pH could change the surface charges they can also influence colloid stability. Furthermore, at high ionic strength, van der Waals attractive forces are dominant, destabilising colloidal particles (i.e. causing them to coagulate and become immobile). Colloids are less stable in the presence of bivalent than in presence of monovalent cations (Grolimund et al. 1998). The predicted calcium concentrations in cement degradation environments will therefore reduce colloidal stability.

Gas variables. The presence of gas bubbles may enhance the transport of colloids that attach to their surfaces. Gas transport of colloids has been invoked as a potential mechanism of radionuclide mobilisation, particularly at the water/gas interface. Indirectly, gas build-up can increase the pressure in the matrix and therefore cause the waste matrix to fracture (see Section 3.4.1), which favours the formation of colloids.

Boundary conditions

The formation of colloids and their stability is an inherent boundary condition of the system. The physical boundaries are set by the geometries of the components involved.

Model studies/experimental studies

Colloid generation and stability

The specific conditions prevailing in a cementitious near-field, i.e. high ionic strength and Ca^{2+} concentrations in the millimolar range, favour colloid coagulation and deposition processes, thus reducing the colloid inventory of the pore water. Favourable chemical conditions for colloid–colloid and colloid–solid phase interactions are retained in stage I and II of the cement degradation (Wieland 2001).

The composition and stability of cementitious colloids have been studied by Fujita et al. (2003). They could relate the stability behaviour of the polydispersed cement particles with the Ca^{2+} concentration in solution by using the DLVO theory. Nevertheless, one has to bear in mind that experiments with colloidal populations are intrinsically difficult due to their meta-stability from a thermodynamic point of view (Alexander and Möri 2003).

Bitumen is a colloidal material and colloids eroding from the waste package may contribute to CFT of radionuclides. There are, to our knowledge, no experimental studies concerning this issue and bitumen analogues have not been investigated with this question in mind. It is expected that bitumen colloids will be destabilised by the presence of the relatively high Ca^{2+} concentrations, but no experimental proof is available. However, the investigations by Rodríguez-Valverde et al. (2003) indicate that bitumen can be dispersed in water and that bitumen particles have large electropheric mobility at high pH values.

Radionuclide intrinsic colloids are usually generated at near neutral pH values and are destabilised in alkaline environments (Neck et al. 2002, Walther et al. 2009), hence we would not expect the formation of colloidal Pu and Am due to the high alkalinity of the cementitious environment and the presence of relatively high Ca^{2+} concentrations. However, recent investigations indicate that aqueous anionic complexes are stabilised in the presence of high concentrations of Ca^{2+} (Altmaier et al. 2008). This effect would only be important in the initial stages of cement degradation, as the stabilisation of anionic complexes occurs at $[Ca^{2+}] > 10^{-2}$ mole/dm^3.

Sorption on bitumen colloids

Van Loon an Kopajtic (1991b, c, d) studied the sorption of Cs^+, Sr^{2+} and Ni^{2+} on bitumen. To this end, a bitumen suspension was prepared under highly alkaline conditions and equilibrated to the desired chemical conditions. The mechanisms of sorption could be identified and a sorption model for the 3 radionuclides was proposed. In the cases of Cs^+ and Sr^{2+}, ion exchange on the deprotonated carboxylic groups of the bitumen was the main sorption mechanism. It could be shown that, in the cases of Cs^+ and Sr^{2+}, competition mainly with Na^+, K^+ and Ca^{2+} present in the cement pore water resulted in very low sorption values on bitumen (Van Loon and Kopajtic 1991b). In the case of Ni^{2+}, surface complexation is the dominating sorption process. For the latter radionuclide, competition with OH^- in solution caused a very low sorption value, because hydrolysed species were found not to sorb on the bitumen surface (Van Loon and Kopajtic 1991d). Model calculations made for U^{6+} and Eu^{3+} showed that also for these elements, only very low sorption values can be expected based on the formation of hydrolysed species in solution that – in analogy with Ni^{2+} – are assumed not to sorb on bitumen (Van Loon and Kopajtic 1991d).

Colloid transport

Colloid transport in the waste forms has not been considered in the safety analyses. The main reason for this is that the concentration of colloids is expected to be low in a cementitious environment (see SKB 2001a, b). This may not be the case in BLA, but the safety case assumes that there are no restrictions to migration inside the BLA (SKB 2001b). This is discussed thoroughly in the Barrier process report (SKB 2014a) and it is only used here as a boundary condition.

Natural analogues/observation from nature

The Maqarin Natural Analogue (in NW Jordan) is an alkaline environment resulting from low temperature leaching of an assemblage of natural cement minerals. The minerals were produced as a result of high temperature/low pressure metamorphism of marls and limestones. Evidence from the Maqarin groundwaters suggests that the numbers of colloids generated in the cement zone will be low, comparable with low pH groundwaters (magnitude of 10^7 colloids · m/dm^3). Sampling for colloids was conducted under oxidising conditions, rather than those representative of the reducing conditions within a repository (Smellie 1998). Nevertheless, as the colloidal particles had no redox sensitive components, the outcome of these investigations could also be used in an anoxic environment.

Time perspective

When water comes into contact with the waste, changes in water composition and hydraulic properties may occur and influence colloid stability and mobility. These changes will be limited to those areas where cement is not available to limit colloidal stability.

In addition, changes in the hydrogeological and geochemical conditions due to uplift and climate change may influence both the stability and transport of colloids. This is particularly true for the future infiltration of dilute groundwaters, as the repository comes under the influence of meteoric waters.

Handling in the safety assessment SR-PSU

Low concentrations of colloids, except for bitumen colloids, are expected in most parts of the repository and hence the influence of colloids on radionuclide transport has been neglected in the main scenario. Although not assessed and explicitly accounted for in the radionuclide transport modelling, the stabilising matrix as well as the concrete packaging have an inherent filtration capacity for colloids. These components therefore provide a cautiously neglected physical and electrostatic barrier which would restrict the transport of any colloidal particles to and from the waste form, and therefore further support this handling.

Bitumen colloids are likely to occur and will be stable and numerous in cementitious environments. However, the extent of radionuclide sorption on bituminous colloids is expected to be low and therefore their potential contribution to radionuclide transport at SFR is deemed to be limited. Hence, no additional consideration for PSU radionuclide transport calculations is made. Since the impact of bitumen colloids on radionuclide transport are negligible, no other impacts of bitumen colloids on the waste form are considered.

The potential impact of colloids upon radionuclide migration is handeled in the scenario describing the potential faster release of radionuclides from the waste form.

Handling of uncertainties the safety assessment SR-PSU

Uncertainties in mechanistic understanding

In general, colloid formation and stability may be neglected, in particular when the Ca^{2+} levels are kept to the expected concentrations, in equilibrium with portlandite.

The influence of organic compounds of the waste on the stability of colloids is uncertain, as no experimental evidence is available. The stability and transport of bitumen colloids is not well understood mechanistically.

Model simplification uncertainty

As colloid formation and stability in the waste forms are in general neglected, the process of transport and filtration of colloids is not taken into account in models.

Input data and data uncertainty

There is significant uncertainty in the data used for the generation and stability of bitumen colloids, as no experimental data are available. The influence of the changing water composition (mainly pH and ionic strength) on colloid generation and mobility are poorly understood. Additionally, the role of organic compounds on the stabilisation of colloids are poorly understood.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.5 Dissolution, precipitation and recrystallisation

Overview/general description

This process description focuses on cement conditioned waste forms and degradation processes affecting cement and concrete in the short- and long-term. Metals in the waste forms are assumed to undergo oxidative dissolution (corrosion), often followed by hydrolysis and precipitation of solid oxides/hydroxides on the metal surface (corrosion products) and the process is described in Section 3.5.9, dissolution of organic material in the waste forms are assumed to follow degradation processes described in Section 3.5.6. Bitumen is used as an immobilisation matrix for certain waste types (mainly ion-exchangers and evaporator salts) since it is considered to provide a physically and chemically stable waste form (IAEA 1993). Bitumen consists of mixtures of mainly aliphatic and aromatic hydrocarbons of high molecular weight and is produced in a range of qualities with different mechanical properties. Bitumen is considered to be highly insoluble in water (Eschrich 1980). However, the material may be subjected to physical, chemical and microbiological processes that influence its retaining properties. These degradation processes are described in various sections in this report, including:

- Chemical and biological degradation of the organic materials (Section 3.5.6 and Section 3.5.8 respectively).
- Degradation due to irradiation (Section 3.1.3).
- Formation of fractures (Section 3.4.1).
- As a result of radiolysis (Section 3.1.3).
- Ageing (Section 3.4.1).
- Water uptake and swelling (Section 3.5.7).

The dissolution and release of evaporator salts and radionuclides from the bitumen waste forms ultimately depends on the extent to which these bitumen degrading processes occur. Since the processes are described elsewhere in this report, they will not be further discussed in this section.

Since many of the fundamental dissolution, precipitation and recrystallisation processes in cement waste matrices are similar to those occurring in the concrete plugs studied for SR-Site, essential parts of the descriptions have been extracted, and when required modified, from the SR-Site Buffer, backfill and closure report (SKB 2010a).

Dissolution–precipitation

Dissolution occurs when a solid chemical compound is undersaturated with respect to the solution it is in contact with, and disintegrates to form dissolved species. Net dissolution can take place as long as the solid phase is present and the solubility limit of the solution is not reached. Conversely, when a solution becomes supersaturated with respect to a solid phase, dissolved species precipitate out of solution. Net precipitation can take place as long as the solution remains oversaturated. The dissolution–precipitation processes continue when the phases are at equilibrium, however the two processes proceed at equal rates which means that the concentrations in solution and the amount of the solid compound remain unchanged.

It should be noted that dissolution can also occur during organic degradation and metal corrosion processes, if the reaction products are soluble under the local conditions (see Section 3.1.3, Section 3.5.6 and Section 3.5.9).

Recrystallisation

Recrystallisation involves a gradual change in the structure of a precipitated compound to achieve a higher degree of crystallinity, while maintaining the same chemical composition. The driving force for the recrystallisation process is the higher thermodynamic stability of the more crystalline structures, which also confers a lower solubility. In a chemical system with a static solution composition, the general tendency is, therefore, to form compounds of increasing crystallinity over time.

In reactive systems, such as in cement during hydration, kinetic factors will have an impact on the compounds that are precipitated. The interfacial free energy (solid mineral – solution) is higher for the more crystalline, lower solubility phases of a certain mineral. Hence, according to the Ostwald step rule (see e.g. Stumm 1992), kinetics will favour precipitation of the least supersaturated compounds from the pore water solution, creating a solid phase that may be metastable compared to more crystalline phases. According to the Ostwald principle, recrystallisation processes may therefore proceed in many small steps, which over time results in increased crystallinity, interfacial free energy, and crystal size. The same principle also applies to the formation of colloids, for further descriptions of the processes of colloid stability and transport, see Section 3.5.4 and the Barrier process report (SKB 2014a).

Recrystallisation processes are of importance for understanding the long-term properties of e.g. CSH-gels[5] in cement. Recrystallisation may have an impact on the pore geometry since the very fine-structured amorphous and/or microcrystalline tobermorite-like and jennite-like mineral phases may gradually change in shape. A change in pore geometry can have a significant impact on both the hydraulic conductivity and diffusivity of the cement.

Conditions controlling dissolution–precipitation

The rate and extent of dissolution–precipitation processes in the cement waste matrix is determined by:

- The rate of advective water transport carrying dissolved species (see Section 3.5.1).
- The rate of diffusive transport of dissolved species (see Section 3.5.2).
- The composition of the cement waste matrix, including the assembly of hydrated cement clinker minerals.
- Any changes in the chemical composition of the cement waste matrix induced by chemical reactions with surrounding materials, porewater or conditioned waste. This may in turn influence the microstructure of the cement waste matrix which would affect its transport properties.
- The composition of cement waste matrix pore water. This is in turn determined by local thermodynamic equilibria between the pore water and the solid hydrated cement minerals.
- Kinetic factors causing metastable equilibria or slow establishment of equilibria.
- The composition of the groundwater and the pore water of adjacent materials (packaging, waste material).

Cement waste matrix

A cement waste matrix consists of hydrated cement clinker minerals and may also contain different filler and ballast materials such as sand, and chemical additives. Different types of conditioned waste materials (e.g. ion exchange resins, salt concentrates and scrap steel) are embedded in the cement matrix.

Additives can be used to modify the properties of the cement, e.g. to improve flow properties and workability of the freshly mixed cement slurry. In some cases significant amounts of filler materials such as slag or fly ash are added to change the mechanical or chemical properties of the cement.

Conditioning cement mixtures commonly have a high amount of cement, about 73 wt-% cement and 27 wt-% water. Details on the actual composition of the cement waste matrices in the SFR repository are presented in the Data report (SKB 2014c).

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[5] See explanation on following pages to the used notations for cement minerals

Composition of cement clinker minerals

Unhydrated cement clinker minerals are formed at high temperature in cement kilns. Typical unhydrated cement clinker minerals[6] and components are:

- Tricalcium silicate, C_3S.
- Dicalcium silicate, C_2S.
- Tricalcium aluminate, C_3A.
- Tetracalcium aluminate ferrite, C_4AF.
- Calcium sulphate (gypsum), $C\hat{s}H_2$ (added as a retardant to the cement).
- Alkali hydroxides, $N + K$.

Details on the actual composition of cement clinker minerals used for manufacture of the cement waste matrices in the SFR repository are presented in the Data report (SKB 2014c).

Hydration processes in cement

The unhydrated cement clinker minerals are highly reactive in contact with water. Hydration is the process by which the anhydrous cement clinker minerals react with water and form the new hydrated solid compounds that give the cement its mechanical strength. The amount of water added to the cement influences the properties of the hardened cement.

The amount of water used relative to dry cement is termed the w/c-ratio. At low w/c-ratios (less than about 0.3), the cement clinker minerals are not completely hydrated. At high w/c-ratios, the water remaining after full hydration has occurred, increases the porosity. In general terms, a low w/c-ratio would give denser and stronger cement than a high w/c-ratio. The choice of mixing proportions is, however, a compromise between factors such as high strength, desire to reach full hydration, workability of the fresh paste and special demands on the permeability. Commonly, a w/c-ratio between 0.3 and 0.6 is used for normal construction work. The w/c-ratio used for conditioning cement in SFR is about 0.37, which is expected to be close to optimum with respect to achieving full hydration and low porosity. A simple model for the hydration of cement is given in Höglund (1992).

The main binding phases of hydrated cement are calcium silicate hydrates (CSH) and calcium hydroxide (CH), which form during hydration. Complex calcium sulpho ferri-aluminates[7] known as AF_t and AF_m are also major hydration products. AF_t and AF_m are produced from reactions involving the calcium aluminate, calcium alumino-ferrite, and calcium sulphate.

The hydrated cement clinker minerals are alkaline. The interstitial solution of an ordinary Portland-cement-based paste will reach chemical equilibrium with the cement constituents, resulting in an alkaline porewater (pH around 13) with high concentrations of Na^+, K^+, Ca^{2+} and OH^- ions.

The hydrated clinker minerals are fairly soluble in comparison with many rock forming silicate minerals, which means that they are more susceptible to dissolution and degradation. The contact of the alkaline cement porewater with dilute groundwater (pH lower than 9) at the exterior of the repository creates large concentration gradients that induce diffusive mass transport (of mainly Na^+, K^+, Ca^{2+} and OH^- ions) outwards from the porous cement paste, see Section 3.5.2 and Section 4.4.2. Initially, the cement waste matrix is protected from the direct influence of groundwater due to buffering by other concrete barriers, including the concrete packaging, although with time the impact by exchange with groundwater is inevitable. Renewal of the external groundwater by advection will carry away the released cement porewater components, and accelerate the outward diffusion of ions and the degradation of remaining solid cement components. See Section 3.5.1 and Section 4.4.1 for descriptions of the advection in the waste form and packaging respectively. However, in many cases the dissolution of one mineral results in the precipitation of another mineral. The high pH created by

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[6] Abbreviations commonly used in cement science for the clinker components:
$C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$, $C\hat{s}H_2 = CaSO_4{\cdot}2H_2O$, $N = Na_2O$, $K = K_2O$

[7] $AF_t = C_6(A,F)X_3H_y$ and $AF_m = C_4(A,F)X_2H_y$, where $C = CaO$, $H = H_2O$, $A = Al_2O_3$, $F = Fe_2O_3$ and $X = CaSO_4$; y = 32 for ettringite and y = 12 for monosulphate.

dissolution of the hydrated cement clinker minerals may also increase the reactivity of other minerals present in the cement waste matrix (e.g. filler materials or other additives), in the waste, in adjacent barriers (e.g. cement components and concrete ballast materials), in the packaging, and/or in the adjacent rock.

During the initial stage, the pore water will be dominated by alkali hydroxides (K^+, Na^+ and OH^- ions) which give alkaline conditions with a pH of about 13, unless the conditioned waste contains substantial amounts of chemical compounds that alter the chemical conditions. Generally, alkali metal hydroxides are soluble, and would therefore be easily leached from the cement waste matrix. Studies of the composition of the solid phases and pore water of concrete show, however, that alkali metal hydroxides are associated (e.g. by sorption) with the solid phases to a significant degree, likely the CSH-gel phases or the ballast (Lagerblad and Trägårdh 1995). Leaching of the alkali metal hydroxides will gradually lower the pH and the solubility of the calcium hydroxide and of the CSH-gel will increase. The durability of cement is affected by the decalcification process, since calcium is the main component of hydrated cement. The continuous outwards diffusion of calcium ions induces dissolution of calcium compounds to maintain chemical equilibrium. The dissolution of calcium hydroxide (portlandite) and CSH-gels leads to an increase in the porosity of the cement, resulting in an enhanced diffusion rate.

The solubility of the CSH-gel is complex due to its amorphous to semicrystalline structure, which can be described in terms of a mixture of tobermorite- and jennite-like phases (Chen et al. 2004). Detailed investigations have shown that CSH-gels have a large variability in their composition, nanostructure and morphology (Richardson 2004). Significant efforts have been made to understand the formation processes and structure of CSH-gels. Several attempts have been made to determine the relationship between solid phase composition and the composition of the porewater in CSH-gels, and a comprehensive overview and compilation of experimental data is presented by Chen et al. (2004). Based on interpretations of these data and new experimental results, Chen et al. (2004) suggest that the observed variability in the solubility of CSH-gels, especially at high Ca/Si-ratios, can be explained by different experimental approaches that may cause differences in the silicate structure, in particular the occurrence of Ca–OH bonds in CSH-gels with jennite-like structure. The results also suggest that CSH solids are present in different metastable phases that are susceptible to transforming (recrystallising) into one another in the long term. In their experimental studies, Baur et al. (2004) used radioisotopes to determine dissolution–precipitation rates for ettringite, monosulphate and CSH under equilibrium conditions, and they found evidence that a complete reconstruction can be achieved in 1–4 years. Experimental investigations using combined small-angle neutron and X-ray scattering data have presented revised data on the density of CSH-gels that differ from previous estimates based on different drying techniques (Allen et al. 2007).

The dissolution of calcium silicate hydrates is accompanied by the leaching of other minerals from the cement. AF_m dissolution releases $Al(OH)_4^-$, which will also be transported by diffusion and could induce precipitation of either secondary AF_m or ettringite (in the presence of excess sulphate). The large molar volumes and crystalline morphologies of these minerals may reduce the porosity and mechanical strength of the cement by producing micro-fractures (Lagerblad 2001). If the external groundwater contains dissolved carbon dioxide, precipitation of calcite might be expected. This has been found to reduce the degradation rate by sealing the pore network on the exposed surface of cement (Pfingsten 2001). Brucite may also be prone to precipitation at the cement–groundwater interface, due to its low solubility at high pH (Lagerblad 2001).

The reactions between certain hydrated cement minerals and dissolved compounds transported in the pore water are also important. The chemical composition of groundwater and the porewaters of other barriers and the waste affect the rate of degradation. Laboratory experiments have shown that the degradation depth is highly dependent on the carbonate concentration of the external solution. A study by Moranville et al. (2004) showed that the leaching depth decreases by a factor of 5 when the external water is in equilibrium with atmospheric CO_2, due to the sealing effect of calcite precipitation at the cement–water interface. An external groundwater containing dissolved sulphate could also have a large impact on the longevity of concrete material (Höglund 2001) due to reaction with calcium aluminates causing ettringite precipitation. Ettringite has the ability to bind large amounts of water as crystallisation water, resulting in this mineral phase having a large molar volume.

This can result in fracturing and mechanical deterioration of the cement. The chloride concentration of the groundwater can also affect the long-term behaviour of the cement due to the precipitation of Friedel's salt (i.e. aluminium and calcium chlorides). A combined attack by sulphate and carbonate at low temperature may lead to precipitation of thaumasite ($Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$) by reaction with AF_m/AF_t phases where silica from CSH-gel has replaced aluminate. This could cause the concrete to deteriorate (Justnes 2003). Different routes have been described for the formation of thaumasite, e.g. i) where ettringite reacts with CSH and calcite, or ii) where CSH reacts with gypsum and calcite as suggested by Bellmann (2004). Solid solutions between ettringite and thaumasite are reported to form where aluminium and silicon can partly replace each other (Barnett et al. 2002). Damidot et al. (2004) investigated the complex system of $CaO–Al_2O_3–SiO_2–CaSO_4–CaCO_3$ and suggested that thaumasite is stable at lower pH than ettringite but requires higher sulphate concentrations. Modelling exercises by Glasser and Matschei (2007) showed a complex reaction sequence involving AF_m, hemi-carbo aluminate, ettringite, mono-carbo aluminate, portlandite and calcite in the initial stages, and mono-carbo aluminate, calcite, strätlingite, ettringite, CSH-gel, thaumasite, aluminium hydroxide, gypsum and amorphous silica in the later stages.

Local supersaturation of minerals in the pore water may occur in response to any rapid change in the external chemical conditions, such as release of dissolved compounds from the waste or changes of the groundwater composition. This could result in the formation of colloidal material in the pore water. However, studies of the alkaline springs in Maqarin, Jordan (Smellie 1998) support the expectation that the colloid concentration would be low due to the high concentration of calcium ions in the vicinity of cement and concrete. The transport of colloids in the waste form and packaging is described in depth in Section 3.5.4 and Section 4.4.4 respectively.

Under hyper-alkaline conditions there is a risk for alkali-silica reactions between the hydroxyl ions leached from the cement and reactive silica in ballast material, if used. This causes formation of alkali-silica gels, which increase in volume by uptake of water and exert an expansive pressure that may eventually lead to fracture formation. This reaction is known to be deleterious for the mechanical strength of cement and concrete. The cements and ballast materials used for waste conditioning and construction concretes in SFR are selected to avoid this type of reaction.

Chemical interactions with the waste

General

The cement waste matrix is in direct contact with the waste. Migration of chemical species from the waste material to the cement waste matrix may initiate chemical reactions that could affect the integrity of the cement matrix. Waste components of particular importance include those that contain significant amounts of soluble salts, degradable materials such as ion exchange resins and organic materials, see Section 3.1.3, Section 3.5.6 and Section 3.5.8. The exchange equilibria of ionic species associated with the exchange sites of spent ion exchange resins may change during stabilisation with cement. IonGradual exchange of pore water caused by groundwater flow may induce ion exchange processes may also occur during/after resaturation due to increased contact with groundwater, and thisthat would release dissolved ions into the cement matrix pore water.

Exposure to increased concentrations of dissolved species from the waste may induce dissolution–precipitation such as: the formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) from the reaction between monosulphate and sulphate; the formation of Friedel's salt ($Ca_2Al(OH)_6(Cl,OH)\cdot 2H_2O$) as result of increased chloride concentrations; or the precipitation of thaumasite ($Ca_3Si(OH)_6(CO_3)(SO_4)\cdot 12H_2O$) as a result of increased exposure to carbon dioxide/dissolved carbonate species and sulphate. The cement waste matrix will also act as a buffer for the surrounding concrete packaging and other concrete barriers against attack by deleterious species in the conditioned waste.

Chemical compounds in the waste

The information available on the specific chemical composition of waste types containing salts, sludges, evaporator concentrates and ashes is fairly sparse.

Cement conditioned ion exchange resins (e.g. waste type F.15) and bitumen conditioned ion exchange resins (e.g. waste type F.17) may contain evaporator concentrates up to 15 wt-% and 65 wt-%, respectively, and these concentrates may contain a significant amount of salts (Almkvist and Gordon 2007). Decontamination sludges may contain iron, nickel and chromium. Waste type B.05 constitutes waste drums with bitumen-conditioned ion exchange resins and contains about 0.2–0.5 kg sodium sulphate (Almkvist and Gordon 2007, Johansson 1999). Sodium sulphate may be released from the bitumen matrix and potentially affect adjacent cement waste matrices in the repository through the formation of the expanding mineral ettringite.

Boric acid, lithium, ammonia and hydrazine are mentioned in the waste characterisation (waste types R.01, R.02, R.15, R.16) (Almkvist and Gordon 2007). Boric acid may retard cement hydration (Conner 1990, Shi and Fernández-Jiménez 2006, Palomo and López de la Fuente 2003), which increases the risk of late hydration and volume expansion of the cement waste matrix. Some information suggests that boron will precipitate under alkaline conditions as calcium hexahydroborite $CaO \cdot B_2O_3 \cdot 6H_2O$, and calcium quadriboroaluminate $3CaO \cdot Al_2O_3 \cdot 2Ca[B(OH)_4]_2 \cdot Ca(OH)_2 \cdot 30H_2O$ (Cau Dit Coumes 2000). Hydrazine (N_2H_4) is a strong reducing agent in alkaline environments (Conner 1990); it is therefore likely to be consumed by reaction with metal ions during cement hydration, e.g. iron or chromium which are common components of cement. Ammonia in the form of ammonium ions may act to ion-exchange for calcium ions resulting in mobilisation of calcium. Ammonium ions in concentrations 15–30 mg/dm^3 are regarded as weakly aggressive to concrete and in concentrations > 100 mg/dm^3 as very aggressive (Fagerlund 2011). Lithium is likely to behave similar to other alkali metals and have small impact on concrete.

Salts of manganese, tin, zinc, copper and lead may reduce the strength of cements, and sodium phosphate may act as a retarder for cement hydration (Conner 1990). Magnesium salts may affect cements through the precipitation of brucite ($Mg(OH)_2$) at the cement surface, followed by formation of gypsym and ettringite, ultimately leading to decalcification of the CSH, producing non-cohesive magnesium silicate hydrates (MSH) (Santhanam et al. 2003). This may result in loss of strength in cement materials.

A literature survey on the effects of salts on cement stability and applicable methods for determining these effects identified that few experimental studies had been carried out although there had been several theoretical modelling studies (SKBdoc 1003223).

Chemical interactions with the other barriers and the groundwater

The presence of other concrete barriers around the cement waste matrix, such as the concrete packaging, the silo wall and concrete walls in BMA, will protect the cement waste matrix from direct attack by deleterious species in the groundwater by buffering the chemical conditions. The chemical conditions at the surface of the cement waste matrix may therefore remain fairly constant, characterised by a high pH, as long as the other barriers can withstand the action of the groundwater. Over time, the effect of the groundwater will become increasingly important as the buffering components of the other concrete barriers become depleted.

Dependencies between process and waste form variables

The following table shows how the Dissolution, precipitation and recrystallisation processes in cement waste matrix influence, and are influenced by, all waste form variables defined in Section 2.1.2.

Influence by Geometry. Yes, a direct influence has been identified. The geometry of the cement waste matrix affects the process through the total volume of cement and the reactive phases it contains. Therefore, the total pool of these mineral phases will affect the geochemical evolution of the system.

The porosity will also have a direct influence on the process, as this controls the solid-to-liquid ratio, which will affect the degradation rate of the cement matrix. Degradation will be slower at higher ratios, as the dissolution of a smaller mass fraction of the minerals will be needed to attain solution saturation. On the other hand, the dissolution–precipitation of cement mineral phases can modify the pore geometry and the total porosity of the system and, thus, modify the degradation rate of the cement waste matrix. The geometry of the cement waste matrix will have a further, indirect influence on the process via the rate of diffusion, which is proportional to the length of the diffusion pathway.

Table 3-14. Direct dependencies between the process "Dissolution, precipitation and recrystallisation" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Waste matrix dimensions and porosity (solid to liquid ratio) directly influence the process.	The waste matrix dimensions are considered. The solid-to-liquid ratio is considered.	Yes. Dissolution, precipitation and recrystallisation of solid phases can modify the porosity of the system.	Porosity changes due to dissolution–precipitation reactions are considered. Changes of the gross volume of the cement waste matrix due to internal chemical reactions with components in the waste are considered.
Radiation intensity	Yes. Radicals can form that may affect chemical bonds in the hydrated cement. The radiation intensity in the SFR waste is generally too low for this influence to be of any practical importance.	Irradiation is expected to affect mainly organic materials see Section 3.1.3. The impact on cement minerals is expected to be negligible for the anticipated radiation intensity.	No. Indirectly by contributing to the shielding of radiation, see Section 3.1.2.	Not relevant.
Temperature	Yes. Temperature affects thermodynamic constants.	Constant reference temperature assumed over long periods.	Yes. Heat effect of initial hydration is expected to take place before disposal in SFR. Long term heat effect expected negligible.	Considered insignificant.
Hydrological variables	Yes. The amount of water has a direct influence on the process. Dehydration of ion exchange resins during cement hydration may cause the resins to shrink.	The water consumption during cement hydration is calculated. Risk for dehydration of ion exchange resins during the early hydration of cement is considered.	No. Indirectly via changes of porosity and pore geometry that effect advection (see Section 3.5.1) and diffusion (see Section 3.5.2).	Not relevant.
Mechanical stresses	Yes. In general, mechanical stresses may affect chemical equilibria where volume changes of solid phases are involved. Indirect influence may occur via stresses causing fracture formation, see Section 3.4.1, which may enhance dissolution.	The direct impact is judged insignificant for the safety analysis of SFR.	Yes. The formation of expansive solid phases, e.g. ettringite, may cause mechanical stresses. Indirect influence may occur via changes in the material composition causing reduction of strength possibly leading to fracture formation, see Section 3.4.1, or ultimately collapse.	Mechanical stresses is handelled by assigning appropiate hydraulic conductivity.
Radionuclide inventory	Yes. Radionuclides are present in the waste but in small quantities.	Not considered.	No. Only indirectly via changes of pore geometry that affects radionuclide mobility and transport, see Section 3.5.1 and Section 3.5.2.	Not relevant.
Material composition	Yes. Cement mass and mineralogy and amount and composition of waste material determines the reactions that may occur.	Included in modelling.	Yes. Modification of mineral composition and reduction in mass. Transformation of certain components in the waste due to reactions with cement matrix.	Included in modelling.
Water composition	Yes. Affects the reactions within the cement matrix. Influences the rate of solute exchange with the surroundings.	Included in modelling.	Yes. Reaction with minerals results in changes in porewater composition.	Included in modelling.
Gas variables	Yes. Formation of CO_2 and H_2 in the waste could affect dissolution–precipitation.	Considered in calculations of gas generation.	Yes. CO_2 will be consumed by reaction with alkaline minerals and form calcite.	Included in modelling.

Influence on Geometry. Yes, a direct influence has been identified. The cement waste matrix geometry can be influenced directly by the gradual dissolution of alkaline minerals. The precipitation of new solid mineral phases may also clog pores in the cement and/or partially or completely fill fractures that may have formed in the cement waste matrix. Recrystallisation causes a gradually increasing porosity and less fine-structured pore geometry. This could also increase the hydraulic conductivity and the diffusivity of the cement, which could result in further changes in the porosity and internal pore structure over time.

The gross volume of the cement waste matrix may change due to internal chemical reactions with waste components, e.g. reactions between calcium aluminates in the cement and sulphate expelled from the waste would result in ettringite formation, potentially leading to an expansion of the waste matrix. For certain waste types (e.g. waste type O.02), the packaging has been equipped with expansion cassettes to allow for expansion of the waste matrix and reduce potential damage to the surrounding barriers.

Influence by Radiation intensity. Yes, a direct influence has been identified. The radiation intensity may theoretically have an influence by forming radicals that could affect chemical bonds in the hydrated cement minerals; however, the radiation intensity in the SFR waste is generally too low for this influence to be of any practical importance.

Influence on Radiation intensity. No direct influence identified. Indirectly, the presence of the cement matrix may enhance radiation shielding, which would affect the radiation intensity, see Section 3.1.2.

Influence by Temperature. Yes, a direct influence has been identified. Thermodynamic constants of chemical reactions are highly dependent on temperature and the reference temperature conditions need to be defined. However, the temperature in the cement waste matrix is not expected to vary significantly in most scenarios, therefore, minimal effects on the geochemical processes are foreseen. Temperature differences between different components in the repository are likely to level out during the operational phase, e.g. the heat of cement hydration and the heat generation due to radioactive decay are likely to have diminished to low levels. The overall judgement is that temperature and temperature variability would have insignificant impact on the dissolution–precipitation processes in the cement waste matrix.

In the long-term, the occurrence of permafrost and glaciations will change the temperature in the repository, which may introduce major changes of importance for the thermodynamic constants. Examples are the changes of stability field of AF_m versus AF_t and the stability of thaumasite with temperature, which could affect the porosity.

Influence on Temperature. Yes, a direct influence has been identified. The dissolution, precipitation and recrystallisation processes in the cement waste matrix during the post-closure phase may cause heat generation/dissipation. However, the magnitude of these processes is judged to have insignificant impact on the temperature in the repository. The cement waste matrix is manufactured off-site and is expected to be essentially fully hydrated when disposed in SFR.

Influence by Hydrological variables. Yes, a direct influence has been identified. The amount of water influences the extent of cement hydration during the early stage. This is accounted for in cement hydration modelling.

A particular issue may be of concern for certain cement conditioned ion exchange resins if too little water was added when mixing the cement and waste, causing dehydration of the resins. During the on-going hydration process, water is expelled from the swollen ion exchange resins, which causes shrinkage of the ion exchanger grains. Indirectly, the hydraulic properties of the cement may be affected as a result of subsequent water uptake during storage or after disposal which may cause the dehydrated ion exchange resins to absorb water, thereby developing a swelling pressure potentially leading to fracture formation in the cement waste matrix, see Section 3.5.7 and Section 3.4.1.

Also the transport of water and solutes will have a very important indirect influence through changes of the water composition which will affect the degradation rate of the cement waste matrix.

Influence on Hydrological variables. No direct influence identified. The dissolution, precipitation and recrystallisation of mineral phases in the cement waste matrix will have an indirect influence on the hydraulic properties of the cement via changes in its porosity and pore structure. Dissolution of minerals may increase the porosity, hydraulic conductivity and diffusivity of the cement waste matrix. Precipitation of secondary minerals may lead to clogging of pores and thus decrease the porosity, hydraulic conductivity and diffusivity of the cement waste matrix. On-going recrystallisation results in a gradually increasing porosity and a less fine-structured pore geometry, which could increase the hydraulic conductivity and diffusivity of the cement. The possible formation of expansive mineral phases, e.g. the formation of ettringite following release of sulphate from certain waste materials, could affect the hydraulic properties of the cement waste matrix indirectly via fracture formation, see Section 3.4.1, which may also affect advective transport, see Section 3.5.1, and diffusion, see Section 3.5.2.

Influence by Mechanical stresses. Yes, a direct influence has been identified. Mechanical stresses may affect chemical equilibria where the volumes of solid minerals change during the reaction. Mechanical stresses may therefore affect the dissolution, precipitation and recrystallisation processes in the cement waste matrix.

There is also an indirect effect since mechanical stresses may also induce fracture formation, which in turn could increase the rate of water flow and thereby the rate of dissolution–precipitation processes, see Section 3.4.1.

Influence on Mechanical stresses. Yes, a direct influence has been identified. Some waste types have the potential to expel significant amounts of sulphate, which may result in the formation of the expanding mineral ettringite which could create mechanical stresses in the cement waste matrix and surrounding barriers. Therefore, the dissolution, precipitation and recrystallisation processes in the cement waste matrix may affect the mechanical stresses in the repository.

Indirectly, dissolution–precipitation processes and to lesser extent recrystallisation processes may indirectly, via changes of the material composition, lead to reduced strength, which could result in fracture formation, see Section 3.4.1, and eventually collapse. Dissolution of portlandite is reported to be the main cause for loss of strength in leached concrete (Carde et al. 1996).

Influence by radionuclide inventory. Yes, a direct influence has been identified. The radionuclide inventory is expected to have a direct influence on the dissolution, precipitation and recrystallisation processes. However, since the mass and solubility of radioactive salts in SFR are low, they will have a negligible influence on both the chemical conditions and dissolution–precipitation reactions in the cement waste matrix.

Influence on radionuclide inventory. No direct influence identified. Dissolution, precipitation and recrystallisation processes may indirectly influence the radionuclide inventory by introducing changes in porosity within the cement waste matrix which may provide a pathway for radionuclide leaching, see Section 3.5.1, Section 3.5.2 and Section 3.6.2.

Influence by Material composition. Yes, a direct influence has been identified. This is one of the most relevant variables influencing this process. The type and amount of minerals are essential considerations that define the dissolution, precipitation and recrystallisation behaviour. They affect the chemical evolution of the system in terms of both the porewater composition and the minerals present in the system (i.e. newly precipitated minerals, amount of existing minerals and gradual recrystallisation of metastable minerals to more stable forms). The influence of material composition is reflected in the selection of material data for the calculations of the chemical evolution of the porewater and the degradation of the cement waste matrix.

Influence on Material composition. Yes, a direct influence has been identified. The dissolution, precipitation and recrystallisation processes will gradually change the material composition. The dissolution–precipitation processes are considered in the chemical modelling. Recrystallisation processes are considered in kinetic modelling.

Influence by Water composition. Yes, a direct influence has been identified. The porewater composition will determine which of the minerals in the system will dissolve or precipitate, and the dissolution–precipitation of these minerals will modify the chemical composition of the porewater. The exchange of porewater with surrounding barriers and waste will introduce changes in the porewater composition which will affect the dissolution–precipitation processes. Input data for chemical modelling reflects the influence of water composition.

A reasonable conceptual model is that the different minerals maintain chemical equilibrium with the water passing through the cement waste matrix; hence the dissolution rate will be proportional to the rate of water exchange which is given by the water flow rates, see Hydrological variables. As the dissolution progresses, some cement minerals may become depleted, thereby leading to changes in the thermodynamic equilibria. Certain mineral phases that form in the cement waste matrix as a result of chemical components expelled by the waste, e.g. chloride-rich salts, have a high solubility in water and hence are more susceptible to dissolution.

The dissolution of CSH-gels needs special consideration. The reason is that the CSH-gels will preferentially leach calcium, leading to an incongruent dissolution of the gels. This has the effect that the remaining gels will become gradually enriched in silica. Simplified, this can be seen as a dissolution–precipitation reaction where the dissolution of a calcium-rich phase is followed directly by the precipitation of a new phase with slightly lower calcium content. A more correct conceptualisation may be that calcium is released from the CSH-gel into solution followed by a rearrangement of the partly calcium-depleted solid silicate phase. Experimental evidence offer some support for this with an increased length of the silicate anion chains in leached CSH-gels (Haga et al. 2002). As with the other dissolution–precipitation processes, the rate of preferential leaching will be controlled by the composition, which in turn is influenced by the transport of water and solutes, see Hydrological variables.

The concept of thermodynamic equilibrium in the system means that no secondary minerals will be precipitated as long as the chemical conditions remain constant. True equilibrium may be hampered by the existence of metastable minerals that recrystallise to more stable phases very slowly. However, whenever chemical gradients are introduced, e.g. as result of chemical exchange with the groundwater, the waste or other barrier materials in the repository, new chemical equilibria may develop and result in supersaturation and precipitation of secondary minerals.

Influence on Water composition. Yes, a direct influence has been identified. The dissolution–precipitation of minerals in the cement, as well as the exchange of porewater in the cement waste matrix with the concrete packaging, the waste and other barriers, will modify the chemical composition of the porewater. Changes in water composition are calculated in the chemical modelling. Recrystallisation processes will only influence the water composition slowly.

Influence by Gas variables. Yes, a direct influence has been identified. Gases can form or dissolve through chemical or biochemical reactions in the waste contained in the cement waste matrix. CO_2 release from the waste or from other barriers is of particular importance as it could either lead to an acidic attack that dissolves alkaline minerals or to the precipitation of calcite, which could clog the pores. Hydrogen may be formed by corrosion of steel and may affect the dissolution–precipitation of redox-sensitive compounds. The partial pressures of different gases and their effects on the thermodynamical stability of minerals are considered in the chemical models. However, it is not expected that any significant amount of gases can form in the cement waste matrix *per se*. Any presence of a gas phase in the waste form is treated in Section 3.3.1. The dissipation of dissolved gases is treated in Section 3.5.10 and in the Barrier process report (SKB 2014a).

Influence on Gas variables. Yes, a direct influence has been identified. The gas composition may be affected by reactions that consume gas, e.g. by reaction of CO_2 with dissolving alkaline minerals and precipitation of calcite. An indirect effect could be the alkaline buffering at high pH that may hamper active microbial gas formation processes, see Section 3.5.8. The very alkaline conditions also mean that hydrogen evolving corrosion of steel in conditioned waste will be slow, see Section 3.5.9 and Section 3.5.10. The possible impact on the gas variables by interactions with the mineral phases is considered in the chemical modelling.

Boundary conditions

There are no particular boundary conditions to discuss for these processes. The relevant boundary conditions for a quantitative treatment of these processes are those of the processes that control solute transport between the cement matrix, the waste, the concrete packaging, the surrounding barriers and the groundwater, as adjacent system components, i.e. the boundary conditions of the processes diffusion (see Section 3.5.2) and advection (see Section 3.5.1).

Model studies/experimental studies

A large amount of relevant research has been reported in the scientific literature involving accelerated laboratory leaching tests of cement matrices; examples of important papers are those of Carde et al. (1996), Faucon et al. (1998a), Catinaud et al. (2000), Saito and Deguchi (2000), Moranville et al. (2004) and Maltais et al. (2004). The influence of the cement particle size for the performance of Portland cement has been studied by Bentz et al. (1999). Different cement hydration models have been evaluated by Bentz (2010).

A relevant decision to be taken in the reactive transport-based models of cement degradation arises from the selection of the geochemical processes to be included, reflected in the selection of basic chemical components. The consideration of the chemical components K^+, Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, OH^-, $Al(OH)_4^-$ and Cl^-, is claimed in Maltais et al. (2004) to be sufficient to describe most degradation processes, although other sets of chemical components have also been proposed, including the addition of Si in e.g. Höglund (2001), Moranville et al. (2004) and Hidalgo et al. (2007), and Fe (Möschner 2007).

In their review, Lagerblad and Trägårdh (1995) pointed out that the early models used to describe the leaching of alkali and calcium hydroxides in the SFR safety assessment were oversimplified. The criticism reflects the simplifications made when calculating the leaching of alkali hydroxides as dissolved substances, and the fact that the counter effect of alkali ions in the groundwater was neglected, leading to a rapid depletion of alkali ions in the concrete material. Furthermore, the leaching of calcium hydroxide and calcium silicate hydrates (CSH-gel) was represented as processes independent of the alkali leaching. Experimental studies by Glasser et al. (1985) indicate retention of sodium and potassium by hydrated cement minerals. Modelling of cement degradation by Berner (1990) addressed the alkali retention by assuming that 5% of the remaining inventory of sodium and potassium is released in each pore water exchange cycle. In the model study by Höglund (2001), the leaching of alkali hydroxides were represented by ion exchange processes, also taking into account the counter ion effect of the surrounding groundwater. The model for the ion exchange processes was calibrated against experimental data by Lagerblad and Trägårdh (1995). These modelling results showed a slower release of the alkali hydroxides which is a more accurate description of the process.

Further, in modelling studies by Höglund (2001) and Moranville et al. (2004) the leaching of different calcium compounds, e.g. portlandite, CSH-gel and AF_m/AF_t-phases, was coupled to the leaching of alkali hydroxides. This has the effect that, during the early period, the leaching of calcium compounds is suppressed by the high pH maintained by the alkali hydroxides in the pore water. The available data for thermodynamic calculations have significantly improved since the early studies for SFR, especially regarding the preferential leaching of calcium from CSH-gels with variable C/S-ratio. Extensive experimental data have also been provided, and combined with modelling, for different chemical systems including different combinations of calcium, silica, aluminium, sulphate, carbonate, sodium, potassium and chloride (e.g. Stronach and Glasser 1997, Perkins and Palmer 1999, Baur et al. 2004, Barbarulo et al. 2007, Birnin-Yauri and Glasser 1998, Damidot et al. 1992, 1994a, b, Damidot and Glasser 1993, 1995, de Silva and Glasser 1993, Glasser et al. 1999). Faucon et al. (1998a) used a combination of experimental studies and modelling to investigate the re-precipitation of secondary minerals including AF_m, ettringite and calcite in a cement exposed to demineralised water. Detailed studies of solid-solutions between Al- and Fe-ettringite minerals have been presented by Möschner (2007), with experimental data also presented for Fe-monosulphate and Fe-monocarbonate. The formation of Fe-ettringite phases is slower than the corresponding Al-ettringite, with time constants on the order of a few months and few weeks respectively (Möschner 2007). It was also found that Al-ettringite is more stable than Fe-ettringite at high pH, Fe-ettringite was gradually replaced by Fe-monosulphate at pH > 13.1 (Möschner 2007).

In early studies for SFR, the limiting C/S-ratio for the CSH-gel was assumed to be 2.5, and this has been shown to be too high (Stronach and Glasser 1997). The CSH-gels are commonly represented by a solid solution series that varies in composition roughly between $C_{1.8}SH$ and $C_{0.8}SH$. Berner (1990) modelled incongruent dissolution of CSH-gels, assuming CaH_2SiO_4 and $Ca(OH)_2$, and SiO_2 and CaH_2SiO_4, respectively as end-members for calcium-rich and calcium-depleted CSH-gels, and adjusting the apparent solubility product as a function of the Ca/Si-ratio. In the study by Höglund (2001), CSH-gel was represented by three discrete CSH mineral phases: $C_{1.8}SH$, $C_{1.1}SH$ and $C_{0.8}SH$. The $C_{1.8}SH$-phase may coexist with portlandite in the more alkaline regime, whereas $C_{0.8}SH$ may coexist with amorphous SiO_2 in highly leached concrete. In the intermediate regime, between highly alkaline and highly leached conditions, $C_{1.1}SH$ coexists with either $C_{1.8}SH$ or $C_{0.8}SH$ depending on the C/S-ratio. The model applied by Höglund (2001) accounts for the gradual transformation of portlandite and CSH-gel between these different mineral phases. Moranville et al. (2004) and Gaucher et al. (2005) used a similar approach.

It has been concluded by Benbow et al. (2007) that cement degradation is complex and will be controlled by the incongruent dissolution of the CSH gel over long periods of time. Benbow et al. (2007) compared three different models representing the gradual degradation of CSH, developed by Börjesson et al. (1997), Walker (2003) and Sugiyama and Fujita (2005). The models by Börjesson et al. (1997) and Walker (2003) determined the solid phase activity coefficients of the solid solutions by calculating the excess energy of the solid solution as a function of its composition whereas Sugiyama and Fujita (2005) applied conditional equilibrium constants related the solid phase activity coefficients. Walker et al. (2007) presented modelling of a non-ideal solid solution aqueous solution applied to a synthetic CSH. The models also differ with respect to the selection of solid-solution end-members; Börjesson et al. (1997) and Walker (2003) considered portlandite and a CSH gel, whereas, Sugiyama and Fujita (2005) considered portlandite and $SiO_2(s)$. A comprehensive literature review of different approaches to represent the CSH-gel in models is given in Soler (2007).

Recently, efforts have been made to improve modelling capabilities with respect to the incongruent dissolution–precipitation of CSH-gel phases in cement (Grandia et al. 2010). Some critisism was made of the earlier modelling attempts in which the incongruent dissolution–precipitation of CSH-gels was modelled as a solid solution process. The main critisism was that the CSH-gels are not crystalline, and hence are not solid solutions. Grandia et al. (2010) have nevertheless used two different methods to estimate equilibrium constants for discrete mineral compositions in the assumed solid solution series to represent the CSH-gels. The approach resembles those used by Höglund (2001) and Gaucher et al. (2005), although it was more detailed with up to 21–30 discrete mineral phases representing the CSH-gels.

The long-term leaching of concrete has been reported to follow a dissolution–precipitation sequence involving the following steps (Hidalgo et al. 2007):

- Dissolution of portlandite.
- Decalcification of CSH-gel.
- Silicate polymerisation.
- Incorporation of tetrahedral and/or hexagonal aluminium in the silica structure to give an aluminosilicate gel.

Model studies of cement degradation have also been used to estimate the impact of leaching on the physical properties of the cement (i.e. porosity, diffusivity) and how these changes affect the leaching process. Some models involve adjusting parameters to fit curves derived from experimental data (Yokozeki et al. 2004) and others are either "pure" random models (Bentz and Garboczi 1992) or "hybrid" models, where randomness is constrained by appropriate user-defined probability distributions (Marchand et al. 2001). A purely mechanistic approach for modelling cement degradation requires the coupling of multi-component solute diffusion with chemical reactions taking place in the system. Dimensionless analyses of diffusion and reaction rates demonstrate the adequacy of a local equilibrium assumption for coupled reactive transport modelling of cement leaching (Barbarulo et al. 2000). This approach allows a mixed non-linear set of equations to be solved numerically. The domain of the problem could be represented either as a homogeneous medium, obtained by averaging the variables of interest over a representative elementary volume, or a pore structure modelled on the basis of microstructural information, such as that provided by mercury intrusion porosimetry, or on the reconstruction of the microstructure by means of random models (Bentz 1999). The latter has been addressed by Moranville et al. (2004).

The possible impacts of the release of different salts from evaporator concentrates intended for disposal in SFR on cement and concrete has been studied by geochemical and reactive transport modeling (SKBdoc 1417785). The importance of sodium, potassium, magnesium, chloride, sulphate, carbonate, nitrate, phosphate, sulphide and ionic strength was evaluated, as well as the effect of pretreating the salt concentrates with lime. Model results indicate the presence of halite

(NaCl), hydroxiapatite ($Ca_5(PO_4)_3OH$), magnesite ($MgCO_3$), thenardit (Na_2SO_4) and thermonatrit ($Na_2CO_3 \cdot H_2O$) in the evaporator concentrates.

Studies have investigated the impact of salts on concrete stability, mimicking the composition of evaporator concentrates in SFR (SKBdoc 1032170). Different cement mixtures were tested and the mechanical strength, weight increase and swelling of test specimens were measured. The results showed no deleterious effects during an initial testing period of one year.

Model studies of the long-term stability of concrete barriers in the SFR repository have addressed the impact of dynamic changes on porosity and diffusivity (Cronstrand 2007). The model calculated the porosity change due to precipitation–dissolution processes and adopted a relationship suggested by Bentz and Garboczi (1992) to describe the effect on diffusivity.

Studies of portlandite and CSH-gel leaching have shown that the depletion of portlandite is responsible for about 70% of the loss of cement strength, whereas only a minor part of the loss can be attributed to leaching of CSH-gel (Carde et al. 1996).

Long-term leaching has also been assessed through the analysis of old, man-made, cementitious structures (Álvarez et al. 2000, Lagerblad 2001, Yokozeki et al. 2004). In the last case, the calcium concentration depth profile suggested that the cement had degraded to a depth of ≈100 mm during 100 years exposure to water (Yokozeki et al. 2004).

New experimental studies have been initialised within the Äspö-project and by Ringhals power station. The emphases of these studies are on reactions and degradation processes in concrete materials. The Äspö experiments are expected to run for up to 40 years (SKB 2010c).

The degradation of ion exchange resins might release compounds that affect the cement matrix, see Section 3.1.3, Section 3.5.6 and Section 3.5.8.

Natural analogues/observations from nature

Natural analogues to alkaline cements have been extensively studied at the hyperalkaline springs in Maqarin in northern Jordan (Pitty and Alexander 2011, Smellie 1998). The Maqarin natural analogue site is considered to be a good representation of the processes occurring in a cementitious repository during portlandite and CSH-gel phase dissolution. Three different stages have been identified:

1. An early, hyperalkaline stage dominated by leaching of sodium and potassium hydroxides.
2. An intermediate stage with a slightly lower pH controlled by dissolution of portlandite.
3. A late and less active stage with a lower pH, dominated by dissolution of silica.

The Maqarin study gives support to theoretical and laboratory studies regarding the overall sequence of mineral loss from the cement clinker, as well as the secondary minerals produced during leaching. Further, carbonation has been extensive in some areas of Maqarin (Linklater et al. 1992). Finally, the observations show that fractures in the cement slowly self-heal, preventing further leaching of the system.

Tobermorite is a naturally occurring mineral (roughly with the composition $Ca_5Si_6O_{16}(OH)_2 \cdot nH_2O$) that can be seen as a crystalline analogue to CSH-gels in cements. Crystalline tobermorite can also be obtained by gently heating CSH-gels in cement (Parsons 2010), indicating the importance of changes in temperature for long-term recrystallisation processes.

CSH-gel has been reported to persist in nature over periods of 10,000 years, despite being metastable with respect to crystalline phases such as tobermorite and jennite (Stronach and Glasser 1997). Very old gels have been reported in natural cements from Scawt Hill, Northern Ireland and Maqarin, Jordan (Milodowski et al. 1989, 1998). These are up to 2 Ma old in Jordan and possibly more than 100 Ma old in N.Ireland and appear to have survived because of becoming isolated from the groundwater.

Mineral characterisation at Scawt Hill and Carneal Plug also indicate the presence of ettringite (Milodowski et al. 2009). The occurrence of different ettringite-group minerals in natural alkaline environments have been reviewed by Möschner (2007), including Al- and Fe-ettringites and analogue phases containing boron, which may be relevant for cement conditioned concentrates/sludges. The minerals considered were as follows: $Ca_6(Si,Al,B)_3(SO_4)_2(O,OH)_{12}(OH)_4 \cdot 26H_2O$, $Ca_6(Al,Si)_2(SO_4)_2(B(OH)_4)(OH)_{12} \cdot 26H_2O$ and $Ca_6(Fe(III)_{1.5}Al_{0.3}Mn(II)_{0.2})_2(SO_{42.3}(B(OH)_4)_{1.2}(OH)_{12} \cdot 25H_2O$.

Time perspective

Chemical reactions related to hydration can occur for as long as unhydrated clinker minerals remain in the cement matrix. Hydration of clinker minerals may continue over extended periods of time, most commonly in cements/concretes with a low w/c-ratio. The w/c-ratio is usually chosen to ensure full hydration, which would be expected within the first year. However, the water content in wastes such as concentrates and sludges may vary, which could result in varying w/c-ratios of the cement waste matrix. Over time, the barrier function relevant for the safety analysis changes as follows:

- For the initial period – short-term, the chemical conditions established by the initial hydration reactions dominate, creating an alkaline porewater of alkali hydroxides and calcium hydroxide. The mechanical strength may be relatively high (depending on the content and the properties of waste mixed into cement matrix) and may be of significant importance for the repository performance. The physical barrier properties may be of relatively high importance, e.g. low hydraulic conductivity and low diffusivity.
- For the short-term – mid-term, e.g. during a few hundred years from closure, the mechanical strength and the physical barrier function may be reduced, e.g. by fractures and leaching, whereas the chemical buffering still would be expected to be significant.
- In the long-term, e.g. during a few thousand years from closure, the mechanical and physical barrier functions may be low. This would result from chemical reactions with components in the groundwater, such as sulphate, and corrosion of reinforcement bars that may cause fracturing of the barriers. Furthermore, the ability of the concrete to maintain highly alkaline conditions may gradually decrease as the amount of the more alkaline calcium minerals are partly reduced by leaching and partly replaced by calcite.
- In the very long-term, e.g. after tens of thousands of years from closure, the cementitious material is likely to be completely degraded and exert a minor impact even on the chemical conditions.

Cement leaching is mainly a coupled diffusion-reaction phenomenon. Therefore, the time needed for complete degradation of the cementitious material will be highly dependent on the relative surface area of the cement matrix where diffusion exchange with the porewater of the surrounding barriers and/or groundwater can take place. This parameter will be related to the geometrical dimensions of the cement matrix/concrete packaging. The change in porosity and permeability due to concrete degradation needs to be taken into account, to avoid an overestimation of the degradation times. It is also emphasised that the conditions may be different due to varying amounts of concrete present in the different parts of the SFR repository.

Long-term climate change will influence the temperature at repository depth. Changes in the temperature will affect the thermodynamic equilibria and may lead to gradual transformation and recrystallisation of the cement minerals. This may impact the mechanical, hydraulic and chemical properties of the cement waste matrix.

Under permafrost conditions, the likelihood of any dissolution, precipitation or recrystallisation processes in the cement waste matrix is negligible. However, freezing may have significant impact on the mechanical integrity of the cement matrix, see Section 3.2.2.

Handling in the safety assessment SR-PSU

The durability of the cement waste matrix is important as its degradation can affect the pH in the near field of the repository. The rate of degradation will essentially define the geochemical conditions of the contained waste and will influence the degradation rate of the concrete packaging and other concrete barriers. Therefore, the durability of the cement waste form is evaluated by long term reactive transport modelling, accounting for the coupling between dissolution–precipitation of minerals and porosity/diffusivity/hydraulic conductivity changes (Höglund 2001, Gaucher et al. 2005, Cronstrand 2007).

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

A major uncertainty is related to the complex solubility behaviour of CSH-phases, which has been represented by increasingly complex modeling approaches in previous studies of cement degradation, see section on Model studies.

Uncertainties also concern the fate and properties of different calcium sulpho-aluminates, calcium sulpho-ferrites (AF_m and AF_t), and similar calcium alumino- and calcium ferrite- mineral phases formed by reactions with chloride and carbonate. The volume change of the solid phases involved in these reactions is of particular interest, as this could result in the clogging of pores, or the formation of expanding minerals causing fracture formation.

Other uncertainties are associated with the long-term evolution of the pore network and the diffusivity in the cement paste. The diffusivity depends strongly on the porosity values, and the coupling between the dissolution processes and the resulting micro-structural changes are not fully understood. However, in the modelling of the chemical degradation of the concrete, the overall effects of the changes in the material properties have been handled by introducing stepwise changes over time.

Certain waste types contain chemical components such as boron, hydrazine, magnesium and other metal salts. The effects of these components have not been previously demonstrated in safety assessments. Potential impacts of cement conditioned waste containing salts, sludges, evaporator concentrates and ashes are not included in the modelling in SR-PSU.

Model simplification uncertainty in SR-PSU

The degradation of the cement matrix is evaluated using a simplified geometry, with the cement matrix surrounded by the packaging and the other concrete barriers.

The solid phases considered are a simplification of the CSH-phases that form during cement hydration. In addition, the representation of the AF_m and AF_t and similar compounds that may form as a result of reactions with sulphate, chloride and carbonate is also simplified. Chemical interactions between concrete and groundwater may also result in precipitation of armouring layers of minerals on the surface of the concrete, e.g. the precipition of calcite due to the carbonate content in the groundwater. This may affect the estimates of the change of porosity and is included in the interpretation of the modelling results.

Input data and data uncertainty in SR-PSU

The main uncertainties concern the composition of the cement matrix and the contained waste, the thermodynamic stability of CSH-gels, as well as AF_m and AF_t and similar compounds that may form as a result of reactions with sulphate, chloride and carbonate. In these calculations, data on and uncertainties related to the content of soluble and/or degradable components of the waste that may result in the release of sulphate, chloride and carbonate in increased concentrations are of particular concern.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.6 Degradation of organic materials

A wide variety of organic materials are present in the waste form. The organic materials mostly arise from activities at the nuclear installations, with smaller contributions originating from research, industry and health care organisations. Therefore, they have different origins, and the types of materials covered in this section are: chemicals used for decontamination and cleaning or emanating from decontamination chemicals; ion exchange resins and similar products such as organic polymers contained in filters; cellulose; bitumen; organic cement additives, and; other organics (described below).

The most important organic compounds in terms of long term performance of SFR are either present in large quantities or have a known ability to complex certain radionuclides. Therefore, degradation of organic material is important both in terms of the breakdown of larger molecules and polymers into smaller, soluble complexing agents that may increase the mobility of radionuclides and the depletion of complexing agents disposed of in the waste. These processes may have a significant impact on the performance of the SFR repository. The organic content of the waste with respect to the overall waste in the different rock vault types at the time of closure (full inventory) varies significantly. Ion-exchange resins and bitumen comprise the bulk of the organic material initially present in all vaults except for BLA, where other organics such as plastics (cable isolation or rubber) and cellulose are the major components. However, cellulose is also a significant contributor to the silo and BMA.

Degradation can occur through chemical, physical, radiolytic and microbial processes. This section describes the chemical degradation of organic material, while radiolytic and microbial degradation processes are covered in Section 3.1.3 and Section 3.5.8, respectively.

Within this section, it is important to note that the stability of species formed between organic complexing agents and radionuclides can be described using equilibrium constants. These can be obtained in some cases from experimental data (Hummel et al. 2005) or using appropriate estimations. A number of studies have been published for common chemicals employed for decontamination and cleaning, allowing an accurate description of the processes. For cellulose degradation products, the situation is less clear although the review in Hummel et al. (2005) and later publications provide information on this subject (see the following sub-sections).

Chemicals used for decontamination and cleaning or emanating from decontamination chemicals

Numerous chelating agents are employed in nuclear decontamination operations. However, the chemical composition of most of these decontamination reagents is proprietary information and is thus difficult to ascertain. With the information available, the main chemicals used for decontamination and cleaning, or emanating from decontamination chemicals, are: EDTA, DTPA, NTA, gluconate, citric acid, oxalic acid, tartaric acid, alkyl sulphonic acids and substituted phenols.

Multidentate chelating agents such as NTA, EDTA, and DTPA are used widely in the nuclear industry for the decontamination of reactors and equipment (Ayres 1971). These aminopolycarboxylic acids, compounds containing several carboxyalkyl groups bound to one or more nitrogen atoms, are especially versatile because of their ability to form stable, water-soluble complexes with a wide range of metal ions.

As previously reported (Means and Alexander 1981), the strength of a metal complex depends on the denticity of the complexing agent. For a given metal, the stability of the complexes generally decrease in the order DTPA > EDTA > NTA > citric acid > oxalic acid > acetic acid. Acetic acid is the weakest complexing agent in this series, as it possesses only one acidic functional group. Although both citric acid and NTA have three ionisable acid groups, NTA is the stronger complexing agent because the nitrogen atom, with its one pair of electrons, also participates in the chelating process. Thus, NTA is a tetradentate ligand and, for the same reason, EDTA is a hexadentate ligand and DTPA is octadentate.

The chemical degradation of these organic complexing agents is expected to be slow. Therefore, they should be considered in terms of their stability constants with radionuclides (Hummel et al. 2005), and may play a role in radionuclide sorption and solubility. This influence is expected to be significantly reduced by the competition between other major ions, such as Ca (and also Fe, Al, Mg), and radionuclides to form stable species with the complexing agents.

Ion exchange resins and similar products such as organic polymers contained in filters

Ion-exchange resins consist of polystyrene chains with amines as the active groups in anion exchangers and sulphonic or carboxylic acids in cation exchangers (Allard and Persson 1985, Allard et al. 2002). It has been shown that ion exchange resins are chemically inert under the chemical conditions anticipated in SFR (Bradbury and Van Loon 1998, Van Loon and Hummel 1999a, b) and hence no organic degradation products are expected or considered relevant at least at short time scales. Furthermore, most ion-exchange resins deposited in SFR will be immobilised in cement or bitumen, which will limit their contact with water and therefore degradation.

Cellulose

Cellulose is a relatively common material in the context of low and intermediate level radioactive repositories, due to its presence in everyday materials such as tissues, cloth and paper. It is a polysaccharide with a linear condensation polymeric chain with the formula $(C_6H_{10}O_5)_n$. It therefore consists of glucose units (D-anhydroglucopyranose units) connected through β-1,4-glycosidic bonds and is also known as β-1,4-D-glucan (polyglucose) (Wertz et al. 2010).

Cellulose molecules interact strongly to form fibres through inter- and intramolecular hydrogen-bonding and van de Waals forces. There are two types of hydrogen bonds in cellulose molecules (see Figure 3-3):

1. Those that form between the C-3OH group and the oxygen in the pyranose ring within the same molecule chain.
2. Those that form between the C-6OH group of one molecule and the oxygen of the glucosidic bond (C-3) of another molecule.

Within the fibres, cellulose molecules are oriented in parallel, with reducing ends of adjacent glucan chains located at the same end of a microfibril. Ordinarily, the beta-1,4 glycosidic bonds themselves are broken relatively easily. However, cellulose is found in amorphous and crystalline forms. Amorphous cellulose allows the penetration of both enzymes (cellulases), produced chiefly by fungi and bacteria, or chemical molecules that induce hydrolysis i.e. OH^-, and hence releases glucose units that can further be degraded. The hydrolysis of these glucosidic bonds, by its very nature, requires water.

The degradation mechanisms and products of cellulose depend on the chemical environment. Cellulose can be degraded aerobically or anaerobically. According to the wastes in SFR, two environments could be differentiated:

1. Anaerobic non-alkaline conditions such as those in BLA.
2. Anaerobic alkaline cementitious environments, as found in the rest of the repository.

In the absence of oxygen and certain other inorganic electron acceptors (such as nitrate, Mn(IV) and Fe(III)), cellulose can be decomposed by anaerobic microbial communities, see Section 3.5.8.

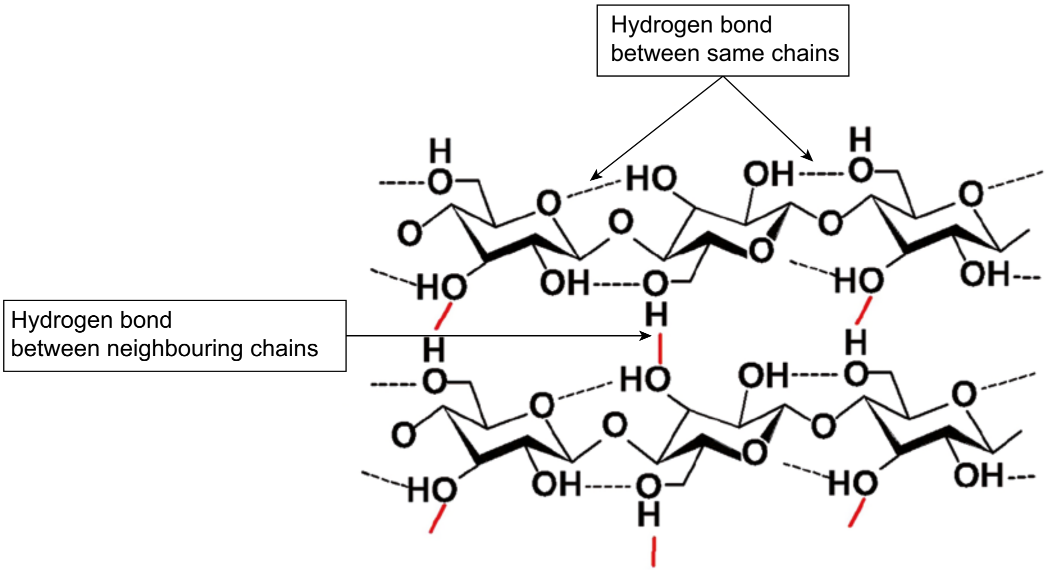


***Figure 3-3.** Hydrogen bond between the same and neighbouring chains.*

Under alkaline, anaerobic conditions, isosaccharinate (ISA) is the main cellulose degradation product formed (Blears et al. 1957, Whistler and BeMiller 1958, Van Loon and Glaus 1998). ISA is a general term for 3-deoxy-2-C-(hydroxymethyl)-D-aldonic acids, which has both α and β diastereoisomers.

Bitumen

Bitumen is used as an immobilisation matrix as it provides both physical and chemical stability (IAEA 1993), and it is abundant in both the BMA and silo. Reviews by the IAEA (IAEA 1993), Nirex (Nirex 2005) and Ojovan and Lee (2005) all agree that bitumen is an appropriate waste encapsulation material and expect long-term degradation and consequent waste release to be slow. Ion exchange resins are the wastes immobilised in bitumen. The technological bitumen used is derived from natural organic materials and consists mainly of a mixture of high molecular weight aliphatic and aromatic hydrocarbons obtained from petroleum. The bitumen composition is controlled both by the composition of the crude oil and the precise distillation process. Consequently, the technical bitumens used for waste immobilisation have a range of compositions, all of which are well characterised, but all of which vary from national programme to national programme. This makes comparison of work from different national programmes difficult and, often, misleading. Bitumenconsists predominantly of carbon (80 to 88% by weight) and hydrogen (8 to 11%), with smaller amounts of oxygen (1 to 12%), sulphur (1 to 7%) and nitrogen (trace to 1.5%) (Savage 1995 from Eschrich 1980). It may be subject to degradation by physical, chemical and microbiological processes. Under the highly alkaline environment characteristic of the SFR repository, bitumen is generally considered to be chemically stable (Petterson and Elert 2001). Therefore, although possible degradation products of bitumen include organic complexing agents (see Section 3.1.3) colloids, degradation is not thought to be important in terms of radionuclide mobilisation (see Section 3.5.4).

Organic cement additives

Cement additives are used to enhance the physical and rheological properties of concretes, and are essential in the construction of a disposal facility for radioactive waste. They are also used in the waste conditioning and the concrete packaging. The potential for radionuclide complexation by cement additives was first noted by Wiborgh (1995) in terms of the superplasticiser planned for use in SFR. This sulphonated melamine polymer was anticipated to comprise up to 3% of the total volume of the cement. The degradation of cement additives might also generate low molecular weight organic materials, and possibly carbon dioxide after extended storage time. Despite this, the organic cement additives studied by SKB (Dario et al. 2004a) and PSI (Glaus and Van Loon 2004b) have led to the conclusion that cement additives will only have a minor influence in comparison with other complexants in the repository such as NTA, EDTA and DTPA (Allard and Persson 1985, Keith-Roach et al. 2014). Cement additives are not thought to be a specific problem for SFR hence their degradation products are not investigated further.

Other organics

Other organics may comprise:

- Both halogenated plastics (polyvinylchloride (PVC) or polytetrafluoroethylene (PTFE) and non-halogenated plastics (polyesters, nylon, epoxy, polyethylene, polypropylene, polystyrene).
- Both halogenated rubbers such as Hypalon (chlorosulphonated polyethylene) and non-halogenated rubbers (like latex or styrene-butadiene).
- Cable isolation.

Plastics are usually resistant towards degradation, but degradation is highly dependent on their size. Small pieces of plastic and plastic dust will be degraded faster than large pieces due to their larger surface area to volume ratios. Rubber is even less degradable than plastic. Any degradation that could occur will, like all other degradation processes, be dependent of water (Hallbeck 2010).

All degradation processes affecting plastic and rubber polymers are associated with molecular weight changes, changes in functional groups and the (release or production) of small molecules as degradation products. There are three relevant types of chemical degradation pathways:

- Long-term thermal processes.
- Thermo-oxidative processes.
- Hydrolysis reactions.

Plausible degradation pathways can be postulated that generate products with complexing ability, however, the yields of these products would be low. Most of the known degradation products of plastics and rubber, e.g. hydrogen, hydrogen chloride, have no significant complexing ability and can therefore be ignored (Heath and Williams 2005).

Dependencies between processes and waste form variables

The influence of some important variables on the process of chemical degradation of the organic material initially present in the SFR and the influence of the process itself on these variables (defined in Section 2.1.2) are summarised in Table 3-15 and discussed in detail below.

Table 3-15. Direct dependencies between the process "Degradation of organic materials" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No. Indirectly through water volume (porosity), depending on the porosity characteristics of the waste.	Not relevant.	Yes. Through changes in porosity	Changes in porosity is handeled as variations in hydraulic conductivity.
Radiation intensity	Yes. May influence and accelerate material degradation. Indirectly, radiolysis can influence the process chemical degradation of organic materials by changing the water composition.	Neglected. This effect is small enough to be neglected here.	No.	Not relevant.
Temperature	Yes. Elevated temperatures are expected to enhance the degradation rate.	Neglected. The expected variation in temperature is not of significance here and is neglected.	Yes. The process itself may influence the temperature.	Neglected. The expected influence on the temperature is relatively low and it is neglected.
Hydrological variables	Yes. Presence of water necessary for the process.	Water is assumed to be initially present.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. The type and amount of organic material of the waste will affect the type and amount of degradation organic products. The composition of material determines the porosity and thus, the water content.	The inventory of waste form materials are input data to calculations/estimations.	Yes.	Changes in material composition are calculated, when possible. An example is the degradation of cellulose.
Water composition	Yes. The chemical composition of the water is one of the important inputs to this process, since it is critical to determine the reactions that take place. Of special, importance are pH, Eh and Ca concentrations.	Yes. pH and Eh of the water directly in contact with the waste is calculated.	Yes.	Accounted for in selection of K_d. Degradation can increase the concentration of soluble organic material, which in turn may enhance radionuclide release.
Gas variables	No. Indirectly through water composition.	Not relevant.	Yes. Increase of gas pressure as a result of degradation of organics.	Gas volumes due to chemical degradation of organics is estimated, see Section 3.5.10.

Geometry. The geometry will not directly affect the chemical degradation of organic material. However, it will have an indirect effect, through the porosity characteristics of the waste, i.e. the volume of water that can penetrate the waste. The potential change in porosity of the waste/bitumen matrix due to the degradation of organic materials is not explicitly addressed in the assessment, but should be covered by the pessimistic selection of radionuclide release rates from the bitumen matrix.

Radiation intensity. The radiation intensity emitted from the waste will accelerate organic material degradation. Radiolytic decomposition of organic materials in the waste form is treated in Section 3.1.3. Bitumen degradation can also be enhanced in the presence of a high radiation field, but as bitumen is usually used to encapsulate low activity wastes, this influence should be of limited importance. The greatest radiation field is in the silo, where the potential for radiation-enhanced bitumen degradation is consequently higher. Nevertheless, it can still be considered as a negligible influence.

However, radiolysis can indirectly influence the process of chemical degradation of organic materials by changing the water composition. In SFR, radiolysis of organic materials (e.g. cellulose and bitumen) will occur in addition to radiolysis of the groundwater. The significance of radiolysis of organic material is related more to a potential increase in material degradation rates than to a control over redox conditions (Section 3.1.3). This effect is small enough to be neglected here.

Temperature. Elevated temperatures might have an impact upon the rate of chemical degradation of organic wastes, the rate of which can be enhanced by the increase in temperature. The expected variation in temperature above the ambient conditions is not of significance here and it is neglected.

Hydrological variables. The presence of a water phase inside the waste, following the intrusion of water through the physical boundary represented by the packaging, is a necessary prerequisite for the production of complexing agents through the degradation of organic materials. This production of complexing agents is the most important consequence of the process of chemical degradation of organic materials. The amount of water (i.e. the degree of saturation) initially present in the backfill of the vaults and in the cement therefore affects the chemical degradation of the organic materials in the waste. Unsaturated conditions could delay the degradation of these organics, although the water content is probably quite high at repository closure (Jarsjö et al. 2001).

Mechanical stress. No direct influences have been identified.

Radionuclide inventory. The radionuclide inventory does not affect the chemical degradation of organic matter.

Material composition. The type and amount of organic material within the waste will affect the type and amount of degradation products, as has been discussed in the introduction. The amount of compounds generated by degradation of organic materials may be calculated/estimated from the amount of these materials initially present in the repository.

Water composition. The chemical characteristics of the groundwater (pH, Eh, and concentrations of dissolved components) intruding into the waste, will govern the rate of organic degradation and the degradation products produced. The most important engineered barrier materials that affect groundwater chemistry are cement (buffering to a high pH), steel (lowering the Eh) and organic material (controlling the concentration of organic complexants and Eh). The groundwater composition in the near-field is thus controlled by the presence of these barrier materials and their degradation (Miller at al. 2002). Under the high pH conditions existing in SFR, organic compounds of low-molecular-weight generated by degradation of organic material may influence radionuclide speciation by their complexing properties, thereby raising solubility limits and affecting sorption processes.

The presence of iron and steel around the waste will affect the Eh of the groundwater. Variation in the redox conditions of the system may enhance or delay the degradation of organic materials, and therefore the amount of organic-radionuclide complexes that may form.

The concentration of calcium in the system is also a key variable that may strongly influence chemical organic material degradation. Portlandite and CSH may provide an effectively unlimited supply of Ca in cementitious environments. A potential effect of high concentrations of Ca would be to promote the formation of Ca-organic complexes, which will result in further degradation of the organic materials. The stability of some Ca-L complexes (L being organic degradation ligands) might be significantly higher under highly alkaline conditions. These may therefore dominate the Ca aqueous speciation and enhance the solubilisation of, for instance, portlandite. The driving force for this process is the complexation of calcium by the organic ligands in the system (for instance acetate, ISA, phthalate, adipate, glutarate).

The reducing sugar end group of the cellulose polymer chain is important in the low temperature alkaline degradation of cellulose. Of the total acid released in the degradation of cellulose, α-ISA and β-ISA are the most abundant. A greater proportion of ISA is formed from degradation in the presence of calcium ions than in the presence of sodium ions (Machell and Richards 1960). Another example that has been experimentally observed elsewhere (Duro et al. 2012a) is that the presence of calcium can more than double the formation of organic degradation products from the UP2 fibre, when all other conditions but calcium remain constant (Duro et al. 2012a).

High Ca concentrations can also result in the precipitation of Ca-organic compounds, when the relevant solubility product is exceeded.

Gas variables. The composition of any gas present as a separate gas phase and/or dissolved in the water phase can have an effect on the redox conditions, for example, which has a direct influence on degradation processes. A clear example is the large amount of hydrogen produced by metal corrosion (mainly iron, aluminium and zinc). The main chemical influence of hydrogen will be to impose reducing conditions in the system. Hydrogen may also be converted to methane by methanogenic bacteria (see Section 3.5.10).

The degradation of an organic material may generate gas, which may change the composition of the water and influence degradation rates. In addition, gas generation through degradation of organics may result in a pressure build-up.

Boundary conditions

A physical boundary is set by the packaging of the waste. Drums and containers of mild steel, and concrete containers are used as packaging.

Liquid water, which is a prerequisite for the process, is assumed to come in contact with the waste as soon as the repository resaturates after closure and sealing.

The chemical properties of the solution phase will influence the degradation of organic materials process in the waste, especially pH, Eh, calcium concentrations and chlorine concentrations.

Although gas generation may create an unsaturated state, a water phase may still be present due to capillary forces in pores and fractures of the waste.

Model studies/experimental studies

This section aims to summarise the available modelling and experimental studies that address the chemical degradation of organic materials present in the SFR waste form. Each type of organic material is discussed in turn. Information is presented on the likely degradation products in a nuclear waste repository along with known degradation mechanisms and reaction rates.

Chemicals used for decontamination and cleaning or emanating from decontamination chemicals

The stability of organic materials has been studied using a non-radioactive simulant of a complex concentrated mixed waste stored at the U.S. Department of Energy's Hanford Site (Toste and Lechner-Fish 1993). The simulant consisted of an alkaline inorganic matrix plus ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylene-diaminetriacetic acid (HEDTA), and citric acid. The simulant's total organic content remained fairly constant (82–102% recoveries) over 171 days at ambient temperature. However, detailed analyses of the organics by gas chromatography/mass spectrometry (GC/MS) showed that, collectively, 61.7% of the parent organics had degraded. Moreover, the individual parent compounds degraded to different degrees, with HEDTA being the most labile. Twenty-one degradation products were identified, consisting mainly of complexing and chelating fragments, with structural similarities to one or more of the parent organics. Since the fragments were smaller than the parent organics, their chelation capacities are lower than that of the non-degraded ligands. The influence of the fragments on radionuclide mobility is therefore expected to be lower than the influence of the parent compounds.

Chelating agents typically require long time scales to breakdown, or severe chemical conditions, or the presence of catalysts (Dario et al. 2004a). One example of the resistance of chelating agents to breakdown is EDTA, which is resistant to radiation-induced degradation and is thermally stable up to 200–250°C (Keith-Roach 2008).

Ion-exchange resins and similar products such as organic polymers contained in filters.

From a chemical point of view, resins are very stable and degrade only under very aggressive conditions. In bitumenised ion-exchange resins bitumen have a protective role on the resins, even under the alkaline pH cement conditions imposed by a cementitious repository (Allard et al. 2002).

Degradation products of a polyacrylonitrile filter aid (UP2, cf. Dario et al. 2004a)) are also of relevance. UP2 will be bituminised prior to disposal (in F.17 type wastes), which is likely to delay the onset of alkaline degradation for some time. Therefore, degradation is expected to take place under portlandite buffered conditions (pH 12.5) and the available evidence (Duro et al. 2012a) suggests that the conditions will limit the extent of degradation. Duro et al. (2012a) investigated the effect of UP2 degradation products on the sorption of Eu-152 to cement. The degradation products obtained at pH 12.5 (buffered by $Ca(OH)_2$) and room temperature, which are the most relevant to SFR, did not affect Eu sorption significantly. The maximum degradation product concentration in this experiment was approximately 8 mg/dm^3 of DOC and was the maximum, plateau concentration obtained in the degradation experiments. The degradation experiments used an initial UP2 fibre concentration of 25 g/dm^3 which is equivalent to the highest UP2 fibre concentration currently disposed in BMA (in compartment 6). Therefore, the data are highly relevant to SFR and indicate that radionuclide mobility will not be affected significantly by UP2 degradation.

Cellulose

Both the mechanism of alkaline cellulose degradation and the products formed have been studied extensively (e.g. Machell and Richards 1957, 1960, Johansson and Samuelson 1975, 1978, Ziderman and Bel-Ayche 1978, Greenfield et al. 1993, 1994, Hurdus and Pilkington 2000, Knill and Kennedy 2003, Van Loon and Glaus 1997, Glaus et al. 1999, Pavasars 1999, Glaus and Van Loon 2004a, b, 2008, Bourbon and Toulhoat 1996, Niemelä 1987, Heath and Williams 2005).

The main cellulose degradation products are summarised in Table 3-16 (Motellier and Charles 1998, Glaus and Van Loon 1999, Hurdus and Pilkington 2000), and include various carboxylic acids and hydrocarboxylic acids (Glaus et al. 1999, Pavasars 1999, Bourbon and Toulhoat 1996, Humphreys et al. 2010). The effective complexing agent ISA has been widely identified as a key product and is therefore one of the most important organic compounds affecting the speciation and mobility of radionuclides in a radioactive waste repository. The other compounds represent low percentages of the total dissolved organic compounds, although they may also complex radionuclides.

Two diastereoisomers of ISA form during alkaline cellulose degradation: 3-deoxy-2-C-hydroxymethyl-D-*erythro*-pentonic acid (α-ISA), and; 3-deoxy-2-C-hydroxymethyl-D-*threo*-pentonic acid (β-ISA) (see Figure 3-4).

Both isomers of ISA were identified following cellulose degradation in the presence of Ordinary Portland Cement (OPC)/Blast Furnace Slag and NRVB (Greenfield et al. 1993, 1994).

Under alkaline, anaerobic conditions at temperatures below 170°C, the predominant mechanism of cellulose degradation involves a reaction that ruptures a 1,4-glycosidic linkage at the end of the polymer chain (Machell and Richards 1960). This releases glucose in a stepwise process known as the peeling or peeling-off reaction. Subsequent rearrangement of these glucose units generates the final degradation products.

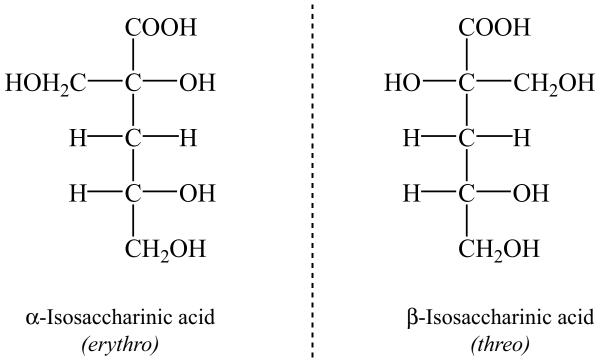


Figure 3-4. *Fischer projection of the two diastereomers of isosaccharinic acid.*

Table 3-16. Overview of short-chain organic products from the alkaline anaerobic degradation of cellulose (from Glaus and Van Loon 1999, Hurdus and Pilkington 2000, Motellier and Charles 1998).

Compound
2-C-(hydroxymethyl)-3-deoxy-D-pentonic acid (ISA)
Formic acid
Lactic acid
Acetic acid
2-hydroxybutanoic acid
Glycolic acid
Pyruvic acid
Glyceric acid
Threonic acid

The rate of alkaline cellulose degradation affects the concentration of cellulose-derived complexing agents such as ISA in solution over time (Chambers et al. 2002, Askarieh et al. 2000). Five well-conducted experimental studies have focussed on the degradation mechanism and kinetics under hyperalkaline conditions (Van Loon and Glaus 1998, Pavasars 1999, Pavasars et al. 2003, Glaus and Van Loon 2004a, b, Glaus and Van Loon 2008). Both research groups (Van Loon and co-workers (Van Loon and Glaus 1998, Glaus and Van Loon 2004a, b), and Pavasars and co-workers (Pavasars 1999, Pavasars et al. 2003)) reached similar conclusions concerning the mechanisms driving the degradation of cellulose, which include the peeling off reaction (see above), stopping reactions and hydrolysis reactions. The stopping reactions involve the formation of chemically stable end groups or reaching an unreactive part of the glucose chain. Hydrolysis is important in the long term degradation of cellulose as it re-initiates the peeling-off reaction.

Early predictions of the long-term fate of cellulose in an alkaline, anaerobic repository environment were contradictory due to the need to extrapolate from experimental data gathered over a few years. This meant that Van Loon and Glaus (1998) concluded that $t > 10^5$ years were needed for cellulose to degrade completely, whereas (Pavasars 1999) concluded that it would only take 150–550 years.

The continuation of Van Loon and Glaus's (1998) experiments allowed degradation to be observed over the longer period of 12 years (Glaus and Van Loon 2008). The authors found that the degradation profile could be divided into a fast reaction phase (2–3 years), dominated by the stepwise conversion of terminal glucose monomeric units to α-ISA and β-ISA, and a slow reaction phase during which the same products were observed to form. The extended time frame increased the reliability of the long-term predictions of alkaline cellulose degradation and showed that neither of the rates estimated previously were appropriate. The best estimate of the time for complete degradation of cellulose under repository conditions is now 1×10^3 to 5×10^3 years.

Bitumen

Chemical oxidation of bitumen leads to the formation of formic, acetic and oxalic acids (Pettersson and Elert 2001). Bitumen also experiences ageing (hardening) effects, due to loss of volatile organics or oxidation, in contact with O_2. Much work has been carried out on the various degradation mechanisms of bitumen over the last decade, especially in Belgium and Japan (e.g. Valcke et al. 2009, 2010, JAEA 2007). Unfortunately, due to the above noted differences in bitumen formulations used worldwide, it remains the case that very little information exists in the literature about products formed from the chemical degradation of bitumen under conditions relevant to SFR.

Organic cement additives

Superplasticisers will only be able to influence radionuclide mobility in the repository if they leach into entrained pore fluids within the cement/concrete. Although superplasticisers may be present at the 1–2% level in the cement, they may pose relatively few problems as radionuclide complexing agents if they are fixed within the cement or on its surfaces.

Degradation of polymeric additives has been studied by Glaus and Van Loon (2004a, b) under cement conditions, although no degradation was detected during the course of the experiments. The authors concluded that the additives should be regarded as stable under cementitious conditions. During a study of the sorption of cement additives to cement, UV-VIS spectra showed that the profile of organics changed (Hur and Schlautman 2003). The authors attributed this to differences in sorption of the different compounds present in the additives, and related this to the phenomenon of molecular fractionation of humic substances during sorption to minerals.

The influence of organic cement additives on radionuclide mobility has been reviewed by Hakanen and Ervanne (2006) and studied further experimentally by Young et al. (2013). All available leaching studies were short-term, and the degradation of these additives has not been shown conclusively under cementitious conditions. Of the 4 main additives used (melamine sulphonates, naphthalene sulphonates, modified lignosulphonates and polycarboxylates), only the naphthalene sulphonates could currently be assumed to be non-problematic. Aggressive leaching tests indicate that admixture leaching from concrete is minimal. Additionally, it has been noted that admixtures may reduce the total leaching by reducing concrete permeability (Dransfield 2005). Young et al. (2013) studied the effect of a commercial superplasticiser of the behaviour of some elements in blended cements. The results of the batch experiments showed that the presence of free superplasticiser in solution reduced the uptake of Ni and Eu by all of the OPC studied. The metal bound in the presence of free superplasticiser is readily remobilised when exposed to fresh cement solution. Contrarily, the metal uptake is almost complete and seems irreversible when exposed to hardened cements prepared with superplasticisers as part of the original mix. Leach experiments on a slag cement monolith containing superplasticisers and metals. The results show that the metals were not effectively immobilised.

Overall, the available experimental and modelling data for additive leaching therefore suggest that additive concentrations in pore fluids in hardened cement pastes are likely to be less than 10^{-5} M, which is much lower than the typical concentrations of 10^{-4} to 10^{-3} M used in radionuclide solubility studies (Greenfield et al. 1995, Bouniol et al. 1994, Glaus et al. 1997).

Nevertheless, one problem which needs to be considered is that the degradation and leaching of additives may change over time, and that it is difficult to assess the rate and type of organic degradation and the extent to which the organics leach into the fluids of cement materials simultaneously. As Bodén and Sievänen (2006) noted *"The additives are commercial products of fairly ill-defined composition and may contain also components other than those indicated in the product safety sheets"*. Also there is limited knowledge on how the additives are incorporated into the grout and the release rates from cement, as well as whether the products are degraded by other processes (e.g. due to microbial activity or cement hydrolysis).

Other organics

There have been relatively few studies examining the degradation of other polymers under the alkaline, reducing chemical conditions anticipated in the near-field of cementitious repositories. For most of the typical synthetic organic polymers present in radioactive waste there is little evidence that alkaline degradation over laboratory timescales has any effect on the mobility of radionuclides. Either the polymers are not susceptible to degradation under these conditions/timescales and longer time scales need to be studied or the degradation products would not be significant complexing agents.

However, Heath et al. (2000) have considered the likely degradation mechanisms for a wide variety of polymers, and proposed chemical structures for the plausible reaction products. The polymers considered ranged from polyethylene to epoxy resin, and included hypalon, neoprene, PVC and polystyrene. Bulk polymers were selected because they comprise the majority of organic materials in the radioactive waste inventory, and the authors focussed on degradation products that could act as complexing agents for radioelements. However, there was a shortage of experimental data that could be used to support the formation of the postulated degradation products, or to estimate likely yields. The authors selected seven model organic complexing agents to represent potential polymer degradation products:

1. Acetic acid, from a number of larger organic molecules and polymers.
2. Glycerol, from polymers such as PVC and neoprene or from epoxy resins.
3. Benzoic acid, from polystyrene and the polymer backbone of certain ion-exchange resins.
4. Ethanolamine, from nylons or anion-exchange resins.
5. 1,2-diaminoethane, also from nylons or anion-exchange resins.
6. Adipic acid, from nylon-6,6.
7. Oxalic acid.

The authors studied the effect of each complexing agent on the solubilities of some radionuclides (Ni, Tc, Th, U and Pu) under both, oxidising and reducing conditions over the pH range 7–13 and concluded that, in general, the model complexants studied were not predicted to increase the solubility of the studied radionuclides more than half an order of magnitude under such conditions. However, the decomposition products containing amine groups (e.g. arising from the degradation of nylons or anion exchange resins) had the potential to cause larger increases in the solubilities of all the radioelements considered.

Natural analogues/observations from nature

Chemicals used for decontamination and cleaning or emanating from decontamination chemicals

There are no relevant observations from nature or natural analogues for decontamination and cleaning chemicals.

Ion exchange resins and similar products such as organic polymers contained in filters

Natural resins are compositionally and structurally different from ion exchange resins and, consequently, do not act as close natural analogues. As discussed in Miller et al. (2000), the only known discussion of natural analogues of polymers and resins is in Hellmuth (1989) and is limited to a brief discussion of resinous plant products. The most common resinous plant product found in the geological environment is amber (Miller et al. 2000). This natural resin is preserved under aerobic and anaerobic sedimentary conditions, as long as the sedimentation rate is not too slow. These resins may also survive under the temperatures associated with the initial stages of coal formation. The occurrence of resins in sedimentary rocks attests to their preservation during erosion and transport in water. However, resins found in less permeable formations like clays demonstrate a better degree of preservation than those found in permeable formations (e.g. sandstones) which suggests that groundwater leaching can enhance their deterioration.

Cellulose

As stated in Miller et al. (2000), there are few high pH, anaerobic sites that can be used in natural analogue studies to investigate cellulose degradation. Therefore, little is known about the long-term behaviour of sedimentary organic matter submitted to alkaline perturbation in natural settings. However, there are some studies worth discussing, particularly with regard to degradation in the non-cementitious BLA.

One example is the Dunarobba fossil forest near Avigliano Umbro, in Italy, which is 1.5 million years old. Examination of the fossil trees at Dunarobba suggests that the rate of cellulose degradation is slow. This wood was buried in sediment and clay, which protected it from degradation, presumably by reducing the flow of water and thereby the transport of electron acceptors and nutrients. This observation might be of relevance in terms of microbial degradation pathways despite the fact that Dunarobba is generally a poor analogue of an alkaline L/ILW repository. As stated in Alexander et al. (2011), the main objective of their work was to provide high-quality quantitative and supporting data relevant to safety and performance assessments for cementitious repositories. Reliable studies based at the Khushaym Matruk site in central Jordanindicated that a combustion event may have induced changes in structural characteristics of the organic matter in the biomicrites underlying the Analogue Cement Zone (ACZ). In addition to thermal stress, hyperalkaline solutions originating from the cement zone are assumed to have percolated through the biomicrites and weathering can also be assumed to occur in such a geological environment. The main problem is that these alteration processes are superimposed in nature and it is often difficult, or even impossible, to differentiate between them without appropriate analytical techniques (Khoury et al. 2011).

Microscopic analyses show the presence of vegetable debris in sediments from Khushaym Matruk that have been altered by migrating alkaline fluids. Delignification alkaline treatments of lignocellulosic materials are used in industry, including in paper pulp manufacturing, agricultural and food industries. Lignocellulose is mainly formed of three closely associated components, hemicellulose, cellulose and lignin. Basically, covalent crosslinkages have been suggested to occur between lignin and carbohydrates (cellulose, hemicellulose) in the form of ester and ether functionalities. One of the delignification reactions occurring at lower temperatures (room temperature to 150°C) includes saponification of intermolecular ester bonds using Ca hydroxide as alkali reagent (Playne 1984, Chang et al. 2001, Kaar and Holtzapple 2000). As reported by Khoury et al. (2011), the extent to which lignocellulosic materials are altered depends on their original chemical and structural composition and, in no small part, the local conditions such as alkaline pH, temperature, reaction time, redox conditions (Draude et al. 2001). Intensive chemical treatments are required to separate cellulose, hemicellulose and lignin. The FTIR spectra recorded in lignocellulosic debris during the studies undertaken in Khoury et al. (2011) indicate major compositional differences.

Infrared spectral features from Khushaym Matruk case study in the 2,000–800 cm^{-1} region and polysaccharide/lignin ratios of microorganic particles from grey biomicrite samples closely match those of unaltered lignocelluloses (Given et al. 1984, Ibarra et al. 2004). The same conclusions were reached by Khoury et al. (2011). These authors reinforce the idea that the spectral feature in the 2,000–800 cm^{-1} region of the lignocellulosic debris from grey biomicrites closely resembles those in the spectra of unaltered lignocelluloses. The aliphatic band in the 3,000–2,800 cm^{-1} region is better resolved, suggesting that the alkyl chains are less cross-linked. The lignocellulosic detritus from transition zone appears strongly depleted in C–O and C–O–C bonds in the sample collected 1 m under the cement zone. On the other hand, the absorption bands assigned to aromatic skeleton vibrations 1,605, 1,510 and 1,460 cm^{-1} and conjugated carboxyl/carbonyl stretching increase.

The abundance of polysaccharides relative to lignin drastically decreases with proximity to the metamorphic zone and this is attributed to the alkaline perturbation. By comparing with industrial delignification processes, high-pH hydrolysis appears to represent the most probable cause of the alteration of lignocellulosic debris. The subsequent degradation of polysaccharides is likely related to the same event since temperature alone would have been too low to induce such a transformation (Glaus et al. 1999, Knill and Kennedy 2003 and references therein).

At the same time, results from Khoury et al. (2011) suggest that any thermal effect due to the combustion event is negligible in the biomicrites and/or the pH of percolating fluids did not enable the degradation of lignocellulose. On the other hand, the relative abundance of the band in the 2,000–800 cm^{-1} region progressively decreases when the cement zone is approached. Two possible scenarios were hence proposed in that work: either hyperalkaline leachates have percolated through the transition zone or the combustion event has partially altered lignocellulose, making it more soluble in hyperalkaline solution. According to the authors, the second scenario would seem more realistic on account of the occurrence of oil migration and petrographic evidence revealing that organic matter from the transition zone has only reached the onset of oil generation. FTIR spectra of lignocellulosic materials reveal that the influence of the hyperalkaline perturbation at Khushaym Matruk is at a maximum at 0 to 1 m under the cement zone, and evidence of progressive pH buffering of the hyperalkaline leachates by mineralogical assemblages along the profile. The extent of hyperalkaline perturbation at the Khushaym Matruk site deduced from this study of organic matter is comparable to values estimated by modelling diffusion of a hyperalkaline plume in a clay barrier (Gaucher et al. 2004).

The temperature ranges studied in Knill and Kennedy (2003) were focussed on the products arising from the degradation of cellulose under alkaline, anaerobic (post-closure) conditions, at temperatures < 170°C, since these conditions predominate with respect to the long-term repository environment. Products that may be obtained under other conditions that may be experienced by the waste prior to closure of the repository (e.g. aerobic oxidative degradation) were also discussed. Glaus et al. (1999) presented data from a long-term degradation experiment of different types of cellulose under conditions close to those existing in a cementitious repository (pH = 13.3 and T ≈ 25°C). The temperature ranges in Khoury et al. (2011) for the Khushaym Matruk case study and the corresponding results cover the range of temperatures: 200°C (0.8–2.5 m) < T < 1,100°C.

Additional experimental studies on the importance of thermal effects on the alkaline delignification of lignocellulosic could be beneficial.

Bitumen

As pointed out in Miller et al. (2000): "Natural bitumens, including asphalts, are found in a number of geological environments and in all climatic zones from tropical to permafrost, in arid to waterlogged conditions. The most impressive are probably the asphalt lakes of Trinidad and Guanoco, Venezuela, but other forms include impregnated sandstones and limestones (e.g. Athabasca, Canada; Utah, USA; Val de Travers, Switzerland and Hannover, Germany) and those in hydrothermal veins (e.g. Derbyshire, UK)." It is also stated that: "In some cases, natural bitumens have been found to have preserved organic material for long periods of time. Perhaps the best examples are the asphalt pits at Rancho la Brea, California and Talara, Peru which contain abundant fossil bone and wood remains (Behrensmeyer and Hill 1980). The Rancho la Brea asphalt pit is the site of the largest find of Pleistocene fossils ever (Rolfe and Brett 1969). The mechanisms that led to the preservation of these organic materials, including the fossil remains, are complex but basically they act to limit microbial decomposition by isolating the organic material from air and water (see Hellmuth 1989 for review). Once again, these examples offer qualitative support to the overall concept of bitumen encapsulation of wastes and should be studied in more detail in any future assessment."

Rocks at Maqarin (Jordan) are late Cretaceous marls and bituminous limestones, known locally as the Bituminous Marl Formation, and contain a rare assemblage of naturally formed cement minerals, including portlandite. These minerals formed in a two stage process: (a) the Bituminous Marl Formation underwent spontaneous combustion at T > 1,000°C to form high temperature mineral assemblages, and (b) the high-temperature minerals were hydrated by interaction with the normal aquifer waters (pH = 8) to form a low-temperature mineral assemblage of gypsum, ettringite, tobermorite and portlandite. The resulting high pH of the groundwater is controlled by the solubility of portlandite and other cement phases, and is a good analogue of a cementitious L/ILW repository. However, natural bituminous marl in Maqarin soil may not resemble the technical bitumen used for conditioning SFR-waste and the soluble organic substances in the two environments may also differ. Strictly, the bitumens used for L/ILW are technological asphalts distilled from crude oil at several hundred degrees C for a few hours. The bitumen composition is controlled both by the composition of the crude oil and the precise distillation process. Natural bitumens are also distilled from crude oils, but by geological processes over much longer time periods and over widely variable temperatures. Consequently, the similarity between technical and natural bitumens is limited (Miller et al. 2000).

Large asphalt blocks (up to several hundred cubic metres) have frequently been found floating in the Dead Sea. This asphalt has leaked from hydrocarbon reservoirs, which are abundant in the region, to the sea floor where it floats to the surface of the water. It has been suggested (Miller et al. 2000) that these blocks and the bitumen coated hulls of ships sunk into anoxic mud could be used as analogues of bitumen leaching. This is probably true if appropriate examples were studied, but they would nevertheless be no more that qualitative illustrations for a wider stakeholder audience.

Miller et al. (2000) also state "One notable attempt has been made to characterise a bitumen–groundwater system in sufficient detail to describe the processes involved and rates of alteration. Hellmuth (1989b) investigated a bitumen impregnated limestone in Germany. This limestone is exposed at the surface but dips beneath permeable sedimentary cover. Variations in the chemical structure, composition and physical properties of the bitumen were measured in samples taken from a range of locations and depths. It was discovered that degradation (oxidation) results in a bleaching of the bitumen as volatile substances are leached from the bitumen but that degradation was confined to only a very shallow near-surface zone. The limited extent of leaching is a consequence of the breakdown process: degradation of the bitumen by oxygen and water is fastest where it is exposed to visible and ultraviolet light, i.e. at the surface only. Deeper penetration is prevented as long as the weathered layers are not mechanically destroyed and removed.

This could be taken to indicate that leaching of bitumen in the repository will be very slow. However, it would not be sensible to reach this conclusion only on the basis of these analogue results because of the gross differences between the chemical conditions of the analogue site and the alkaline near-field of a L/ILW repository."

Qualitatively, the many geological and archaeological occurrences of bitumens point to their stability under a wide range of physico-chemical conditions as well as their ability to isolate materials from water for long periods of time. However, as Miller et al. (2000) point out, the differences in the composition of natural and industrial bitumens means that no natural analogue studies of direct relevance have been carried out to date. The review of Hellmuth (1989), for example, cites over one hundred publications but not one deals with the long-term behaviour of bitumen under the alkaline conditions expected in the near-field of the SFR 1 repository. This is clearly an area worth further study but there are currently no known relevant analogue sites.

Organic cement additives

No observations from nature or natural analogues are known for the degradation of organic cement additives.

Time perspective

Cellulose

The rate of alkaline degradation is the main factor determining the concentration of cellulose-derived complexants such as ISA in solution in cementitious repositories (Chambers et al. 2002, Askarieh et al. 2000).

The assessment of potential influence of ISA on the safety case is based on model calculations on the rate of cellulose degradation. In view of the new data for cellulose degradation rates and the model presented in Glaus and Van Loon (2008), from experiments run for up to 12 years, further evaluation is needed. From the work of Glaus and Van Loon (2008), it can be concluded that both estimates previously made for the complete degradation of cellulose in the alkaline environment of a cementitious repository Pavasars et al. (2003) and Van Loon and Glaus (1998) are not appropriate. The review made by Humpreys et al. (2010) agrees that the data from Glaus and Van Loon (2008) do not fit with the previous two phase model (Van Loon and Glaus 1998) and discusses data that show there is a definite stopping of cellulose degradation at 90°C, which suggests that mid-chain scission is being inhibited by the crystalline regions of cellulose. Data collected at 25°C (Glaus and Van Loon 2008) do not demonstrate a stopping of cellulose degradation and the authors suggest that other reactions maintain cellulose degradation at these extended timeframes, such as the transformation of crystalline to amorphous cellulose.

It is important to higlight that the total cellulose degradation time based on these extended reactions is still significantly shorter that the expected life of a repository.

In view of the new data and the model presented in Glaus and Van Loon (2008) the range of uncertainty for complete degradation of cellulose under repository conditions can be narrowed down to a best estimate of 1×10^3 to 5×10^3 years.

Organic cement additives

Long-term safety aspects of the use of superplasticisers (SP) and other cement paste components were studied in the joint Nagra – NUMO – SKB – Posiva project (Andersson et al. 2008), with the aim of developing an evaluation methodology. The main long-term safety issue is whether the superplasticisers and/or other organic components of cement pastes might affect the transport properties of radionuclides. Very weak sorption of SP onto granite has been observed. There is currently insufficient data to evaluate whether superplasticisers can be used in a high-level nuclear waste repository, but superplasticisers have been classified according to their impact on radionuclide sorption (Andersson et al. 2008). According to these authors, an increase in directly added SP has generally been reported to decrease sorption of Eu^{3+} to granite, while grout leaching solutions have had no observable effect. Sorption experiments with Ni^{2+}, Eu^{3+} and Th^{4+} on a cation exchange resin indicate that the admixtures may form strong complexes in solution with the aforementioned radionuclides. Nevertheless, no influence on the uptake of radionuclides by cement paste was observed (Andersson et al. 2008).

According to Hallbeck (2010), any degradation of concrete additives will occur early on, from the time of construction to 100 years after repository closure. This is in agreement with the recommendations and conclusions of Andersson et al. (2008), that a small part of the organics and SP leach out in the early period. Therefore, they recommended that the time dependent behaviour of SP should be further investigated by both experimental and modelling studies, in order to be able to estimate their potential impact at the different timescales needed.

Handling in the safety assessment SR-PSU

Although ISA is not the only alkaline degradation product of cellulose, it is the only one found to be of significance for safety assessment. Cellulose degradation is assumed to start immediately after the closure and sealing of the repository, as a result of resaturation with water that has been chemically altered by cement. The concentration of ISA inside the waste packages is calculated from the estimated concentrations of cellulose in different waste types using the latest degradation results from Glaus and Van Loon (2008).

Other chemicals present in SFR, e.g. EDTA, NTA, Citric acid, gluconate, oxalate and organic cement additives are deemed to be stable under the conditions prevailing in SFR (Dario et al. 2004a, Keith-Roach 2008). Hence their ability to mobilise radionuclides are evaluated as the original compounds throughout the safety assessment.

All uncertainties regarding the source term of complexing agents are covered in the scenario "high levels of complexing agents" (SR-PSU Main report (SKB 2014k)). This scenario also addresses the uncertainties regarding cellulose degradation.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The mechanistic understanding of the degradation of organic matter might be considered sufficient for the needs of safety assessment. Indeed, one of the main uncertainties concerning the complete degradation of cellulose under repository conditions can be minimised as a result of the recent experimental results from Glaus and Van Loon (2008).

Uncertainties in mechanistic understanding are not very important in terms of the chemical degradation of organic materials present in SFR. The most important uncertainties are related to the understanding on how organic degradation processes might generate ligands that affect radionuclide speciation and behaviour. Accurate predictions of radionuclide speciation should include data on the stability of complexes with organic ligands present in SFR.

Relatively little systematic work has addressed reactions between cement and organic ligands, e.g. reactions which decrease the concentration of organic ligands in a cement environment (Stronach and Glasser 1997). Preliminary indications suggest that the influence of some organic ligands on radionuclide mobility may be limited by competing processes in a repository environment. Some organics precipitate in cement environments, e.g. oxalate as its Ca salt, limiting the aqueous concentration. Other organics, e.g. citrate, is decomposed. The result of this is that the concentration of organics is reduced in aqueous solution, with a lower capacity to complex and transport radionuclides.

Model simplification uncertainty

Some of the uncertainties are covered by pessimistic assumptions of reaction rates and total ligand concentrations as a function of time.

The main components subjected to degradation processes are cellulosic materials, ion exchange resins and bitumen. Of these, only cellulose degradation has been proven to produce degradation products with strong complexing properties. Under highly alkaline conditions, cellulose slowly degrades to low molecular weight compounds and ISA (both stereoisomers, α- and β-) is considered the main product of cellulose degradation.

Carboxylic acids formed during radiolytic degradation of bitumen are reported to be weak complexing agents and are considered to not have significant influence on the sorption of radionuclides onto cementitious materials (Allard and Persson 1985, Bradbury and Van Loon 1998).

Similarly, the degradation products from ion exchange resins as amines and oxalic acid have not been considered to have a significant influence on radionuclides (Van Loon and Hummel 1999a, b).

The degradation of nylon, polystyrene and polyvinylchloride has a small effect on radionuclide in comparison with cellulose degradation products.

In Fanger et al. (2001), the main complexing agents assumed to affect the migration of radionuclides are EDTA, citric acid, fatty acids, NTA, lignine and derivatives from cement additives, cellulose and its degradation products (ISA), oxalic acid, gluconic acid and picolinic acid.

Under alkaline, anaerobic conditions, cellulose degrades partially over experimental timescales. Therefore, it is possible to relate the effects of the leachate on radioelement behaviour to a known degree of degradation (and thus, indirectly, a concentration of complexing agents). This can be then extrapolated to estimate the magnitude of the effects that would occur on greater or full degradation of cellulose over longer timescales of relevance for repository conditions. The extrapolation of experimental degradation data to repository timescales introduces uncertainties.

Input data and data uncertainty

The major input data uncertainty is related to the amounts of complexing agents deposited in SFR. Generally, the amounts of organic substances such as EDTA, NTA are based on the estimated amounts of detergents used on the active side of each nuclear site. The amount of the complexing agents used that has actually been deposited in SFR remains uncertain. It should be pointed out that, according to Fanger et al. (2001), the estimates of concentrations in different waste types are based on a number of conservative assumptions. The actual concentrations are therefore probably lower than the calculated ones.

The uncertainties relating to the quantities of cellulose deposited in the repository mainly arise from cellulose containing materials, e.g. clothing, which may not consist of 100% cellulose. This introduces a large uncertainty of the potential amounts of ISA formed in SFR. The assumption that all cloth materials are 100% cellulose is the conservative approach when assessing the effect of ISA on radionuclide mobility. Furthermore, the limited knowledge of the % of the α- and β-ISA formed by the chemical degradation of cellulose, and the assumption that they have the same affinity for radionuclides might be potential sources of uncertainties, which are not well studied.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.7 Water uptake/swelling

Overview/general description

Waste materials in contact with water, both in liquid form and as vapour, can take up water and swell. This can occur in both bitumen and cement stabilised wastes. This section will treat water uptake and subsequent swelling in bituminised waste only. Hydration of cement stabilised waste is treated in Section 3.5.5.

Bitumen is a complex mixture of high molecular polycyclic aromatic hydrocarbons and is produced in a range of qualities with different mechanical properties, ranging from low viscosity soft bitumens (distilled, straight-run) to hard more plastic elastic bitumens (blown, oxidised). Only distilled bitumens are used for solidified waste placed in SFR. The mechanical properties of the bitumen are also affected by age, radiation and the production of gas within the waste matrix. Thus, the swelling behaviour can differ to a large extent between different types of bituminised waste.

In SFR, bitumen is used to solidify ion-exchange resin waste. Evaporate salts are to varying degree present in these wastes. The bituminised waste is allocated to the silo, BMA and BLA. In the bituminisation process, waste is mixed into hot bitumen resulting in a bitumen matrix with a dispersion of embedded waste particles. Although pure bitumen is a hydrophobic material, water can be transported into a bitumen matrix. In pure bitumen the water uptake is very low, since the driving forces are very small, although not nil due to the presence of a small amount of electrolyte in the bitumen (Read and Whiteoak 2003). However, the bituminised ion exchange resins and evaporator salts are hygroscopic, and thus provide a driving force for diffusion of water into the bitumen matrix. Since water can move through the bitumen, but the constituents in the waste material cannot, the bitumen acts as a semi-permeable membrane and the process can be considered to be osmotic.

The driving force for water uptake can be described in several ways, as a gradient in chemical potential (Sercombe et al. 2006), water vapour pressure or water concentration (Brodersen 1999). However, the different descriptions give similar results and the driving force is determined by the specific properties of each waste. For evaporate salts, the chemical composition and solubility of the waste is important. Salts with relatively high solubility such as $NaNO_3$ and Na_2SO_4 can create low chemical potentials, while more insoluble salts such as $BaSO_4$ or sludges are relatively inert. For ion-exchange resins, the situation is more complex and depends on the type of resin (cation or anion, powder or bead, degree of cross-linking), the extent of drying of the resin and the pretreatment of the resin by, for example, heat treatment (Petterson and Elert 2001).

When salts and ion exchange resins absorb water they expand in volume (Snellman and Valkiainen 1985, Nilsson et al. 1988, Brodersen et al. 1998). The degree of expansion of the waste particles will depend on the type of waste. The increase in volume between the dry salt and the saturated solution at a temperature of 20°C is 3.5 times for $NaNO_3$ and about 14 times for Na_2SO_4, calculated from the density of the dry salt and the salt content of the saturated solution (Petterson and Elert 2001). The potential change in volume from water uptake for a cation ion exchange resin is about 2.4 times.

The swelling of the waste particles will affect the stress conditions in the bitumen matrix and cause internal changes leading to the formation of fractures. As a consequence, an interconnected porosity may form in the bitumen matrix. If an open porosity forms, soluble salts can diffuse out of the matrix and the gradient in chemical potential will decrease. The case is somewhat different for bituminised ion-exchange resins as they are not mobile and the lowering of the chemical potential is in this case achieved only by the continuing uptake of water.

The degree of swelling will depend on the mechanical properties of the bitumen, the waste loading and the homogeneity of the waste product. The internal swelling and the formation of an open porosity will affect a number of hydraulic and chemical processes in the waste matrix. The change in volume and the pressure it creates may be sufficient to affect the volume, dimensions and stability of the surrounding packaging.

In an unaffected bitumen matrix, the release of radionuclides is negligible. However, the water uptake and swelling will create a network of pores or fractures in the bitumen matrix. Once a communicating porosity is established, dissolved radionuclides can be released from the bitumen matrix by diffusion. Highly soluble radionuclides in ion-exchange resins or evaporator concentrates can be assumed to be released at the same rate as highly soluble salts. Any sparingly soluble radionuclides or nuclides in sparingly soluble salts could remain in the pore system for a long time.

Dependencies between process and waste form variables

The following table shows how the process influences, and is influenced by, all waste variables defined in Section 2.1.2.

Table 3-17. Direct dependencies between the process "Water uptake and swelling" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Depends on surface/volume ratio and is affected by internal geometry.	Included in swelling calculations.	Yes. Swelling changes internal and external geometry.	Estimated swelling is compared to void space in package.
Radiation intensity	Yes. High absorbed doses affect the chemical and physical properties of bitumen and ion-exchange resins.	Not relevant. Radiation effects judged to be negligible at absorbed doses less than 0.1 MGy. Majority of SFR-waste has long-term doses less than 0.1 MGy, see Section 3.1.3.	No.	Not relevant.
Temperature	Yes. Temperature affects potential for water uptake.	Considered in swelling calculations.	Yes	Neglected. Negligible heat effects due to water uptake.
Hydrological variables	Yes.	Enough water assumed to be present to induce swelling.	Yes. Influence on the local scale.	Neglected. Negligible on repository scale.
Mechanical stresses	No. Indirectly via matrix geometry.	Not relevant.	Yes. Swelling may cause stress in the waste form.	Result of the swelling calculations.
Radionuclide inventory	No. Indirectly through radiation intensity.	Not relevant.	No. Indirectly via changes in geometry that can provide pathways for leaching.	Not relevant.
Material composition	Yes. The type and amount of waste are the most important factors.	Considered in swelling calculations.	Yes. Water uptake changes properties of ion-exchange resins and salts. Also, indirectly through leaching of waste constituents.	Considered in swelling calculations.
Water composition	Yes. Water composition will to a small degree affect potential for water uptake.	Neglected. Neglecting solutes in water gives a conservative assumption of water uptake.	No. Indirectly since salt and small amounts of organic substances may leach from bitumen.	Not relevant.
Gas variables	No. Indirectly. High gas pressures can lead to mechanical stresses causing pores, cracks or bubbles in bitumen matrix.	Not relevant.	No.	Not relevant.

Influence by geometry. Water uptake is a surface process, thus the area available for water uptake is important. Swelling due to water uptake primarily affects the outer parts of the waste matrix and is more important for small waste packages due to their larger surface-to-volume ratio. Decreasing the surface-to-volume ratio decreases the swelling (Brodersen et al. 1991, Valcke et al. 1999).

Water uptake and swelling is affected by the internal structure of the waste matrix, for example the size and shape of waste particles and the loading of waste in the bitumen.

Influence on geometry. Swelling changes the geometry of the waste matrix. In the bitumenisation process, a void space is left in the waste package to make room for the additional volume. Thus, only a volume increase exceeding the void space would affect the waste package and its surrounding barriers. Swelling of bitumen may also lead to formation of a network of pores or fractures in the bitumen matrix, see Section 3.4.1.

Influence by radiation intensity. Irradiation of bitumen may have several negative effects on the bitumen properties, through the generation of radiolytic gases (mainly hydrogen), but it may also lead to a hardening of the bitumen. The changes in the bitumen matrix have an indirect effect on the uptake of water and the subsequent swelling. Experiments with bituminised ion-exchange resins have shown that irradiated resins (0.1 MGy) have an order of magnitude faster water uptake than unirradiated resins (Aittola and Kleveland 1982). See also Section 3.1.3. Radiolysis has been found to have a negligible effect for an absorbed dose less than 0.1 MGy; for absorbed doses between 0.1 and 2 MGy, generation of gases should be considered in the design, and at absorbed doses higher than 2 MGy, substantial swelling can take place (Eschrich 1980). The acceptance criteria for bituminised waste to be placed in SFR is 1 MGy. The estimated absorbed dose in the bituminised waste placed in SFR is about 0.01 to 0.1 MGy, but a fraction of the packages may obtain a dose exceeding 0.1 MGy (Pettersson and Elert 2001).

Influence on radiation intensity. Water uptake and swelling has a negligible effect on the radiation intensity.

Influence by temperature. Temperature affects the potential for water uptake and the bitumen properties. The chemical potential of water increases with temperature, furthermore an increase of temperature will increase the solubility of most salts and will thus decrease the chemical potential of the waste. Thus, the driving force for water uptake by salts is expected to increase with increasing temperature. For an anionic resin the swelling behaviour at 0°C is expected to be the same as at 25°C based on the free energies of formation of different hydrates (Nilsson et al. 1988).

Temperature will also have an influence on the bitumen properties. At higher temperatures bitumen softens, which may increase the potential for swelling. However, at lower temperatures bitumen becomes harder and fractures can more easily form.

Experimentally, the swelling of bitumen mixed with evaporator concentrate and reprocessing sludge has been shown to depend on temperature (Sneyers and van Iseghem 1998). The volume increase at 40°C was three to seven times higher than at 23°C. These results are supported by Brodersen et al. (1998).

The effect of temperature and waste-to-bitumen ratio on water uptake and swelling has been studied using a cation exchange resin in bitumen that was immersed in water for up to one month (Brodén and Wingefors 1992). For a matrix containing 40 percent resin by weight, almost no water uptake or swelling was observed at temperatures between 3 and 30°C. At higher resin concentrations, the water uptake increased with increasing resin concentration, but there was no significant difference between experiments carried out at 20 and 30°C. However at 3°C, water uptake was found to be considerably higher. A possible explanation is fracturing of the matrix at low temperatures. The authors note that similar results have also been obtained in a study by Buckley (1985).

Influence on temperature. The dissolution of salts can be an exothermic reaction. However, the amount of heat generated is very small.

Influence by hydrological variables. The amount of water (degree of saturation) surrounding the waste/bitumen matrix may have some influence on water uptake. However, the chemical potential of water in vapour form is high enough to create the necessary driving force for water uptake.

Experimentally, bituminised waste samples have been shown to take up water and swell if placed in humid air (Brodersen et al. 1998).

Influence on hydrological variables. The swelling of bitumen within a confined space may close pores in the surrounding barriers, thus reducing their permeability. If the swelling is large, it may lead to mechanical stresses within the waste matrix forming an open porosity (fractures). This may have indirect effects on the magnitude, direction and distribution of the water flow in the waste matrix and surrounding barriers on a local scale. However, it will not affect water flow within the repository on a larger scale.

Influence by mechanical stresses. Indirect effect via changes in the internal matrix structure. Internal swelling caused by gas generation may create mechanical stresses that give rise to fracturing and bubble formation, which may increase the rate of water uptake into the bituminised waste. This effect can be important at high radiation levels (absorbed dose well above 0.1 MGy). Experiments on pure bitumen have shown that irradiation of soft (distilled) bitumen leads to bubble formation and that irradiation of hard (oxidised) bitumen leads to the formation of pores and fractures (Phillips et al. 1984).

When bituminised waste is confined, for example in a drum, swelling is prevented and an osmotic pressure is generated. Increased pressure may re-compress the bitumen matrix and reduce further swelling (Valcke et al. 2010). However, this has not yet been proven in experiments. Investigations of confined swelling show that the swelling rate of soft bitumens is about the same for confined and unconfined conditions (Brodersen et al. 1998). For hard bitumen, the swelling rates were found to be higher in confined conditions compared to unconfined conditions.

Influence on mechanical stresses. Swelling due to water uptake gives rise to mechanical stresses in the waste form. Excessive swelling of the bituminised waste may cause mechanical stresses on the surrounding packaging and barriers, see Section 4.3.1.

Influence by radionuclide inventory. The radionuclide inventory is not believed to have a direct influence on the water uptake and swelling, since the mass and solubility of radioactive salts is small and will have a negligible influence on the chemical potential of the waste. The indirect effect caused by radiation is treated above (Radiation intensity).

Influence on radionuclide inventory. The water uptake and swelling may give an indirect influence by changing the geometry, providing an interconnected porosity within the bitumen matrix that will be a pathway for radionuclides leaching from the waste.

Influence by material composition. The type of waste embedded in the bitumen matrix has a significant influence on water uptake, and thus the degree of swelling. For ion-exchange resins, important considerations include whether it is a cation or anion, powdered or bead resin, the degree of cross-linking, the extent to which the resin has been dried, and pretreatment of the resin by for example heat. The chemical content of the evaporator concentrate is important, e.g. sodium nitrate, sodium sulphate. The relative volume increase is higher for an evaporator concentrate, and specifically for sodium sulphate, than for an ion-exchange resin. The water uptake rate is one order of magnitude faster for irradiated bituminised resins than for non-irradiated resins (Aittola and Kleveland 1982). The authors have also found that addition of decontamination chemicals such as EDTA, citric acid, oxalic acid and ascorbic acid in the waste increases the swelling rate. However, the reason for this effect was not investigated.

The process of water uptake also depends on the amount of waste in the matrix. It has been shown (Aittola and Kleveland 1982) that at a waste loading of less than 50%, there is a slight increase in swelling with increasing amount of resin, but when the ratio exceeds 50% there is a strong effect on swelling.

Results presented by Brodersen et al. (1998) indicate that the unconfined swelling rate of soft bitumen is higher than that for a hard bitumen. However, confinement (for example in a waste drum) increases the extent to which hard bitumen swells, but has no effect on soft bitumen. Therefore, when the bituminised waste is confined, swelling of hard bitumen is similar to that of soft bitumen.

Influence on material composition. Water uptake and swelling may lead to changes in the properties of ion-exchange resins and salts. It also has an indirect effect as it makes possible the leaching of waste constituents.

Influence by water composition. Dissolved chemical substances may decrease the chemical potential of the water in contact with the bituminised waste matrix. This effect has been shown experimentally (Gwinner et al. 2006). However, the impact of this has generally been neglected. Furthermore, the presence of complexing agents in the water, which is dependent on the material composition to some degree, has in experiments been shown to affect the swelling properties of the waste (see Influence by material properties).

Influence on water composition. Water uptake and swelling of bituminised waste may lead to the leaching of organic constituents from the bitumen. The effect is influenced by radiation, aging and microbial processes.

Influence by gas variables. Internal pressures induced by gas formation may have an indirect effect by causing fracturing and bubble formation. However, the effects have been found to have negligible effects for an absorbed energy of less than 0.1 MGy.

Influence on gas variables. Water uptake and swelling does not have a direct influence on gas composition. However, water uptake may lead to increased microbiological degradation.

Boundary conditions

The boundary condition for water uptake is the exterior surface of the waste package. Water uptake may start directly after emplacement of waste, due to the presence of air humidity. However, in the early stages water uptake will be hindered by the packaging. The waste package is also the boundary condition for swelling, although in extreme cases swelling may also affect surrounding barriers.

Model studies/experimental studies

Extensive experimental studies were performed between 1980–1990 on water uptake and swelling and subsequent leaching of bituminised waste in the Nordic countries (Snellman and Valkiainen 1985), Denmark (Brodersen et al. 1998), Finland (Valkiainen and Vuorinen 1985, 1989, Aalto and Valkiainen 2004), France (Bernard et al. 1982, Nomine and Ferriot 1996) and Belgium (Sneyers and van Iseghem 1998, Valcke et al. 1999). A Euroatom R&D program has dealt with the characterisation of bituminised waste (Brodersen et al. 1998). Summaries of research on bitumen have been published (Eschrich 1980, IAEA 1993). A characterisation of bituminised waste in SFR is presented in Pettersson and Elert (2001). More recent research focussed on bituminised waste has been performed in Belgium (Mariën et al. 2008, 2013, Valcke et al. 2010) and in France (Sercombe et al. 2006, Gwinner et al. 2006). Most of the research concerns the swelling of bitumen-embedded salts. Although the process of water uptake into these salts is similar to that for ion-exchange resins, there is a major difference in that the salts give rise to an osmotic pressure and can leach out of the waste. Comparatively little work has been done on swelling and pressure build-up within wastes containing ion-exchange resins (Valkiainen and Vuorinen 1985, 1989, Nilsson et al. 1988, Masuda et al. 1992).

A relatively limited number of modelling studies of water uptake and swelling of bituminised waste have been carried out. Brodersen (1999) set up a pore scale model of water uptake from hygroscopic materials in bitumen. More recently, mathematical models have been set up for understanding the mechanical behaviour of bituminised waste products (Mokni et al. 2010, 2011) and the swelling and water uptake under unconfined (Sercombe et al. 2006) and confined conditions (Gwinner et al. 2006, Valcke et al. 2010, Mokni 2011). Models have also been applied to predict the long-term properties of bituminised waste and its effect on the repository environment (Weetjens et al. 2010).

Natural analogues/observations from nature

Natural geological occurrences of bitumen (e.g. asphalt lakes and the Oklo uranium deposits) have been targeted as natural analogue studies. The natural deposits of bitumen and similar materials are the result of complex, largely unknown long-term geological processes. They therefore vary significantly in composition. Bitumen used to solidify radioactive waste is produced industrially under controlled conditions, and is therefore well characterised in terms of both composition and properties. Thus, a direct comparison is problematic and this limits the value of natural analogue studies for bituminised waste. However, natural analogues have been used to obtain qualitative information on the stability of bitumen under a wide range of physical and chemical conditions, but not as a direct analogue for water uptake and swelling.

Most natural analogue studies focus on the long-term isolation properties of bitumen, for example in Oklo, where uraninite is embedded in graphite, that may originally have consisted of bitumen, but has been substantially altered to form almost pure graphite due to the loss of volatiles (Miller et al. 2000). Studies at Oklo carried out by Nagy et al. (1991, 1993) and Mossman and Nagy (1996) have concluded that graphite produced during the period of nuclear criticality has immobilised uraninite and fission-generated isotopes. One potential criticism here is that the standard laboratory techniques employed above subject the bitumen samples to a massive, externally applied radiation dose. This effectively gives the bitumen sample its predicted lifetime (i.e. several hundred years) dose in two or three months (for details, see Burnay 1987, Kopajtic et al. 1989). Uranium orebodies and other metallic orebodies with enhanced radionuclide concentrations are sometimes accompanied by bitumen or kerogen (e.g. Parnell et al. 1993, Smellie 2012). A good example of this association is the Oklo natural fission reactors (Nagy et al. 1991, Nagy 1993) where natural graphitic bitumen and uraninite occur together in some of the reactor zones. The bitumen at Oklo is derived from syngenetic kerogen through hydrothermal processes during criticality (Gauthier-Lafaye and Weber 1993). Initially the bitumen was liquid, and its presence caused the reduction of uranium in aqueous solution to form uraninite and some of these newly formed uraninite crystals were enveloped in the bitumen which subsequently hardened into a solid graphite.

Comparison of the retention of fission products between uraninite crystals enclosed in this graphitic bitumen and those enclosed in clay minerals clearly demonstrates that containment was greater in the graphite. This is despite the irradiation of the graphite which must have occurred around the uraninite crystals. In simple qualitative terms, this is an interesting supporting observation, but it should not be used to quantify the stability of bitumen in the repository because there are too many important differences between the SFR 1 repository and Oklo systems.

Most importantly, the bitumen at Oklo has been substantially altered to form almost pure graphite due to the loss of volatiles with time. In addition, the uraninite exists as discrete crystals or aggregates of crystals in the graphitic bitumen, leading to highly localised radiation effects, whereas in the SFR 1 waste, radioactive material is homogeneously dispersed throughout the the bitumenised waste package leading to low, non-localised doses.

There are archaeological and anthropogenic examples of the preservation and durability of bitumen-type materials which have been discussed by Miller et al. (2000). Examples include the preservation of wood and fossil bones in tar pits in California and Peru, and the ancient use of pitch to seal boats and graves.

Time perspective

Water uptake and swelling of bitumen will start early on as water can be taken up from air humidity, although possibly at a lower rate. After closure, void spaces in drifts and vaults will be saturated with water rapidly by inflowing groundwater. Due to the low hydraulic conductivity of the bentonite and concrete in the silo, as well as the impact of entrapment of gases in the silo, the water saturation of the silo is expected to be a slower process (25–100 years).

Models for water uptake in bituminised waste predict that the rate will be proportional to the square root of time. Laboratory experiments on small scale samples indicate swelling rates in the order of 10–20% after a period 4 years (Valcke et al. 2010). These experiments indicated a slow decline in the swelling rate. The thickness of the leached layer after 3–4 years was in the order of a few millimetres (Valcke et al. 2010, Gwinner et al. 2006). For repository conditions with full-scale waste packages, water uptake and swelling may continue for several hundreds of years.

Handling in the safety assessment SR-PSU

In previous risk assessments the maximum theoretical swelling was calculated and compared with the available void volume. Theese comparsions showed that there was enough void volume in the surroundings to accomedate the volume increase. In the safety assessment for SR-PSU knowledge of the swelling pressure as a function of volume expansion is used to evaluate the pressure exerted on structures and barriers surrounding the bituminised waste in the SFR. Consideration will be taken to the geometry and the composition of the waste.

The effect of water uptake on the subsequent release of radionuclides is handled by assigning appropriate release rates for the radionuclides.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The processes involved in the water uptake and swelling of bituminised salts and evaporator salts are well understood. However, less research has been carried out investigating the swelling of bituminised ion-exchange resins. The complex interactions between the bitumen matrix and the waste are not well understood. For example, whether a counter pressure could lead to a re-compression of the bitumen matrix when swelling occurs in a confined space.

Model simplification uncertainty

The process models for water uptake and swelling are rather complex and have been developed for long-term predictions of results of laboratory experiments. Models for safety assessment contain a number of simplifications, but aim at explaining the major interactions between processes often based on experimental data.

Input data and data uncertainty

Not all input data are well known. A source of uncertainty is the variability in waste package properties. Waste packages can have an inhomogeneous waste loading, which may lead to water uptake and swelling that deviate from the "normal". Also, long term changes in the waste matrix such as settling of waste particles may need to be considered.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. A majority of the references are published material that has been reviewed by SKB and/or by refereed scientific journals. Some references are reports from research institutes.

3.5.8 Microbial processes

Overview/general description

Biological processes include many reactions that are very slow or do not occur in sterile lifeless chemical systems, e.g. the reduction of sulphate to sulphide (Goldstein and Aizenshtat 1994, Cross et al. 2004). This is because life has the ability to over-run activation energy barriers and other energetic circumstances that block spontaneous chemical reactions. Life is possible from –20°C up to above 113°C, where in general all life processes stop. Life is also possible within a large pH range, from pH 1 up to at least pH 12 (Yumoto 2007, Pedersen et al. 2004). However, the highest growth pH in alkaliphiles was reported to be 12.5 (Takai et al. 2001) for *Alkaliphilus transvaalensis* isolated from a deep African goldmine. At present, pH in the drainage waters from the repository rock walls in SFR, has been measured to be in the range pH 8 to 9.4, which provide excellent conditions for microbial growth as most alkaliphilic bacteria have optimal pH in the range 8–10 (Yumoto 2007). On the assumption that there will be no microenvironments, the pH in the water in contact with the waste is expected to follow the concrete degradation stages, i. e. starting pH 13.3, which rapidly decreases to 12.5 for the concrete containing repository parts. Upon recharge (advection), nutrients will be added to the system and biofilm growth inside the barriers will be stimulated.

During the saturation phase that will last for a couple of years (25–100 years for the silo), the water pH is likely to be equal to that of Baltic Sea water until saturation is reached. In the parts that are saturated with water, the pH will reach the same level as the cement porewater, i.e. 12.5. Microbial growth will increase as a result of the addition of energy (e.g. H_2 which mainly is an energy source for SRB among others) dissolved nutrients, but will slow down when saturation is reached and the recharge ceases. Alkaline condition is assumed to be the result when saturation is reached and is likely to last during the lifetime of the SFR repository. During that time, microbial activities are expected to significantly slow down. However, it must be kept in mind that survival is not the same as being active. As the pH in SFR will decrease over time (Small et al. 2008), the influence of microbial processes will increase in magnitude concomitantly and could result in further decrease in pH due to acidogenic activity such as fermentation.

Microbial processes comprise the decomposition and the production of organic molecules with different electron donors, energy sources and electron acceptors. Organic carbon in wastes and reduced inorganic molecules such as hydrogen from anaerobic corrosion processes and methane from organic substances are possible electron donors and energy sources for microbial processes in the SFR. During the microbial oxidation of these energy sources, microorganisms preferentially reduce electron acceptors in a particular order as shown in Figure 3-5. First oxygen, and thereafter nitrate, Mn(IV), Fe(III), sulphate, sulphur and carbon dioxide are reduced. In other words when the electron acceptors from oxygen down to sulphur are available methanogenesis is suppressed. Simultaneously, fermentative processes supply the metabolising microorganisms with, for example, hydrogen and short-chain organic acids such as acetate. Fermentation, in comparison with respiration, does not require an external electron acceptor, the oxidation-reduction process comprises rearrangement of electrons in exogenic modes, thereby releasing energy for life processes. As the solubility of oxygen in water is low, and because oxygen is the preferred electron acceptor of many bacteria that utilise organic compounds in shallow water, anaerobic environments and processes usually dominate below the water table. The reduction of microbial electron acceptors may significantly alter the variables water composition and gas composition, see Table 3-18. Dissolved nitrate is reduced to dinitrogen (N_2) and nitrous oxide gases which dissolve in water. Solid iron oxides in wastes and corroding reinforcements and steel components are reduced to dissolved ferrous iron, and the sulphur in sulphate is reduced to sulphide which is corrosive to metals. In addition, the metabolic processes of some autotrophic microorganisms produce organic carbon, such as acetate, from the inorganic gases carbon dioxide and hydrogen, while other microorganisms produce methane from these gases; all microbial processes generally lower the redox potential, Eh.

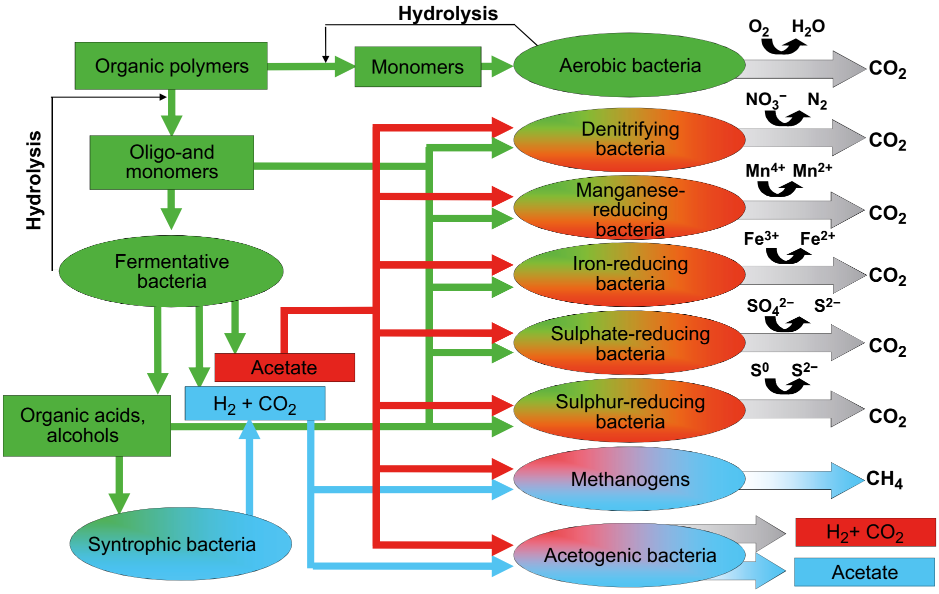


***Figure 3-5.** Possible pathways for the flow of carbon in the SFR environment. Organic carbon (green and red) is respired to carbon dioxide with oxygen (black/grey), if present, or else fermentation (green) and anaerobic respiration (black/grey) occurs with an array of different electron acceptors. Autotrophic processes (blue) generate methane and acetate from carbon dioxide and hydrogen.*

Growth

The variables material composition, water composition and gas composition can be influenced by microbial growth, as microorganisms oxidise organic and inorganic energy sources. The harvested energy is used to synthesise new cell components such as cell walls, proteins, fat, carbohydrates and nucleic acids. The microorganisms produce organic molecules that can be expelled to the environment for purposes such as chelating agents for trace elements needed for growth and polymers enhancing attachment and biofilm formation. The chelating agents can mobilise radionuclides (Anderson et al. 2011). During growth, many microorganisms excrete waste products such as alcohols, organic acids and carbon dioxide.

Respiration

A general microbial process is respiration, which must proceed in all active microorganisms, except for those using a fermentative metabolism. Respiration is a membrane-bound process where electrons from metabolic, dissimilatory, oxidative processes are expelled from the cell via the reduction of different electron acceptors. The electron donors to the metabolic processes can be either organic compounds or inorganic, reduced molecules. Respiration mainly influences the variables water composition and gas composition. This is because the process of respiration changes the state of oxidation, and commonly also the state of aggregation, of the respective electron acceptor, as presented next. In addition, respiratory processes that degrade organic material generate carbon dioxide from wastes. Therefore, all microbial processes influence the variable material composition.

Oxygen; Oxygen is the preferred electron acceptor by many microorganisms, because the free energy change available in oxidation of electron and energy donors is larger when oxygen is used compared to all other metabolic electron acceptors. Oxygen is a gas that is reduced to water; the state of aggregation changes from gas (dissolved) to liquid in this process. This process thereby influences the variable gas composition. The oxidising character of oxygen is removed. This process, consequently, removes oxygen from any system where aerobic respiration (with oxygen) is possible, resulting in a decreasing Eh.

Nitrate; In oxygen depleted (anaerobic) systems, nitrogen in nitrate is the preferred electron acceptor in microbial respiration. Nitrate is present in some SFR wastes such as ion-exchange resins. The reduction of nitrogen in nitrate can result in different products depending on the environmental conditions for this respiratory microbial process. Commonly, the end product is nitrous oxide and/or dinitrogen gas; when the carbon and energy source is plentiful relative to nitrate, the process tends to end with ammonia. In the high pH waters of SFR, ammonia will dissolve and form the ammonium ion (NH_4^+) leaving behind OH^- from the water. Such conditions may occur when large loads of organic material are combined with nitrate and is thus expected to occur to greater extent in the waste and to a lesser extent, if at all, in the vaults and backfill despite the less harsh conditions. As concluded above, oxygen is rapidly removed by microbial respiration processes. When oxygen is used up, nitrate will be reduced and gas will be produced. This process thereby influences the variable gas composition

Iron and manganese; Solids with iron(III) oxides and manganese(IV) oxides, such as iron corrosion products under oxic conditions, can serve as electron acceptors in microbial respiratory processes that degrade organic carbon compounds (Lovley 1991). In this process, the state of aggregation is changed from solid to dissolved and the variable water composition is influenced. The microorganisms can dissolve fracture minerals such as iron and manganese oxides either by direct contact or by excretion of chelating agents such as siderophores (ligands with high affinity for ferric iron) and organic acids. Some microbes produce conductive nanowires (Reguera et al. 2005) in order to be able to transport electrons to extracellular electron acceptors such as ferric iron in iron(III) oxides.

Sulphate, sulphur; In oxygen and nitrate depleted systems, sulphate commonly becomes the preferred electron acceptor, if available, for microbial respiration. Sulphate is a dissolved species that is reduced to the gas hydrogen sulphide in presence of SRB. The preferred energy source is H_2. Hydrogen sulphide dissolves readily in water with a significant dependence on pH. The reductant can be organic carbon or methane (Boetius et al. 2000). In this process, the state of aggregation is changed from dissolved to gas and possibly also to solids in the form of metal sulphides. The variables water composition and gas composition are influenced. The biological nature of sulphate reduction in natural and engineered systems is well investigated (Muyzer and Stams 2008) and the process is ubiquitous in most anaerobic aquatic systems with temperatures below 110°C. The corrosive nature of sulphide for metals makes this process important to understand and quantify. In cases where oxygen is present from air and reacts with sulphide, sulphuric acid is formed which will degrade concrete. Oxygen will only be present initially as it is a very potent electron acceptor for microbes and will therefore be consumed rapidly. Under anaerobic condtions nitrate could work as an oxidant. However, as long as the SFR is saturated, alkaline conditions are likely to prevail in the whole repository and degradation of concrete will thus be very local.

Methylation and alkylation of radionuclides

Some metals and metalloids can be converted by a variety of microorganisms to their volatile methyl derivates (Bentley and Chasteen 2002). This conversion of metals to methylated forms can be mediated by microbes under both aerobic and anaerobic conditions. In aerobic environments, this activity appears to be principally (but not exclusively) associated with fungi. Under anaerobic conditions, methylation can be carried out by a variety of bacteria (e.g. clostridia, sulphate reducing bacteria, methanogens). Microbial methylation and alkylation of radionuclides can be regarded as a special case of radionuclide mobilisation. The radionuclide is not only mobilised as a dissolved gas, but also its bioavailability and radiotoxicity could change, as the process can change an aqueous soluble metal cation into a metal-organic molecule soluble in organic solvents (such as fat).

Biofilm formation

Many microorganisms attach and grow on surfaces of all types in aquatic systems. The resulting cover of microorganisms on the surface is commonly denoted biofilm (Marshall 1976, Characklis and Marshall 1990). Microbial biofilms have been demonstrated to interact with the process of speciation and sorption (Anderson et al. 2006). Typically, microbial biofilms form where gradients of nutrients and sources of energy are present. This can be on surfaces that are exposed to flowing water, and on solid materials, such as SFR wastes and bitumen, where the solid itself constitutes the nutrient and energy source. Pedersen et al. (2004) observed that attached cells seemed to be more active than the unattached ones. However, under alkaline conditions, i.e. pH 12–13, cells did attach to surfaces, but did not grow. If pH decreases one or two units, microbial growth is likely to occur. As a biofilm consists mainly of exudates (e.g. extra cellular polymers) and various precipitates in addition to bacterial cells, it also protects the cells from drying and other extreme conditions.

Anabolic processes

Anabolism is the processes by which microorganisms synthesise the vast array of chemical substances of which they are composed. Autotrophic microorganisms can synthesise all organic cell components such as proteins, fat, carbohydrates and nucleic acids, needed for growth with inorganic energy and electron donors and carbon dioxide as carbon source

Acetogenesis; Autotrophic acetogens produce acetate from hydrogen and carbon dioxide during growth (Wood and Ljungdahl 1991). They produce more acetate than needed for anabolic processes and acetate is, therefore, expelled to the environment. This process influences mainly gas and water composition.

Methanogenesis; Autotrophic methanogens produce methane from hydrogen and carbon dioxide during growth (Wood and Ljungdahl 1991). The methane is expelled to the environment. This process influences mainly gas composition.

Extracellular metabolites, enzymes, complexing agents; Many microorganism synthesise organic components that are expelled to the outside of the cell. These compounds can be enzymes for the degradation of polymers and complexing agents of trace elements including radionuclides (Lloyd and Macaskie 2002). The complexing agents mainly interact with the SFR processes of radionuclide inventory and speciation and sorption. Other microorganisms excrete acids under fermentative conditions which is a process that may interact with degradation of grout (Diercks et al. 1991). Microorganisms produce various kinds of chelating compounds to increase the bioavailability of essential elements needed for metabolism, such as siderophores (Liermann et al. 2000, Anderson et al. 2011). These ligands are not always highly specific, and several of them will also mobilise other elements such as heavy metals and radionuclides (Johnsson et al. 2006, Essén et al. 2007). However, natural concentrations of siderophores are often at nanomolar concentrations and are therefore neglected as other processes are likely to dominate.

Dependencies between microbial processes and waste form variables

Table 3-18 shows how microbial processes are influenced by and influence all waste form variables defined in Section 2.1.2. The handling in SR-PSU is indicated in the table and further described below.

Geometry. There are no relevant direct effects of waste form geometry on microbial processes as the microbial activity will be low under alkaline conditions.

Radiation intensity. The radiation intensity is not expected to be high enough to influence microbial processes.

Temperature. The rate of all microbial processes discussed here increases with increasing temperature from below 0°C up to above 113°C. The degradation of waste material will be more rapid at high temperatures. In cases with high microbial activity, significant heat can be generated. However, the microbial activity is expected to be low.

Table 3-18. Direct dependencies between the process "Microbial processes" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes.	Neglected as the microbial activity will be low under alkaline conditions.	Yes.	Neglected as the microbial activity will be low under alkaline conditions.
Radiation intensity	Yes.	Not handled due to low radiation intensity.	No.	Not relevant.
Temperature	Yes.	Neglected. Negligible effect in expected temperature interval	Yes.In cases with high microbial activity, heat is generated	Neglected as the microbial activity will be low under alkaline conditions.
Hydrological variables	Yes. The extent of microbial processes increases with increasing flow.	Neglected as the microbial activity will be low under alkaline conditions.	No. Indirectly via geometry since, microbial biofilms may clog flow paths.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. Microbial process rates depend on the composition of waste materials.	Neglected as the microbial activity will be low under alkaline conditions.	Yes. Microbial processes will degrade waste material.	Neglected as the microbial activity will be low under alkaline conditions.
Water composition	Yes. The content of carbon sources, electron donors and acceptors will influence microbial processes.	Neglected. Negligible effect, in the expected high pH, low redox range of waters expected.	Yes. Microbial processes will influence concentrations of water components, dissolved gases, Eh and to some extent pH.	Neglected as the microbial activity will be low under alkaline conditions.
Gas variables	Yes. Hydrogen, CO_2 and methane in gas phases can be utilised by microbial processes.	Neglected as the microbial activity will be low under alkaline conditions.	Yes. Microbial processes generate gases, but they also consume gases.	Estimation of gas production is described in Section 3.5.10. Methanogenesis will be out competed by other microbes, such as SRB,s long as there is a pool of electron acceptors yielding more energy than CO_2.

Hydrological variables. After closure, flow rates are expected to be slow and the biofilm formation process will be reduced. The pressure will not be affected on the long term as the produced gas is assumed to migrate out of the system.

Mechanical stresses. There are no relevant direct effects of mechanical stresses on microbial processes and the reverse.

Radionuclide inventory. There are several microbial processes such as methylation and alkylation (Bentley and Chasteen 2002), complexation and chelation (Anderson et al. 2011) that can influence the radionuclide mobility.

Material composition. Microbial processes degrade organic material and can contribute to the corrosion of metals and the degradation of concrete and bitumen. The type and amounts of different materials will influence the rate and extent of microbial processes.

Water composition. The concentrations of substrates such as carbon sources, electron donors and electron acceptors in repository water will favour certain microbial processes. The active processes will persist for as long as the respective substrates for different processes are available. Microbial processes will influence water composition significantly by their reduction of electron donors during respiration, which will change states of oxidation and aggregation of important water components. Removal of oxygen, nitrate and hydrogen from the water composition and production of nitrous oxide and nitrogen gas, ammonium, sulphide, ferrous iron, carbon dioxide and methane will have a profound influence on water composition. Microbial processes will also influence Eh and to some extent pH. This is of particular importance to BLA, where the pH depends on the production of acids from fermentation and the oxidation of sulphide to sulphuric acid, sulphide oxidation can occur aerobically or anaerobically, coupled with nitratereduction.

Gas variables. Microbial processes utilise hydrogen from corrosion processes of material in SFR. Hydrogen gas thereby will have a profound influence on the extent and rate of microbial processes in SFR. Many microbial processes generate gases such as carbon dioxide, dinitrogen, nitrous oxide and methane. Significant pressure build-up can consequently occur as a result of microbial processes.

Boundary conditions

The most important boundary conditions are most likely access to water and the high pH in the repository once it is filled with water, since most of the waste is either encapsulated in concrete/cement or at least in close contact with it. The system is thus buffered with $Ca(OH)_2$, sustaining the high pH. It has been demonstrated that microorganisms could grow and be metabolically active under aerobic as well as anaerobic alkaline conditions, i.e. at pH 10–11 (Pedersen et al. 2004) and even higher (Yumoto 2007). The optimal growth pH for most alkaliphiles lie within the range 8–10 (Yumoto 2007), thus pH above 11 is not expected to give favourable conditions even for the majority of this group of microbes. The most favourable position for microbes, with respect to available energy, is inside the BLA containers with a lot of organic waste. However, restricted availability of electron acceptors and the build-up of toxic degradation products may limit the types and number of microbes that may proliferate inside containers. Many degradation products are relatively non-toxic, but become toxic upon accumulation (e.g. Ingram et al. 1987).

Bitumen can be degraded by microbes and is therefore a possible substrate for microbial activity, but only to minor extent in BLA, as the dominating substrate is cellulose. The growth of microbes would predominantly occur on bitumen surfaces inside steel packages, locally generating large numbers of microbes. The availability of electron acceptors will be controlling microbial processes inside the containers in BLA, as discussed further below.

The amount of organic carbon, nutrients and electron acceptors in the water interacting with the waste influences the microbial activity. Of great importance is the availability of electron acceptors, such as oxygen nitrate, ferric iron, sulphate and carbon dioxide. The SFR is rich in nutrients and energy and these components will not be limiting for microbial activity *per se*. The magnitude, direction and distribution of water flow in the different SFR components will influence the transport of microbes and, much more importantly, the transport of electron acceptors to, and degradation products from, microbes dwelling in SFR waste form locations. This interaction is judged to be the most important in relation to most other interactions involving microbes. The species distribution changes over temperature as the growth interval for a single microbe generally comprises no more than 20–30°C. After closure the expected repository temperature will be the same as ambient rock temperatures.

Microbial growth is possible in a waste form that has been solidified with cement. The growth may be significant if an advective flow supplies the microbes with electron acceptors, removes degradation products and leaches the concrete. Under stagnant hydraulic conditions, the effect may be less significant. Specific species of bacteria can produce sulphuric and nitric acid, which may deteriorate cement and concrete. Microbial growth is possible as biofilms on the surfaces of bitumen-contained waste. The growth may be significant if there is an advective flow to supply the microbes with electron acceptors and remove degradation products. The bitumen will be degraded at a slow rate if conditions are anaerobic; access to oxygen is then an important boundary condition. Degradation is much higher under aerobic conditions. Advective flow and availability of electron acceptors will control these processes.

Non-solidified waste has the greatest potential for microbial degradation. The organic carbon content is very high and pH will be less alkaline than in cement-solidified waste. The large mobility of microbes and waste components inside a container suggests that gas production may become significant here. Microbial growth is possible on the outside of cement containers. The pH gradients will control microbial growth, the limit is not well known.

Microbial corrosion is a well-established process and pitting corrosion by sulphate-reducing bacteria (SRB) may rapidly corrode holes into the steel containers. The growth and corrosion may be significant if there is an advective flow to support microbes locally with sulphate and organic substrates. In the backfill, too, microbial growth is possible, and may be significant in the presence of an advective flow. The effect will, however, be low under stagnant hydraulic conditions. Acidic exudates excreted from bacteria will deteriorate cement and concrete. Microbial growth is possible on concrete structures and may be significant in the presence of an advective flow. It is also possible that there is microbial activity within the cemented waste form (Gorbunova and Barinov 2012). These boundary conditions are not well known.

Model studies/experimental studies

Bitumen waste form is a complex system consisting of a mixture of mainly high molecular aliphatic and aromatic hydrocarbons. It consists mainly of four different compound groups; saturated hydrocarbons, cyclic hydrocarbons, resins and dispersed particles named asphaltenes. The chemical composition of bitumen lies normally in the following ranges: C, 80–88%, H, 8–11%, O, 1–12%, S, 1–7%, N, 0–1.5% (Eschrich 1980). Roffey and Nordqvist (1991) concluded that biofilm formation on bitumen occurred both under aerobic and anaerobic conditions. A pH of 9.8 did not inhibit growth on bitumen by aerobic microorganisms. The source of microorganisms in their study was enrichment cultures from rock caverns used for storage of heavy fuel oil. Degradation studies of bitumen have shown that parts of the hydrocarbons in bitumen are biodegradable. Potter and Duval (2001) could measure a 50% decrease in the aromatic and aliphatic fractions in a bitumen-based fuel sample (trade-name Orimulsion). The bitumen had a large surface area, glass beads were covered with the substance, and the degradation was aerobic. Factors that affect the degradation rate are surface area, temperature, availability of additional nutrients like nitrogen and phosphorous and of course the access to oxygen.

Water in the bitumen–waste mixture will increase the possibility for microbial degradation of the hydrocarbons in the bitumen concomitant with degradation of the waste product, because water is needed for microbial processes to proceed.

Cement waste form and concrete waste: is often composed of Portland cement, with different additives and water. Microbial processes that can degrade concrete are the production of acids and chelators. Both organic and inorganic acids, are produced by different types of microorganisms in their metabolisms. Organic acids can be produced by fermenting bacteria and fungi. Formic, acetic, butyric, oxalic and many other types of organic acids can be produced, sometimes together with carbon dioxide and/or hydrogen (Madigan and Martinko 2006). Kato et al. (2005) noted that, even if all the saturated and aromatic compounds in the bitumen were to be completely decomposed to

CO_2 and this reacted with cement (i.e. carbonation), there would be no significant impact on the pH buffering capacity (and therefore radionuclide speciation) of a L/ILW repository in Japan.

In Gorbunova and Barinov (2012) a drilled core sample was taken from a cement monolith from a low and intermediate level radioactive repository at the depth interval 0.1–8 m. After 15–45 years of storage all specimens regardless of depth were found to have increased porosity, indicating degradation of the cement matrix. Microbial tests showed presence of nitrate reducing bacteria (NRB), iron reducing bacteria (IRB), sulphate reducing bacteria (SRB), fermenting bacteria and fungi. An experimental study conducted at optimal conditions with with denitrifying bacteria isolated from 2 g (≈1 cm^3) of the withdrawn cement specimen showed that they are capable of releasing 0.9–4.1 µmole acetic acid, 3.8 µmole propionic and 1.5–5.6 µmole butyric acid per day. Their main conclusion was that biodegradation, due to formation of organic acids and acid gases (CO_2 and H_2S) reacting with the cement matrix, could along with seasonal variations of moisture and temperature from positive to negative centigrade values, be factors responsible for changes in the crystal structure of hydrated cement minerals and for disturbances in the microstructure of the cement matrix.

According to the modelling performed by Cronstrand (2007) the initial pH of 13.5 will decrease to 12.5, for the silo and the cement encapsulated waste in 1 BMA. This pH will be maintained for 100,000 years depending on hydraulic flow. Little or negligible microbial activity is expected as long as pH remain above 12.5. Microbial activity at alkaline conditions are in general significantly slower than in the pH range 8–10, where most alkaliphiles have their optimal growth pH (Yumoto 2007).

Cellulose and lignin (1BLA). In 1BLA there is cellulose, which is a compound that is easily degraded by microbial processes. It is also degraded abiotically under alkaline conditions (Van Loon and Glaus 1997, Glaus et al. 1999, Van Loon et al. 1999, Humphreys et al. 2010) to e.g. isosaccharinate (ISA), which is a good complexing agent or to compounds that can further be degraded by microbial processes (Bailey 1986). However, the pH in 1BLA will be neutral to slightly alkaline as set by the intruding water and presence of shotcrete and as there will be some moisture in the material heterotrophic degradation by mould and bacteria will be facilitated as long as there is oxygen present in the repository. During the aerobic respiration water is formed which *enhances* further degradation of the cellulose material. When oxygen has been consumed, fermenting processes are likely to start (Bailey 1986). These processes produce acids like acetic, citric, oxalic together with carbon dioxide. In addition, anaerobic respiration processes can occur such as nitrate-reduction, iron-reduction and sulphate-reduction depending on how the ion-exchange resin was prepared, for instance with Na-salts like nitrate or sulphate. Lignin is an organic substance binding the cells, which constitute wood. It is one of the most abundant organic polymers on Earth. This compound is mostly degraded by fungi named “white rot”. In BLA no barriers are accredited for in the safety assessment and when it comes to leaching of radionuclides. However, dilution will be so extensive that no high concentration plumes will occur.

Engineered analogues of the degradation of cellulose include spills of “black liquor”, a waste product of the Kraft paper pulping process. Soil and lake sediments polluted by black liquor have been found to contain several microbial strains capable of metabolising ISA under near-neutral chemical conditions (Bailey 1986, 1987).

Plastics, rubber, cable insulation (BLA, some in BMA and silo). 99% of this type of waste is located in BLA and the remaining 1% is located in the BMA and silo). The degradation of plastic polymers is often a slow process but initially, when oxygen is present, microbial degradation will produce smaller units that can be utilised in anaerobic microbial degradation processes. Polyethene is degraded by lignin degrading white rot fungi by the action of a manganese peroxidase (Iiyoshi et al. 1998). In an aerobic environment microbial degradation of polymers via de-polymerisation will occur. The initial degradation is mediated by de-polymerases which break down the long polymer into oligo-, di- and monomers (Gu 2003 and references therein). The closer to a natural polymer the structure of the plastic polymer it is, the easier the microbial degradation proceeds. The aerobic degradation end products are carbon dioxide and water. Microbial degradation of plastic polymers occurs in anaerobic environments as well. The degradation products in anaerobic processes are organic acids, carbon dioxide, methane and water (Gu 2003 and references therein).

Ion-exchange resins (BTF, BMA, silo and little in BLA). Most of the ion-exchange resins are stored in the BTF and about 1% is stored in the BMA and silo. The ion-exchangers used in nuclear power plants are usually strongly acidic with styrene resin. One type of ion-exchange is Amberlite IR-120 which is a strong acidic ion-exchanger with sulphonic acid groups on a styrene resin (Pettersson and Elert 2001). Styrene (vinyl-benzene) is a polymer and it is a natural component in plants. It is aerobically degradable by different types of bacteria (Omori et al. 1974, 1975, Sielicki et al. 1978, Shirai and Hisatsuka 1979, Grbić-Galić et al. 1990). It has also been shown to be degraded by an anaerobic consortium of microorganisms (Grbić-Galić et al. 1990).

Insulation (BLA). Glass-wool and mineral-wool are examples of insulation materials that are deposited in SFR. During the production of the insulations phenol-plastic (Bakelite) is used as binding agent. From this addition phenol and formaldehyde is produced into the insulation products. These compounds are organics that can be degraded by microorganisms both aerobically and anaerobically (Flyvbjerg et al. 1993).

Metals (BMA, silo, BTF, BRT, BLA). Anaerobic corrosion of iron/steel will end up with solid iron oxides/hydroxides and hydrogen gas (see Section 3.5.9). The oxidised iron is a possible electron acceptor in the anaerobic respiration performed by iron-reducing bacteria. These bacteria are mostly heterotrophs and use organic acids as carbon and electron source but some can use H_2 with CO_2 as energy and carbon source respectively. There are no known microbial processes where aluminium is involved. Aluminium can corrode anaerobically and H_2 can be produced in this process. The H_2 is an excellent energy source for many microorganisms such as methanogens, acetogens and SRB (Pedersen 2012a, b).

Natural analogues/observations from nature

Cellulose degradation. *Alkaline conditions analogue:* Microbes capable of degrading ISA under alkaline conditions have been extracted from alkaline lakes in Africa (Greenfield et al. 1995). However, while these studies indicate that such metabolising bacteria exist, no information is available for repository-relevant alkaline environments. Work has been carried out on microbes at the Maqarin site in Jordan (e.g. West et al. 1995, Pedersen et al. 2004) but no ISA metabolisers were identified, although the researchers noted that the methods utilised were not optimal for being used in alkaline environments and that their results, should not be taken as definite proof. However, cellulose is only present in 1BLA, where near neutral pH conditions are expected.

Bitumen degradation. Natural bitumen can be degraded by microorganisms as revealed when the composition of the bitumen is analysed during the degradation process. Mass-chromatograms of bitumen from natural bitumen fields in the northeast of the Siberian Platform, showed that the amount of n-alkanes were drastically reduced and most terpanes were a homologous series of 25-norhopanes, which is evidence for intense bacterial degradation of the hydrocarbon pool (Kashirtsev et al. 2010). Degradation of bitumen then appears to be relevant in the presence of water. Another example of microbial degradation of crude oil is that in the Saskatchewan oil fileds (Bailey et al. 1973), where samples ranging progressively from non-degraded to highly-degraded could be clearly related to the influx of microbe-bearing surface waters. The above examples have environments that are very different from the conditions we have in SFR. However, it has been noted by several authors that the degradation of bitumens is very slow under anaerobic conditions (Mayberry et al. 1993, Pedersen 2001, JAEA 2007).

Fermentation. Fermentation processes occur in environments and systems where there are large amounts of organic material but low supply of compounds that can act as electron acceptors. Examples of such systems are composts and municipal waste sites. Inorganic acids can be nitric acid, nitrous acid and sulphuric acid. Nitric acid is produced by ammonium and nitrous oxide oxidising bacteria. Sulphuric acid is produced by oxidation of hydrogen sulphide by sulphide-oxidising bacteria. The oxidation can be both aerobic and anaerobic with nitrate. Little or negligible microbial activity is expected in 2–5BLA, BRT and BTF as long as pH remain above 12.5.

Alkaline environments. The alkaline, high-Ca^{2+} springs of Maqarin, Jordan have been studied as an analogue for various microbial processes at high pH generated by cement and concrete (Coombs et al. 1998, Pedersen et al. 2004). Leaching of natural cement clinker in Maqarin has produced current, hyper-alkaline water with a maximum pH of 12.9. The study demonstrated that both aerobic and anaerobic microorganisms from the alkaline water could be cultured at low but significant numbers. Uptake studies with radioactively labelled compounds confirmed that the microorganisms were active in the alkaline environment but slow growth, low numbers and a generally low metabolic activity were found. The low total numbers of unattached cells relative to Fennoscanian Shield water and the absence of attached cell growth suggest that the microorganisms found in the investigated alkaline waters are inactive, though not necessarily dead (Pedersen et al. 2004). Alkaline environments hosting living extremophilic microbes such as *Alkaliphilus transvaalensis* have been found in South African goldmines (growth range pH 8.5–12.5) (Takai et al. 2001). Lee et al. (2002) described an alkaliphilic bacterium *Paenibacillus daejeonensis* sp. nov.isolated from a soil in Korea able to grow at as high pH as 13. It must be kept in mind that, even if microbes are able to grow at extreme pH, it does not mean that they thrive or grow well. Most alkaliphiles have their optimal growth pH in the range 8–10.

Time perspective

The rate of non-alkaline degradation of cellulose will be strongly affected by the presence of enzymes from microbes able to catalyse the hydrolysis of the internal bonds of the molecule. The hydrolysis rate is much faster when it is microbially mediated.

In addition, the chemical compounds surrounding cellulose, for example lignin in wood, limit the diffusion of enzymes into reactive sites and play an important role in determining the rate of hydrolysis.

The time scale or time scales on which microbial processes occur is related to the amount of available nutrients and energy sources in the system, but in order to understand this in detail more research is needed.

Handling in the safety assessment SR-PSU

From the safety assessment perspective the effect of microbial processes on repository function is neglected. Gas generation due to microbal processes are estimated in Moreno et al. (2001).

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The potential for the mobilisation of radionuclides from repository environments such as SFR by bacterially produced ligands is considered neglibable as the production of microbial ligands often lies in the nanomolar range (Bi et al. 2010). This process is neglected in SR-PSU as other chelators are assumed to dominate (see Section 3.5.3 and Section 3.5.6). Microbial ligands may only be relevant if the barrier fails and for 1BLA, where there are no barriers. If some nuclides are mobilised, they will be so diluted that high concentration plumes will not occur. In other words, this will have no effect from a safety perspective.

Microbial degradation of the bitumen waste form in SFR is possible. The degradation rates may not be high but there will certainly be changes in the composition of the bitumen after thousands of years because of microbial activity. Within the safety analysis it is assumed that bitumen does not retain any of the radionuclides. The effect from high pH is suggested to mitigate microbial processes in all repository parts where concrete is highly abundant in all repository parts except in 1BLA where pH will be close to neutral. However, several investigations suggest that pH will decrease to about 12.5 (Cronstrand 2007) in all repository parts where concrete is highly abundant. How long this will take can only be estimated by models. The longer the pH remains above 12.5, the more reduced the inventory of radionuclides will be before microbial activities will be significant. Even if there are microbes found growing at such extreme conditions as pH > 12.5 (Takai et al. 2001, Lee et al. 2002) and within cement monoliths (Gorbunova and Barinov 2012), it should be remembered that most alkaliphilic microbes have their optimum pH in the pH interval 8–10 (Yumoto 2007) and have reduced activity above this pH.

Experiments cited in Pedersen (2001) indicate that microbial gas formation due to degradation of organic materials under conditions expected to prevail in SFR after closure is initially fast but decreases after the initial phase. Gas formation in SFR could be limited by the supply of oxidants and nutrients and the removal of reaction products. Under alkaline pH, the microbial activity will be slow (Pedersen et al. 2004) or not occur at all, so no or little gas will be generated from microbial processes. Far more gas will be produced from corrosion of metals in all repository parts where concrete is highly abundant, i.e. in all parts except 1BLA. Because of microbial activity in 1BLA gas will be produced, but it will probably seep out and therefore never build up a pressure inside the container.

Methanogenes are in general out-competed if other electron acceptors, such as oxygen, and thereafter nitrate, Mn(IV), Fe(III), sulphate and sulphur are present. In other words when the electron acceptors from oxygen down to sulphur are available methanogenesis is suppressed. Thus production of methane is not expected to occur to large extent or even at all until the pool of other electron acceptors than CO_2 is emptied. However if acetate is used as substrate the total gas volume will increase. This could, in a simplified way, be expressed as:

Acetate + electronacceptor (Fe^{3+} or SO_4^{2-} + H_2) = reduced species (Fe^{2+} or H_2S) + CO_2

Autotrophic acetogens use H_2 and CO_2 to form acetate, thus gas is consumed.

When it comes to the degradation of plastic and polymers, questions regarding rates of aerobic as well as anaerobic degradation and how fast degradation products are formed that potentially could be used as a carbon source for microbes still remain. This is something that could be included in the next R&D program for Safety assessment.

Model simplification uncertainty

Since there is so little relevant microbial data at this stage, it is not possible to develop a meaningful model where microbial processes are taken into account.

Input data and data uncertainty

Is unimportant in all repository parts where concrete is highly abundant except in 1BLA, where it is neglected. Not considered to be a radiological risk.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU. All supporting references are either peer-reviewed articles or documents which have undergone factual review.

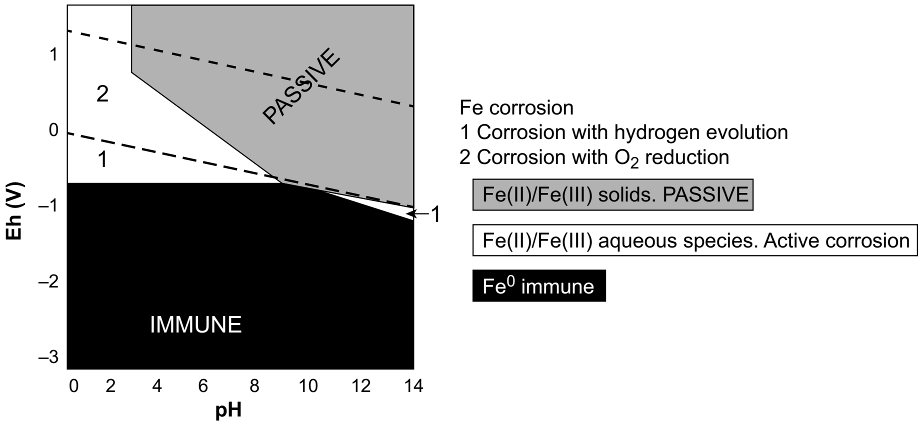
3.5.9 Metal corrosion

A significant portion of the waste volume in SFR 1 consists of metals, mainly carbon steel and stainless steel. Around 10^4 tonnes of iron/steel and almost 10^2 tonnes of aluminium/zinc will be present in the waste and packaging (SKB 2008b). There will be even more metal in the extension of SFR (SKB 2013a).

Overview/general description of the process

Pourbaix diagrams are commonly used to show the range of conditions under which a metal corrodes. Figure 3-6 shows Pourbaix diagrams for iron and aluminium, two metals of interest in SFR from the perspective of corrosion. The zones labelled “immune” show the conditions under which the zerovalent metal is stable and thus will not corrode. Zones labelled “passive” indicate conditions favourable for the formation of solid oxides or hydroxides of the metal, since the formation of a protective layer passivates the surface. Dashed lines bound the stability field of water. Within the stability field of water, metal corrosion involves reaction with oxygen (Zone 2), while below the stability field of water, metal corrosion involves redox reactions with water, generating hydrogen (Zone 1).

In some cases, passivation is disrupted by localised corrosion. Examples include pitting corrosion, scratches on the protective surface layer, or the development of fractures in the surface layer, all of which can expose the bare metal surface to corrosive conditions.



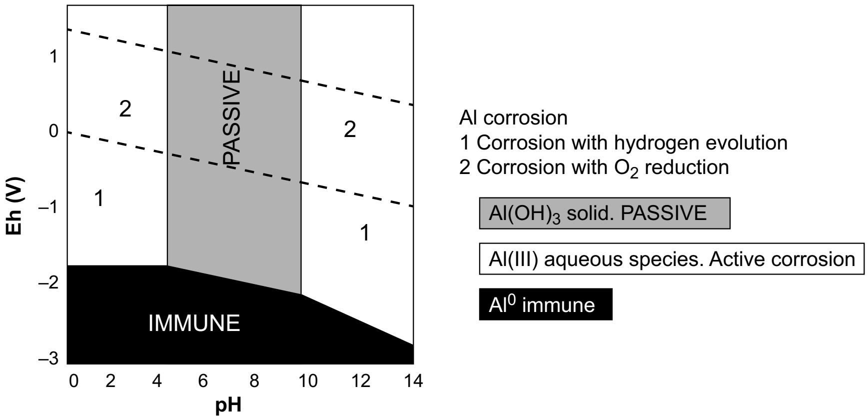


Figure 3-6. *Pourbaix diagrams of iron and aluminium showing the zones for corrosion, passivation and immunity of the metals. The diagrams have been calculated for a concentration of the metal of* 10^{-5} *M.*

Although the oxidation of these metals by water is thermodynamically favoured, the reactions are kinetically controlled, with many factors affecting their progress.

The existing Fenno-Skan cable (underwater cable between Sweden and Finland) or equivalent future equipment generates earth currents that may lead to galvanic corrosion and thereby influence corrosion rates.

Aerobic corrosion

Oxygen will be available during the repository operational period and aerobic corrosion of the metals will occur. From the estimations of the amount of metal and initial oxygen trapped in the repository, it is assumed that all oxygen will have been consumed shortly after repository closure.

Under aerobic conditions, oxygen is the main oxidant in metal corrosion. The two generic reduction and oxidation processes are shown in the two following half-reactions:

Reduction (cathodic reaction):

$O_2 + 2\ H_2O + 4\ e^- = 4\ OH^-$

Oxidation (anodic reaction):

$M = M^{n+} + n\ e^-$

The overall reaction therefore involves hydrolysis with precipitation of oxy-hydroxides as the metal corrosion products. Under the hyperalkaline conditions of interest in SFR, precipitation will be especially favoured. For iron, the half reactions are:

$Fe^0 + 3\ OH^- = Fe(OH)_3(s) + 3\ e^-$

$O_2 + 2\ H_2O + 4\ e^- = 4\ OH^-$

Resulting in the following overall redox reaction:

$4\ Fe^0 + 3\ O_2 + 6\ H_2O = 4\ Fe(OH)_3(s)$

When aluminium is exposed to air, an oxide layer forms that provides protection against further corrosion. The same is true for zinc. Nevertheless, under alkaline conditions, the dissolution of the oxide layers can reactivate the metal surfaces. The reactions for Al and Zn would be:

Oxidation	Reduction	Overall redox	Redissolution at high pH
$Al^0 + 3OH^- \rightarrow Al(OH)_3(s) + 3e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$4Al^0 + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3(s)$	$Al(OH)_3(s) + OH^- \rightleftharpoons Al(OH)_4^-$
$Zn^0 + 2OH^- \rightarrow Zn(OH)_2(s) + 2e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$2Zn^0 + O_2 + 4H_2O \rightarrow 2Zn(OH)_2(s)$	$Zn(OH)_2(s) + OH^- \rightleftharpoons Zn(OH)_4^-$

–Although oxygen is a strong oxidant, other species such as sulphate or chloride can also enhance the corrosion of metals, depending on the environmental conditions.

Anaerobic corrosion

Once oxygen has been exhausted, metals present in the repository will corrode anaerobically, with water as the main oxidant. The presence of microorganisms can also favour corrosion through sulphate and carbonate reduction. In this case, hydrogen sulphide and/or methane could be formed as products of the reduction of sulphate and carbonate. The presence of microorganisms in the repository is discussed in Section 3.5.8.

Most transition metals, such as Fe, are thermodynamically unstable in the presence of water, so their oxidation (corrosion) is expected to occur in the presence of air moisture. The half reaction for the reduction of water is:

$2\ H_2O + 2\ e^- = H_2(g) + 2\ OH^-$

Although gaseous hydrogen is written, the formation of a gaseous phase depends on the activity of hydrogen generated, the overall pressure of the system and the ability of dissolved hydrogen to diffuse out of the confined system, among other parameters.

The corrosion of iron by water under anaerobic conditions produces hydrogen and iron(II) hydroxide, according to the following reaction:

$Fe(s) + 2\ H_2O = Fe(OH)_2(s) + H_2(g)$

$Fe(OH)_2(s)$ is metastable and with time it evolves towards the formation of a spinel-like structure oxide. The composition of the oxide formed on the surface of iron is not known exactly, although it has been suggested that it consists of $Fe_{3-x}O_4$ varying in composition from Fe_3O_4 (magnetite), in oxygen-free solutions, to $Fe_{2.67}O_4$ in the presence of oxygen (Stumm and Morgan 1996, p 1022). The reaction is exemplified by magnetite, in the Schikorr reaction:

$3\ Fe(OH)_2(s) = Fe_3O_4 + H_2 + 2\ H_2O$

The global redox reaction for the transformation of iron into magnetite under anaerobic conditions can then be written as follows:

$3\ Fe(s) + 4\ H_2O = Fe_3O_4(s) + 4\ H_2(g)$

Anaerobic steel corrosion in alkaline environments proceeds at a much slower rate than under pH neutral conditions (Grauer 1988).

Iron/steel corrosion can also occur in the presence of carbonates and sulphides. In this case, the corrosion products may change from magnetite to iron sulphides and/or carbonates (siderite) and, in the presence of chloride, other phases such as green rusts may form.

Aluminium corrodes under anaerobic conditions, generating hydrogen gas as follows:

$2\ Al(s) + 3\ H_2O = Al_2O_3(s) + 3\ H_2(g)$

This results in the formation of a highly protective passivating layer that prevents further oxidation. However, an increase in pH to alkaline conditions dissolves this oxide layer thus exposing the bare metal. Corrosion under alkaline conditions produces soluble aluminium hydroxide and hydrogen gas.

$2\ Al(s) + 2\ OH^- + 10\ H_2O = 2\ [Al(OH)_4 \cdot 2H_2O]^- + 3\ H_2(g)$

The aluminium hydroxide product is soluble under alkaline conditions, promoting on-going corrosion. Since alkaline conditions are expected in most of SFR, aluminium metal is expected to corrode rapidly.

Zinc corrodes anoxically through the formation of Zn hydroxides:

$Zn(s) + 2\ H_2O = Zn(OH)_2(s) + H_2(g)$

Zinc hydroxide dissolves under alkaline conditions, again promoting corrosion.

Volume changes

In the presence of cementitious materials, metal corrosion products are less dense than the metal and hence occupy more space. This can create mechanical stresses and produce fractures, thus enhancing the contact between water and the wastes. A plot of the relative molar volume of the different corrosion products formed under aerobic/oxic (OX) and anaerobic/anoxic (AN) conditions is presented in Figure 3-7. This allows the increase in the volume of the system and/or the stress generation to be calculated.

Dependencies between process and waste form variables

The direct dependencies between metal corrosion and the defined waste form variables (defined in Section 2.1.2) are summarised in Table 3-19 and some comments are given in the text below.

Geometry. The geometry can affect corrosion processes. The pore characteristics will influence the contact between the water and metallic parts.

Radiation intensity. Radiation intensity only has an indirect effect on metal corrosion in the waste. Radiolysis may produce reactive species that affect the corrosion rates and corrosion products. However, this effect has only been demonstrated using dose rates expected in high level wastes.

Temperature. Temperature affects corrosion rates and the type of corrosion products formed. However, the temperature within SFR is only expected to vary by a few degrees prior to glaciation. Therefore, this effect can be neglected. Aluminium corrosion is an exothermic process, although it is estimated not to produce any relevant temperature increase on the overall temperature of the vaults

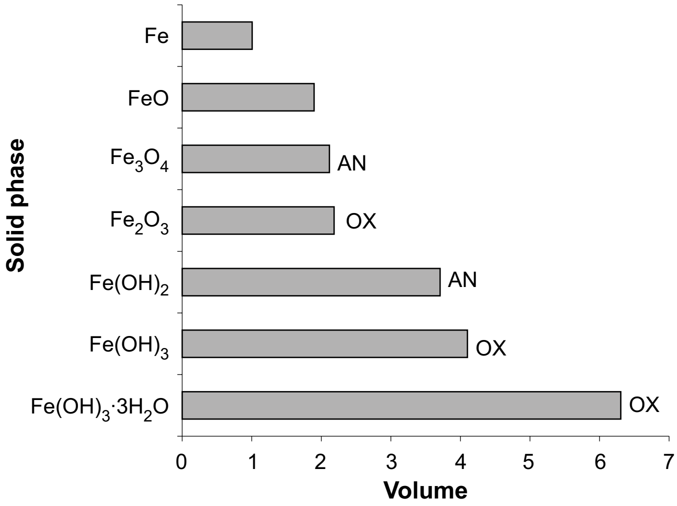


Figure 3-7. *Relative molar volume for different iron solid phases. AN: most likely formed from corrosion under anoxic conditions; OX: most likely formed under oxic conditions.*

Table 3-19. Dependencies between the process "Metal corrosion" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry and pore space will affect water access to the metal components.	Not considered explicitly. Incorporated within the uncertainties associated with the corrosion rates.	No. Indirectly formation of secondary products may affect the pore space and create fractures.	Not relevant.
Radiation intensity	No. There is only an indirect effect since radiolysis generates aggressive oxidants and/or radicals that affect corrosion.	Not relevant.	No.	Not relevant.
Temperature	Yes. Temperature affects corrosion rates and products.	Not considered due to the narrow temperature range expected. Uncertainties associated with the corrosion rates include the possible variations due to temperature.	Corrosion of aluminium can increase the temperature.	Not considered. Thermal effect due to aluminium oxidation predicted to be low, see Section 3.1.2.
Hydrological variables	Yes. Saturation degree affects metal corrosion.	The system is assumed to be saturated instantaneously.	No. Indirectly via geometry.	Not relevant.
Mechanical stresses	No.Indirectly via geometry, since mechanical stresses can create new pathways enhancing water flow to metals.	Not relevant.	Yes. Formation of corrosion products with different molar volumes may create mechanical stress.	Considered in the selection of hydraulic conductivity see Section 3.4.1.
Radionuclide inventory	No. Only indirectly, see radiation intensity.	Not relevant.	No.	Not relevant.
Material composition	Yes. The composition of the material determines the corrosion rates and products.	The range of corrosion rates used include different material composition.	Yes. The composition of the material will change due to the formation of corrosion products.	Considered in the redox modelling.
Water composition	Yes. Water composition can affect corrosion rates and products.	Not specifically handled. Included in the range of corrosion rates considered.	Yes. Corrosion will create more reducing conditions.	Considered in the Redox modelling.
Gas variables	No. Indirectly, affecting rates and corrosion products.	Not relevant.	Yes. Corrosion under anaerobic conditions will cause hydrogen build-up.	The gas production is treated in Section 3.5.10.

Hydrological variables. Hydrological variables only have an indirect effect on the corrosion of metals in the waste. The flow and degree of saturation will affect corrosion in terms of the flux of water and other chemical species that can influence corrosion in and out of the system.

Mechanical stresses. Mechanical stresses only influence metal corrosion in the wastes indirectly via fracturing, generating new water pathways and changing the metallic surface area exposed to water.

Radionuclide inventory. The radionuclide inventory only influences corrosion indirectly, via radiolysis (see Radiation intensity).

Material composition. The type of metals present in the repository will affect the rate and extent of the corrosion process. This uncertainty is included in the range of corrosion rates considered.

Water composition. The water composition will affect the corrosion process, specifically the rate and the products formed. The presence of high concentrations of Cl^- favours localised corrosion under oxidising conditions. The presence of dissolved carbon dioxide increases the corrosion rate of iron in water by decreasing the pH of the water. The presence of complexing agents in the porewater may affect corrosion through the dissolution of protective corrosion product layers on the metal surfaces. The presence of alkaline conditions may cause depassivation of metallic surfaces. The corrosion processes will generate more reducing conditions. This effect is accounted for by geochemical modelling.

Gas variables. The gas composition will indirectly affect the corrosion rate and the type of secondary products formed, via the groundwater composition. Corrosion processes, on their part, can generate gases (see Section 3.5.10).

Boundary conditions

The boundary conditions are the initial oxygen content of the repository, the ingress of water, the conditions associated with water flow and the groundwater composition.

Model studies/experimental studies

There is a wide body of literature on the corrosion of steels, although the majority of data have been obtained under non-alkaline conditions.

The studies presented here are organised according to the following:

- Corrosion rates and related factors.
- Corrosion products.

Corrosion rates and related factors

Corrosion rates are highly dependent on the type of steel and the environmental conditions.

A high pH usually decreases the rate of corrosion of steels, which is attributed to the low solubility of iron corrosion products at high pH. However, this trend is reversed at pH values sufficiently high to support the formation of soluble hydrolysed species, as this dissolves the protective corrosion product surface layer. Experiments running for 60 days under anaerobic, alkaline conditions (Fujiwara et al. 2001) showed that pH values close to 14 increased the corrosion rate due to the formation of soluble $HFeO_2^-$ species.

During the COBECOMA project (Kursten et al. 2004) corrosion rates of different steels were measured under alkaline conditions. Hydrogen overpressures of 1 to 100 atm did not alter the anaerobic corrosion rate of carbon steel discernibly under anoxic, alkaline conditions. Kursten et al. (2004) report that the critical chloride concentration for the initiation of pitting corrosion of carbon steel in cement was around 6,000 to 28,000 mg/dm^3 (0.2 to 0.8 mole/dm^3) at room temperature. Increasing the temperatures to around 80°C decreased the critical chloride concentration to between 4,000 (0.11 mole/dm^3) and 300 mg/dm^3 (8×10^{-3} mole/dm^3). According to these results, the main factor limiting the propagation of pitting corrosion was the ability of the cementitious matrix to immobilise chloride ions.

For stainless steels, the corrosion rates determined in anaerobic, alkaline media varied from 0.001 to 0.4 μm/y. Under aerobic conditions, the rates varied between 0.03 and 0.5 μm/y. All the stainless steel samples tested were resistant to pitting corrosion up to 100,000 mg/dm^3 of chloride (2.8 mole/dm^3) at room temperature, and up to 50,000 mg/dm^3 (1.4 mole/dm^3) at 45 and 70°C. The likelihood of stress corrosion fracturing of stainless steel was judged to be very low from the experimental results obtained (Kursten et al. 2004).

In the review conducted by Smart (2010) it is indicated that pitting corrosion of stainless steel is not relevant until the ratio Cl^- to OH^- exceeds a value of 14. Data suggests that the resistance to localised corrosion is high for cements with chloride concentrations below 5%.

Aluminium is highly reactive under alkaline conditions, with rates of corrosion over 100 μm/y, according to the measurements by Volckaert and Mallants (1999).

Corrosion rates and their uncertainties are discussed in detail in the Data report (SKB 2014c).

Corrosion products

Carbon steel and stainless steel were exposed to cementitious, anaerobic conditions for 2 years and then the corrosion products were characterised by Laser Raman Spectroscopy. The black film that formed on the surface of carbon steel was identified as magnetite. However, the corrosion product layer on the surface of the stainless steel was too thin to identify (Kursten et al. 2004 and references therein).

Setiadi et al. (2004) observed the expansion and fracturing of ordinary portland cement after a few hours contact with aluminium, due to the formation of aluminium hydroxide phases. After some weeks, cement expansion decreased.

Green rusts can form when steel corrodes in the presence of certain groundwater ions. The term green rust (GR) refers to a series of compounds that belong to the layered double hydroxide (LDH) family. The green rust compounds are composed of positively charged brucite-like layers of Fe(II)–Fe(III) hydroxide that alternate with interlayers of water molecules and anions, such as SO_4^{2-}, CO_3^{2-} and Cl^-. GR is stable at pH above 6 and may form naturally at iron redox boundaries, but destabilises at very high pH and under oxidising conditions (Skovbjerg et al. 2006, Christiansen et al. 2009).

In general, the long-term corrosion product formed under anoxic conditions is a spinel-type solid, exemplified by magnetite (Fe_3O_4), and under oxic conditions goethite (α-FeOOH) forms.

Natural analogues/observation from nature

Natural analogues for the corrosion of iron materials are available in the literature. A short review of these can be found in the SR-Site fuel and canister process report (SKB 2010b).

Data from archaeological analogues compare well with those from short-term laboratory experiments under anaerobic conditions. Johnson and Francis (1980) presented data on more than forty iron archaeological objects and estimated corrosion rates between 0.1 and 10 µm per year, similar to the values derived from experiments. It is more difficult to find natural analogues for metallic corrosion under alkaline conditions. There are some analogues for cementitious environments, such as Maqarin in Jordan, although there are not many data for relevant metals in the site that can be used to support the selection of corrosion rates.

Both Nagra and JAEA have directly compared laboratory data with natural analogues for iron corrosion and used these data to provide boundary conditions in the Kristallin-1, H12 and H17 SA (see Table 3-20).

Time perspective

Aerobic corrosion will occur during the initial stages of the repository due to the trapped oxygen. It has been estimated that the trapped oxygen will be consumed within a few years after saturation of the repository system (Duro et al. 2012c).

Therefore, anaerobic corrosion will probably be the most relevant process by which metals will corrode in the repository, as has been discussed previously. The rate of anaerobic corrosion will probably decrease over the life of the repository as protective layers form on the metals.

Table 3-20. Comparsion between laboratory data and data from natural analogues for iron corrosion.

Form of data	Corrosion depth (per 1,000a)	Reference	Comments
Short-term lab	31.8 mm	JNC (2000)	Uniform corrosion of carbon steel. Base Case value
Short-term lab	29 mm	NWGCT (1984)	Conservative corrosion rate, including an allowance for pitting. Base Case value
Natural analogue	0.09×10^{-3} mm	Hellmuth (1991)	Weathering of native iron in basalt (Disko Island). These are very low values which may reflect the site complexity. See discussion in Hellmuth (1991) and Miller et al. (2000).
Archaeological analogue	10 mm	Range of studies cited in Nagra (1994)	Uniform corrosion of iron and steel
Archaeological analogue	< 15 mm	Range of studies cited in JNC (2000)	Uniform corrosion of iron and steel
Archaeological analogue	0.1–10	David (2001)	Literature review of archaeological samples
Archaeological analogue	< 10 mm	Range of studies cited in JNC (2005)	Uniform corrosion of iron and steel

Handling in the safety assessment SR-PSU

Formation of fractures due to production of less dense corrosion products are considered in the selection of hydraulic conductivities.

Corrosion of metal waste, as well as other metals in the repository, is considered in terms of its role in establishing reducing conditions.

The process of metal corrosion is considered to be one of the main gas producing processes in the repository. The handling of gas production due to corrosion is described in Section 3.5.10.

No credit is given to corrosion products in terms of potential radionuclide retardation see Section 3.5.3.

Handling of uncertainties in the safety assessment SR-PSU

The handling of uncertainties is focused on the modelling of the development of the redox conditions, reported in Duro et al. (2012c), which is largely dependant on metal corrosion modelling.

Uncertainties in mechanistic understanding

The uncertainties in the mechanistic understanding of metal corrosion mainly reflect the corrosion rates and the corrosion products formed, which are directly related to the amount of gas generated.

Model simplification uncertainty

The model of the development of the redox conditions is based on metal corrosion processes to a large extent. The main uncertainties resulting from the model simplifications are detailed below:

- The water saturation of the system is considered instantaneous, therefore the system is always considered to be completely saturated.
- Initially, the porewater of the wastes is considered to be in equilibrium with atmospheric oxygen and oxic corrosion is assumed to be instantaneous, rather than kinetically controlled.
- The corrosion products considered are goethite, when oxygen is present, and magnetite when the steel corrodes under anoxic conditions.
- In the model, there is always sufficient water as to allow anoxic corrosion of steel.
- Mechanical changes are not considered to affect the integrity of the system, in this context this means that the surface characteristics of the metallic wastes are not considered to change.
- Temperature is considered to be constant at 25°C, since including temperature variations would introduce further uncertainties and the actual variations are bound by probabilistic analyses of the corrosion rate.
- Steel is considered to be homogeneous, with no difference in the composition of different steels.
- Under anoxic conditions, steel is considered to corrode at a constant rate over time.
- Pitting corrosion is not explicitly considered.
- Al and Zn corrosion has not been considered in the numerical model. This results in an underestimation of the reducing capacity of the system, thus producing conservative estimations of the evolution of the redox state of the repository.
- In the numerical model, corrosion of metal components has been assumed to occur under the alkaline conditions imposed by equilibrium with portlandite. This simplifies the concrete degradation process in SFR and resultant pH conditions, introducing uncertainties for metal corrosion. These uncertainties have been bound through a probabilistic analysis on the corrosion rates.

Input data and data uncertainty

The main data uncertainties correspond to the corrosion rates of the metals present in the repository. These uncertainties are bound through sensitivity analyses.

The uncertainties associated with the corrosion rates affect the estimations of the reducing capacity of the system, which removes oxidant intrusions to the system. This, and other related issues, are explained and developed in detail in Duro et al. (2012c) and references therein.

Other uncertainties arise indirectly from several other data:

- Uncertainties in the temperature over time are not important due to the narrow temperature range considered at SFR.
- Uncertainties in the salinity, mainly chloride, and microbial activity, which are able to enhance localised corrosion and thus increase the corrosion rate, are not expected to be very important due to the low tendency of steels to undergo localised corrosion under anoxic alkaline conditions. However, this is relevant for oxic events.
- The amount of surface area exposed to corrosive fluids introduces important uncertainties. From the perspective of the modelling, this has been bound with the help of sensitivity analyses on the corrosion rate.
- The type and amount of metals also introduces important uncertainties. Carbon and stainless steel have different corrosion rates. This uncertainty is also bound by sensitivity analyses also on the corrosion rate.
- Uncertainties in the composition of the water in contact with the metallic wastes highlight the relevance of scenario definition.
- Uncertainties in the groundwater flow expected in the repository will affect the mass balance of oxidants intruding into the repository and, therefore, can have an influence on the extent of metal corrosion.
- Uncertainties in the corrosion products formed are important and are likely to be overcome through different model approximations.

Most of the waste foreseen to be disposed in SFR has not yet been produced. The prognosis of the amounts of metal waste in the repository used in the model is therefore an important source of uncertainty.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.5.10 Gas formation and transport

Overview/general description

Gas can be formed in SFR wastes through several (bio)chemical processes. The most relevant ones are:

- Metal corrosion.
- Microbial degradation of organic materials.
- Radiolysis.

The gas generated can also be transported out from the waste form through a variety of processes, such as:

- Gas diffusion.
- Diffusion and advection as dissolved gas.
- Two-phase flow.
- Gas advection through preferential fractures open in the waste form.

A short description of these processes follows.

Gas formation

Gas formation through metal corrosion

After repository closure, trapped oxygen is rapidly consumed. Hydrogen gas can then form due to anaerobic metal corrosion. The main metals present in the repository are the iron-based steel present both in the waste and in the packaging materials, and aluminium and zinc in the waste.

The reactions exemplifying anaerobic corrosion of these metals with gas generation are as follows:

$3\ Fe(s) + 4\ H_2O = Fe_3O_4(s) + 4\ H_2(g)$

$2\ Al(s) + 3\ H_2O = Al_2O_3(s) + 3\ H_2(g)$

$Zn(s) + 2\ H_2O = Zn(OH)_2(s) + H_2(g)$

A detailed discussion on corrosion processes and their impact on gas formation is given in Section 3.5.9.

Gas formation through microbial degradation of organic materials

Organic materials present in the waste can be degraded by microbial activity. Although the expected pH conditions are highly alkaline due to the presence of cementitious materials in most of SFR, microbes are known to be adaptable and this process cannot be ruled out. There are different estimations of the rate of microbial gas production in a repository, although the uncertainties are large due to, among other factors, the heterogeneity of the wastes, the different type of microbial communities that can be present and the lack of data on the rate of degradation of some organic substrates present in the wastes.

According to Section 3.5.8, non-conditioned waste has the greatest potential for microbial degradation due to the high organic carbon concentrations and the possibly lower pH values than in cementitious wastes.

Organic material in SFR can be divided into two groups regarding potential gas generation:

- Cellulose-based materials with a large surface to volume ratio.
- Other organic materials (including ion exchange resins, plastic, rubber, bitumen, etc) that have a low surface to volume ratio and higher chemical stability against degradation, and thus lower potential for gas generation.

Degradation of organic materials is expected to produce hydrogen, methane, and CO_2 as gaseous products.

Cellulose hydrolyses to glucose under near-neutral pH conditions, which in the presence of microbes and oxygen can degrade to CO_2, and in the absence of oxygen forms alcohols, ketones, carboxylic acids, CO_2 and H_2.

The effect of microbes on the system is further described in Section 3.5.8.

Gas formation due to radiolysis

Radiation from the waste may cause water radiolysis, which leads to the formation of hydrogen and oxygen gases. Water radiolysis is described as a separate process in Section 3.1.4. Radiation causees radiolysis of organic material which may lead to the formation of small amounts of gases, see Section 3.1.3.

The alpha field is presumably too low in SFR as to be of any relevance for hydrogen production. Therefore only gamma radiation (low Linear Energy Transfer and thus long range) should be considered in terms of water radiolysis. Gas formation due to radiolysis will be much lower than that produced by anaerobic metal corrosion.

To summarise, the main gases generated in the repository will be hydrogen, carbon dioxide and methane.

- The main chemical influence of hydrogen will be to impose reducing conditions in the system. If tritium is present as part of the water molecule, incorporation into hydrogen gas can enhance its migration.
- Methane production is not thought to have any relevant chemical influence in the system, unless methylation of radionuclides occurs. If so, volatile species may form that can enhance radionuclide migration. Equally, the formation of gaseous $^{14}CO_2$ may, either enhance C-14 migration or reduce it through retention on the newly formed carbonates created by the carbonation of cement.
- The main chemical influence of CO_2 can be the carbonation of cementitious materials and a possible local decrease in the alkalinity of the system. Although carbonate complexation can enhance the mobility of some radionuclides, the high calcium concentrations arising from cement will favour carbonate precipitation as calcite. Migration of C-14 will also be of relevance. This is further described in Section 3.6.3.
- The generation of gases can create overpressures in the system and generate fractures that could affect the structural integrity of the repository. This has been acknowledged in the design of the repository, for example when closing the silo it is planned to include specific pipes for gas evacuation.

Gas transport

Gases generated in SFR will initially dissolve in the water according to their solubility equilibria (Henry's law). Dissolved gas can be transported across the waste form to the packaging through diffusion or advection processes. If the solubility of the gas is exceeded, bubbles can form and create a discrete gas phase. The formation of a differentiated gas phase can produce a two-phase flow gas migration. Enhanced pressure introduced by a trapped gas phase may expell water from the system, enhancing the migration of dissolved radionuclides and lowering the degree of saturation in the repository. The generation of a gas phase can also facilitate transport of gaseous radionuclides.

When the gas pressure exceeds the hydrostatic pressure to the extent that the gas is released from the system, preferential water pathways can be created. For solid materials, it has been proposed that a cycle of preferential path opening and closing occurs: the internal pressure increases until it overcomes the stress resistance of the material and a fracture forms, gas breaks through until the overpressure is reduced sufficiently for the fracture to close, and then the gas pressure builds again. Although this has been observed in several materials, including bentonite, closure of the generated fractures in cementitious materials has not been investigated so extensively. Wang et al. (2004) developed a model to calculate the rate of gas leakage through reinforced concrete shear walls and provide several references on studies of gas leakage rates through damaged concrete structures.

Gas transport through the porous material of the matrices will follow the same laws as gas transport through the backfill and engineering barriers of the repository.

Transport of gas will only occur after the gas pressure exceeds the local hydrostatic pressure. The rate of gas generation, which is directly related to the corrosion and organic degradation rates, clearly affects the rate at which gas pressure increases.

The possible formation of methane hydrate has been shown to be negligible due to the pressures needed for the formation, see the Geosphere process report (SKB 2014e).

Dependencies between process and waste form variables

The direct dependencies between the process and the defined waste form variables (defined in Section 2.1.2) are summarised in Table 3-21.

Geometry. Geometry affects gas transport and indirectly also gas formation processes. For example, corrosion is dependent on the available surface area and geometry also affects gas generation by determining the access of water to the metallic parts of the waste. The geometry will also affect the contact between water and organic materials of the waste, as well as radiolysis processes.

Table 3-21. Direct dependencies between the process "Gas formation and transport" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Gas formation is influenced, since the geometry may affect contact of water with the waste, and thus gas generation processes. Geometry also affect gas transport.	Geometry is included in the gas generation calculations. The waste form is assumed to offer negligible resistance to gas transport.	No. Indirectly via mechanical stresses.	Not relevant.
Radiation intensity	No. Indirectly via radiolysis. Gas transport is not affected by the variable.	Not relevant.	No.	Not relevant.
Temperature	Yes. Temperature affects gas solubilities.	Neglected due to the limited variations in temperature.	Yes.	Neglected. Gas formation is expected to have a negligible effect on temperature, see Section 3.2.1.
Hydrological variables	Yes. The formation of a separate gas phase depends on pressure and flows, and this affects gas transport.	Discussed conceptually and bounding cases are modelled.	No. indirectlyvia gas pressure see Section 3.3.2.	Not relevant.
Mechanical stresses	No. Indirectly, since stresses may create preferential paths (geometry) for water and thereby affect gas generation and transport processes.	Not relevant.	Yes. Mechanical stresses created through the generation of a separated gas phase.	See fracturing processes (Section 3.4.1).
Radionuclide inventory	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. The composition of the material determines the total amount of gas volume generated, as well as the rate at which it is generated. The gas transport is also affected by the material composition.	The material composition is used as input data for the gas generation. The waste form is assumed to offer negligible resistance to gas transport.	No.	Not relevant.
Water composition	Yes. Water composition can affect gas/liquid equilibria and indirectly gas formation rates.	Gas solubilities are accounted for in the modelling of the redox evolution of the repository.	Yes. The gas generated can dissolve in water and change the water composition.	Neglected in gas transport calculations. The formed gas is assumed to remain in the gas phase. Included in the modelling of the redox evolution.
Gas variables	Yes.	Incorporated in the gas/liquid equilibria. The waste form is assumed to offer negligible resistance to gas transport.	Yes.	Neglected in gas transport calculations. The formed gas is assumed to remain in the gas phase. Included in the modelling of the redox evolution. Amount of gas generated is calculated.

Radiation intensity. Radiation intensity can indirectly affect gas generation mainly through radiolysis of organic materials and water (see Section 3.1.3 and Section 3.1.4). These gas generation processes are, however, of minor relevance compared to metal corrosion. Gas generation is not considered to affect the intensity of the radiation.

Temperature. Temperature can affect gas solubility in groundwater and therefore the composition of gas in equilibrium with water and the point at which two phase flow starts. It can also indirectly affect the rates of gas generation through metal corrosion and degradation of organic materials. Temperature variations within the range expected in the repository are considered to be too minor to include in the assessment. Gas generation processes are not likely to influence the temperature of the waste. The influence of aluminium corrosion on temperature has been evaluated see Section 3.1.2.

Hydrological variables. Pressure and flows will affect the amount of water that eventually accesses the material, thus the gas generation rate. Due to the low amounts of water needed for gas build-up, this is not considered a limiting factor, and assessment backs up this assumption (Mallants and Jacques 2004). Hydrological variables will also affect the rate at which water is expelled from the system to allow gas migration. Therefore, this will affect the rate at which gas leaves the system and may also affect the rate of gas generation. Gas build-up in the system may create overpressures and indirectly generate new water/gas pathways.

Mechanical stresses. Stresses may create preferential paths for water and then indirectly affect gas generation processes. They will also affect gas migration out of the waste through preferential paths. Gas generation may indirectly via gas pressure build up and create mechanical stresses leading to fractures.

Radionuclide inventory. See Radiation intensity. Gas generation does not affect radionuclide inventory.

Material composition. The composition of the material determines the total volume of gas that can be generated, as well as the rate. The generation of CO_2 gas can indirectly affect the material composition, via water composition, due to carbonation of the cementitious materials in the matrix. The composition of the material can also influence the transport of gas out of the waste form.

Water composition. Water composition can affect gas/liquid equilibria and indirectly the rate and total amount of gas build-up and gas formation can affect water composition. For example, the generation of hydrogen may impose reducing conditions in the system and the generation of CO_2 may locally decrease the alkalinity of the system.

Gas variables. The composition of the gases will affect the process of gas transport and vice versa, through the displacement of gas/liquid equilibria and creating the necessary pressures for gas transport.

Boundary conditions

Boundary conditions defining the role of gas transport within the waste form are given by the pressures (heads) as well as the concentrations/gradients of gases within the waste. The pressure of gas needed to exceed its solubility in water, and the diffusive transport capacity is a boundary condition for gas transport. Temperature should also be defined in the boundary conditions given that it controls the physical state of system components as well as the pressure and water properties. The hydrostatic pressure is also a boundary condition for the generation of fractures and the possible expulsion of the gas generated.

Model studies/experimental studies

Gas generation in SFR has been modelled by Moreno et al. (2001) and the results were then recalculated and reported in SAR-08 (SKB 2008b), to reflect the updated waste inventory. The same hypothesis and assumptions were used in both calculations. The gas generation model considers the three gas sources previously described: metal corrosion, microbial degradation of organic matter and water radiolysis. Gas generation rates are based on rate of metal corrosion, rate of cellulose degradation and radiolysis (G-values). The calculations show that metal corrosion generates the most of the gas volumes in SFR. Given the low amount of water needed for gas generation through metal corrosion, water availability is not considered to be a limiting factor.

Duro et al. (2012c) developed a model for the assessment of the evolution of the redox conditions in the SFR, from which the amounts of gas produced can be estimated. The numerical model was implemented in the PHREEQC code. Gas phases were allowed to form once the gas fugacity exceeded the hydrostatic pressure, although gas transport was not dealt with specifically. The main contributors to gas generation were found to be organic matter degradation in the short term and metal corrosion in the medium to long term. However, aluminium corrosion is not included in the model and will contribute to a large extent to the gas formation in the short term. Hydrogen is the most abundant gas formed in the system (silo, 1-2BTF, BMA and BLA), while methane is mostly formed during the initial anaerobic stages of the repository, due to microbial degradation of organic materials. Wastes in the BLA are not conditioned in concrete, and the only concrete components of this vault are the concrete floor and the shotcrete lining of the walls and the roof. Therefore, the $CO_2(g)$ generated will not be removed through cement carbonation, and the volume of $CO_2(g)$ produced in BLA is likely to be higher than in the other vaults.

Other models applied by SERCO for the UK Nuclear Decommissioning Agency use the GAMMON code to calculate gas generation and TOUGH2 for the migration of gases (Rodwell et al. 2002). In these simulations, the CO_2 generated in the system was considered to react with the cementitious phases, so that no CO_2 evolution occurred, although as the authors highlight, this is an issue deserving further investigation.

Streatfield et al. (2006) used the MAGGAS model to assess gas formation in MAGNOX wastes. As at SFR, the main gas-producing process was considered to be metal corrosion, with smaller contributions from radiolysis and microbial degradation. The code consists of a set of excel spreadsheets where the processes and the corresponding parameters are implemented.

The 7th FP EC FORGE project started in 2010 to investigate the generation of gases in radioactive waste repositories. The findings of this project will be important for assessing the impact of gas formation (Norris et al. 2010), although most of the studies relate to high level nuclear waste repositories.

Ortiz et al. (2002) found experimentally that hydrogen produced by metal corrosion can be converted to methane by methanogenic bacteria, something which would decrease the volume of gas, according to:

$CO_2(aq) + 4\ H_2 = CH_4 + 2\ H_2O$

The formation of a gas phase can decrease the saturation degree of the waste form, which will affect the rate of gas generation. Mallants and Jacques (2004) compared the amount of water available in the near field of a repository with the assumed rate of hydrogen generation and they concluded that there was enough water in the system to sustain the assumed gas generation rate, in agreement with the assumptions in Moreno et al. (2001) and in the more recent Duro et al. (2012c).

Several models have estimated that 50 times more hydrogen will be produced than the sum of other gases in the UK ILLW repository (Rees and Rodwell 1988), which is consistent with the assumption that metal corrosion will be the most important gas generation process.

Gas generation rates in a deep (300–400 m depth) L/ILW repository in the Opalinus Clay of Northern Switzerland were calculated using the sum of the hydrogen gas produced by anaerobic metal corrosion and the methane produced by microbial degradation of organic waste components (Nagra 2008). All carbon dioxide was considered to be consumed in the carbonation of cementitious materials.

Norris et al. (2010) reviewed the different models used in performance assessment exercises to predict gas generation and transport. According to the review, there is a general lack of experimental data on gas transport through cementitious materials. Therefore, most of the predictions have large degrees of uncertainty.

According to the waste types defined for SFR, gas transport through the wastes must consider different materials: wastes conditioned with cement/mortar; wastes conditioned with bitumen and non-conditioned wastes. Several studies have investigated gas transport through concrete and mortars, but determining the gas permeabilities of these types of materials is challenging, as recognised in Loosveldt et al. (2002). Therefore, insufficient data are available to estimate the transport of gas through cementitious environments. Also, the evacuation of gases from the waste form will depend on the state of the waste containers and the backfill of the vaults, which are also concrete based in many cases.

Natural analogues/observation from nature

As mentioned in Miller et al. (2000), no natural analogues for gas generation have been studied. Although natural or anthropogenic analogues for metal corrosion processes can be found, as presented in Section 3.5.9, the associated gas generation is very difficult to quantify. The same is true for gas generation though organic degradation.

Overviews such as the one provided by Etiope and Martinelly (2002) can be useful in supporting gas transport through porous and fractured media.

Time perspective

Gases can be generated throughout the time of interest for the safety assessment (100,000 years in the SR-PSU).

The most relevant gas generating processes in SFR are anaerobic metallic corrosion, followed by degradation of organic materials and water radiolysis. According to the calculations in Duro et al. (2012c), the initial rate of gas generation is governed by microbial degradation of organic materials, while in the medium and long-term the generation of hydrogen due to anaerobic metal corrosion is the most important. Aluminium and zinc were not included in the model. Metallic aluminium and zinc will be the largest contributors to the gas generation at the initial stages, due to their much faster corrosion rates, around 100 times faster than those for steel. At the end of the assessment period, the volume of gases generated is estimated to exceed 1 million cubic meters (calculated at STP).

Microbial degradation of organic materials will be dominated by cellulose degradation during the first hundred years. Other more complex organic materials, such as ionic exchange resins and bitumen, will probably degrade more slowly.

The generation of gas by water radiolysis produces very small quantities of gas and the process will be important only during 20 years after saturation (SKB 2008b).

Handling in the safety assessment SR-PSU

The volume of gas generated is calculated in a similar way to previous assessments (Moreno et al. 2001) with the updated inventory (SKB 2013a) and updated data on corrosion rates see the Data report (SKB 2014c). More detailed information regarding gas generation is also obtained from the redox evolution model (Duro et al. 2012c)

Gas transport in the waste is not handled specifically. The wastes are only considered as a source of gas, which will be transported to the engineered barriers (see the Barrier process report (SKB 2014a)).

Handling of uncertainties in the safety assessment SR-PSU

The handling of uncertainties is focused on the updated calculations of gas volumes based on Moreno et al. (2001). The handling of the uncertainties in the redox evolution model (Duro et al. 2012c) is treated in Section 3.5.9 Metal corrosion.

Uncertainties in mechanistic understanding

As discussed, the three main sources of gas generation in SFR are microbial degradation of organic materials, anaerobic corrosion of metals and radiolysis. All uncertainties affecting the mechanistic understanding of these processes will therefore affect gas formation.

According to Norris et al. (2010), the assumption that equal quantities of CO_2 and CH_4 are produced during organic material degradation under anaerobic, methanogenic conditions, while production of other gases is negligible, might not be realistic. The percentage of CO_2 that will react with cementitious materials is not clear. The rates and amounts of microbially mediated gas generation from organic wastes are difficult to assess in current repository safety studies. This and many other safety assessments rely on simple bounding estimates of gas generation rates based on available experimental data to attempt to ensure that the rates used are upper limits.

The heterogeneity of the organic material deposited (or planned to be deposited) in SFR adds uncertainty to the understanding of the mechanisms responsible for gas generation. For example, the degradation processes of bitumen and ionic exchange resins are not well understood; the materials are normally considered to be very stable with low degradation rates.

The extreme conditions under which the material will degrade in the SFR, in terms of compaction and high pH values, may also affect the mechanisms of degradation. The most well-characterised process is the alkaline degradation of cellulose, where the uncertainties affect the data and parameters more than the mechanism.

The mechanism of anoxic metal corrosion, which is the dominant process in terms of gas generation in the repository, is fairly well known. Nevertheless, the existing uncertainties in the actual corrosion reactions taking place in the system, and the corrosion products formed, can affect the estimation of the amount of gas generated. The uncertainty on whether the bare metal surface is in contact with water, and the time taken for a layer of rust to form that makes this contact difficult, may be overcome through sensitivity analyses on the corrosion rate.

Uncertainties in the understanding of gas generation through water radiolysis are not expected to influence the general process, given the low contribution of this process to overall gas formation.

As recognised in the different performance assessment exercises, there is a lack of data and high uncertainty on gas migration processes through cementitious components.

Given that the initial stage of gas transport will involve diffusion and advection of dissolved gas, it is important to know the extent to which the gas generated can be solubilised in water. When a separate gas phase forms, the uncertainties associated with dual phase flow are important, for example gas permeability, heads and pressures in the system, and the stress on the external barriers to the wastes.

Model simplification uncertainty

The main simplifications used in the gas generation models their uncertainties are described below:

General

All packages are assumed to be saturated immediately after the repository is sealed. This means that the gas generation processes start immediately. If saturation was assumed to occur later, it would delay the start of gas generation.

Simplifications and qualitative uncertainties in gas formation via metal corrosion

i) Instantaneous oxic corrosion of the metals, generating anaerobic conditions immediately after repository closure.

ii) Sufficient water is always available for anaerobic corrosion of the metals present. As mentioned above, this assumption is supported by scoping mass balance calculations suggesting that gas formation would not lead to unsaturated conditions (Mallants and Jacques 2004). If water is not supplied at a rate sufficient to support anaerobic corrosion of metals, gas generation would be slower.

iii) Iron (e.g. in steel) is assumed to corrode to magnetite. The uncertainties associated with this assumption are discussed in Section 3.5.9. Calculated gas generation rates depend on the stoichiometry of the assumed process. This uncertainty can be assessed by using bounding cases.

iv) The rate of metal corrosion is assumed to be constant over time. This uncertainty can be assessed by bounding calculations for the likely range of corrosion rates, thus of gas generation rates.

v) The temperature is assumed to be constant, which is not thought to introduce significant uncertainty beyond the uncertainties in the corrosion rates.

vi) Hyperalkaline conditions are assumed to prevail in all of the repository system except in the waste packages deposited in the BLA vault.

Simplifications and qualitative uncertainties in gas formation via degradation of organic material

i) Microbes able to degrade waste organic materials are assumed to be present. This is an important uncertainty that is addressed through bounding case approach.

ii) It is assumed that cellulose is degraded through microbial degradation with subsequent gas generation, although abiotic degradation is expected to dominate under alkaline conditions, which does not generate gas.

iii) The degree of saturation of the wastes can also be considered a source of uncertainty.

iv) For gas transport, the main simplification is that wastes are only considered as a source of gas, and the waste form are considered to offer no restriction to gas transport.

Uncertainties related to gas transport

Gas transport process uncertainties reflect those of gas generation, as this will affect the time when the gas solubility is exceeded and a separate gas phase forms. Other uncertainties affecting gas transport are not expected to be of relevance for the assessment given that wastes are considered as sources of gas, and transport is only assumed to occur through the backfills and external engineering barriers and the geosphere. However, these would include the hydrodynamic properties of the waste matrices, gas diffusivity in the waste matrices, pressures and heads, as well as the conditions at the boundary of the wastes. The state of the waste containers and the hydrodynamic properties of the backfilling media in which the waste packages are located and uncertainties on water flows also affect gas transport. Resistance of the material to fracturing for the creation of the preferential pathways for gas transport and evacuation of gas from the wastes is another uncertainty.

Input data and data uncertainty

Most of the waste that will be deposited in SFR has not yet been produced and hence the final inventory is based on prognosis. The uncertainty in the amounts of materials in the waste used in the model is therefore a source of uncertainty. The updated inventory and estimated uncertainties (SKB 2013a) will be used in SR-PSU.

Uncertainties relating to the presence and type of microbial activity directly affect the predicted biotic organic degradation processes and, therefore, the rates of gas generation through these processes.

Other input data uncertainties are mainly related to rates of corrosion. The uncertainties related to these input data are further evaluated in the Data report (SKB 2014c).

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.6 Radionuclide transport

3.6.1 Speciation of radionuclides

Overview/general description

Chemical speciation refers to the distribution of an element amongst defined chemical species in a given system. For instance, in the alkaline waters expected in some parts of the SFR repository, metal ions will be mainly hydrolysed building aqueous hydroxide complexes, as well as complexes with the organic ligands present in the waste. Both types of ligands will have to compete for metals and also for the large calcium content of the contacting waters. Hence, there is not straightforward way to define a priori the chemical speciation of radionuclides in the different parts of the SFR system and thermodynamic modelling is required to ascertain the chemical distribution of radionuclides under these conditions.

Aquatic chemical speciation is the outcome of expert thermodynamic modelling together with dedicated spectroscopic methods, which are now able to unravel the stoichiometry and structure of dissolved species down to the nanomolar level (Kalmykov et al. 2008, Michel et al. 2009). The combination of atomic and molecular spectroscopy with quantum chemical modelling has also provided insights and back up of the macroscopic thermodynamic modelling assumptions (Vallet et al. 2006)

One of the key assumptions in thermodynamic modelling is the existence of local equilibrium. This is, that the residence time of contacting waters is sufficiently large that kinetic constrains are not relevant. This is somewhat questionable in the SFR repository system due to the relatively short residence times of groundwaters and in particular for heterogeneous electron transfer reactions (Bruno 1997), like the anaerobic corrosion of iron, the sulphate/pyrite reaction or the selenium redox system. For selenium it is known that reduction from selenate, Se(VI), to lower oxidation states is rather slow. The mobility of the selenium, and other elements, at different oxidation states differs. However, the presence of bacteria can indeed accelerate these sluggish reactions (3.5.8).

The outcome of (geo-)chemical modelling is never better than the thermodynamic (and kinetic) data bases used. In this context, quality assessed thermodynamic data bases are therefore essential. The compilation work performed by the NEA-TDB project has been a key building stone of the process. Particularly relevant for this Process report, are the books referred to organic ligands (Hummel et al. 2005) and the actinide update. Unfortunately, NEA-TDB compilations for key radionuclides in SFR, like Ni and Se are still missing, however quality assured compilations performed for other repository systems contain the necessary data, e.g. Thermochemie TDB (Duro et al. 2012b)

Knowledge of the speciation of a certain radionuclide under given conditions is also important for assessing its sorption to solid surfaces present in the system, and its diffusion. Sorption is addressed separately in Section 3.5.3). The pH and the organic ligand content in the repository changes over time, thus the aqueous speciation of certain radionuclides will change and their sorption capacity will be affected.

Speciation also affects the distribution of volatile elements in the gaseous phase, i.e. C-14, which may be present as CO_2(g) and/or CH_4(g) radionuclides may be present as gases. In this case, their distribution between the dissolved and gas phases is controlled by Henry's law.

Much of the activity in SFR is in the water-containing waste, i.e. bead resin, powder resin, mechanical filter aids, evaporator concentrates and precipitation sludge (SKB 2013a). The ion exchange resins consist of organic polymers with acidic or basic groups that make them capable of cation or anion exchange. Non-radioactive species are also captured in the ion exchange resins during operation, examples being organic complexing agents such as citrate, gluconate and *N*,*N*-bis(carboxymethyl) glycine (NTA), and various cations such as Fe^{2+}/Fe^{3+}, Ni^{2+} and Zn^{2+}. Organic complexing agents may influence the speciation and sorption of certain radionuclides, and therefore affect radionuclide transport out of the repository. A low redox potential will be maintained in the different repository parts due to the anaerobic corrosion of steel (Duro et al. 2012c). However, since SFR is located relatively close to the surface, the possibility cannot be excluded that oxidising conditions will be introduced by a colder future climate, for example due to penetration of melt water from permafrost or an ice sheet into the repository. If oxidising conditions occur, redox-sensitive elements will be oxidised and their speciation and mobility will change.

Dependencies between processes and waste form variables

The following Table 3-22 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Temperature. The effect of temperature on radionuclide aqueous speciation is relatively well understood and can be handled (within the relatively narrow range expected for the repository) by speciation models (Stumm and Morgan 1996, Puigdomenech et al. 1997). The effect on solubility can be more difficult to predict, especially in cases where the corresponding solid phases become relevant (Puigdomenech et al. 1997). For effects on sorption, see Section 3.5.3.

Table 3-22. Direct dependencies between the process "Speciation of radionuclides" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No. Speciation is a molecular-level chemical process which is not influenced by macroscopic geometry.	Not relevant.	No.	Not relevant.
Radiation intensity	No.	Not relevant.	No.	Not relevant.
Temperature	Yes. Temperature will have effect on speciation.	Neglected. Thermodynamic data is used at the temperature given in the thermodynamic data set.	No.	Not relevant.
Hydrological variables	No.	Not relevant.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	No. Indirectly by different mobility properties of radionuclides.	Not relevant.	No.	Not relevant.
Material composition	No. Indirectly through porewater composition.	Not relevant.	No. Radionuclides are present only at trace concentrations.	Not relevant.
Water composition	Yes. Water composition directly affects speciation.	Included in the speciation calculations and considered in the selection of K_d see Section 3.5.3.	Yes. Speciation affects the chemical form of the dissolved radionuclides.	Included in the speciation calculations and considered in the selection of K_d see Section 3.5.3.
Gas variables	No. Indirectly by influencing water composition).	Not relevant.	No.	Not relevant.

Water composition is the main factor influencing speciation. Therefore, other variables that influence water composition (such as the composition of solids and gas) will affect radionuclide speciation indirectly. Conversely, trace concentrations of radionuclides entering the waste form void volume will not have a notable effect on bulk water properties. Speciation affects the chemical form of the dissolved radionuclides, this is handled in the selection of K_d values see Section 3.5.3.

Boundary conditions

Boundary conditions for radionuclide speciation are the inventory as well as the physical-chemical conditions (water composition and related variables, temperature).

Model studies/experimental studies

Most of the relevant aqueous equilibria involving radionuclides have been studied in detail, and corresponding equilibrium constants are available, see Guillaumont et al. (2003) and Hummel et al. (2005). When the water chemistry is known, the speciation of radionuclides can be calculated with a thermodynamic equilibrium model, such as PHREEQC (Parkhurst and Appelo 1999). For nuclides that are considered to be redox sensitive (Se, Tc, Pu and Np) thermodynamic modeling of the speciation, Duro et al. (2012c) suggest that under the conditions expected to prevail in SFR Se exists as Se(–II), Tc as Tc(IV), Np as Np(IV) and Pu as both Pu(III) and Pu(IV).

Kinetic constrains have to be taken into consideration. For instance, in diffusion experiments in Boom Clay (reducing conditions), selenate ions, $Se(VI)O_4^{2-}$, did not get reduced along their migration pathway (Beauwens et al. 2005, Alexander et al. 2009) even though Se(IV) and Se(–II) were the thermodynamically stable oxidations states hence thermodynamical modeling might overestimate the predominance of Se(–II) and Se(IV) species. However, selenite, $Se(IV)O_3^{2-}$, has been observed to change redox-state during diffusion through argillites and limestones (Descostes et al. 2008). It has also been observed that $Se(VI)O_4^{2-}$ can be reduced to Se(0) in the presence of green rust formed from an Fe(II) solution. When Se(VI) was present during green rust precipitation, the reduction kinetics to Se(0) were reasonably fast (< 150 h) and depended on the pH conditions (faster at alkaline than near-neutral pH) (Myneni et al. 1997).

Natural analogues/observations from nature

There have been a number of Natural Analogue projects where blind predictive modelling exercises have been used to test the capabilities of the geochemical codes and associated thermodynamic databases to predict radionuclide speciation in diverse geochemical environments. This kind of exercises were initiated at the Poços de Caldas Natural Analogue (Bruno et al. 1992) and where put in full use in subsequent Natural Analogue projects (Bruno et al. 1998). The Maqarin analogue is perhaps the most relevant for the cementitious environment (Alexander 1992, Smellie 1998), in that study there was also a blind predictive modelling exercise (Linklater et al. 1996). By and large the testing of the geochemical codes was quite satisfactory giving support to the proposed radionuclide speciation methodology.

Time perspective

This process is relevant for the whole assessment period. It can be considered fast in comparison to transport processes, i.e. local equilibrium can be assumed (Stumm and Morgan 1996, NEA 2012a).

Handling in the safety assessment SR-PSU

The speciation of the redox sensitive radionuclides Se, Tc, Np and Pu is calculated using thermodynamic data (i.e. equilibrium assumption) (Duro et al. 2012c).

In the safety assessment solubility limiting thermodynamic calculations are not accounted for as a retardation mechanism instead K_d-values are used to represent the retardation of radionuclides on cement in the radionuclide transport modelling as speciation is indirectly accounted for in the selection of K_d values.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

The basic understanding of the process is well developed. For some RN, there are still uncertainties in understanding their interactions with certain ligands (e.g. dissolved silica, mixed hydroxo-carbonato complexes, organic complexing agents), especially at high pH. For uncertainties related to K_d see Section 3.5.3.

Model simplifications uncertainties

The speciation is mainly accounted for in the selection of K_d values. Typically the determination of K_d values are done under high pH conditions similar to those assumed to prevail within SFR. The experimental determination of K_d is typically done under controlled redox-conditions. For the redox sensitive radionuclides thermodynamically modelling determines the oxidation state of the radionuclide hence it influence the selection of the experimentally determined K_d values.

Input data and data uncertainties

Input data for the quantitative description of the process are thermodynamic and water composition data. The uncertainty of thermodynamic data (or of the calculations) can be estimated. Uncertainties in water composition can be handled by considering bounding conditions.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

3.6.2 Transport of radionuclides in the water phase

Overview/general description

The main radionuclide transport related processes identified in the waste form are:

- Decay and ingrowth (see Section 3.1.1).
- Advection (see Section 3.5.1).
- Diffusion (see Section 3.5.2).
- Dispersion (see Section 3.5.1).
- Sorption/uptake (see Section 3.5.3).
- Solubility limitations (see Section 3.6.1).
- Speciation (see Section 3.6.1).
- Colloid transport (see Section 3.5.4).
- Corrosion (see Section 3.5.9).

Decay and ingrowth, advection, diffusion, sorption/uptake, corrosion and solubility limitations are included explicitly in the radionuclide transport model. Sorption/uptake is handled using element specific K_d values. Effects of colloid facilitated transport are considered negligible due to the reasoning in Section 3.5.4. Dispersion is not handled explicitly in the model since the chosen modelling approach introduces greater numerical dispersion than the expected physical dispersion, negating the need for a specific dispersion term.

Modelling of radionuclide transport

Radionuclide transport in the waste is calculated using radionuclide transport models developed in the Ecolego modelling tool. Details of the Ecolego modelling tool can be found in the Model summary report (SKB 2014i), detailed descriptions of the models developed for SR-PSU can be found in the Radionuclide transport report (SKB 2014j). The following text gives a brief general description of how the models are implemented. Equation 3-9 describes the rate of change of the radionuclide inventory in each compartment:

$$\frac{dA_i^n}{dt} = \sum_j Tr_{ji} - \sum_j Tr_{ij} + \lambda^n A_i^p - \lambda^n A_i^n \qquad \text{Equation 3-9}$$

where:

A_i^n = Amount of nuclide n in compartment i [Bq].

Tr_{ji} = Transfer from compartment j to compartment i [Bq/year].

λ^n = Decay rate of nuclide [year^{-1}].

The transfer terms in Equation 3-9 represent various physical and chemical radionuclide transport processes. The mathematical descriptions of these processes are given below.

Radioactive decay and in-growth

Radioactive decay and in-growth are well known physical processes with exact mathematical descriptions (see Section 3.1.1), which make the modelling trivial. These processes are included in the model via nuclide specific decay constants and branching ratios (see Equation 3-9).

Advective transport of dissolved species

Detailed hydrological calculations for the near-field have been performed (Molinero et al. 2013), and these identified a number of water fluxes in the waste domain of the repository. The fluxes are used as parameters in the Ecolego model together with the relevant volumes and retardation factors to calculate advection driven transport of radionuclides in the waste and barriers.

The advective transfer between compartments is expressed as:

$$Tr_{adv\_ij} = \frac{q_{ij}}{Capacity_i} A_i^n$$ Equation 3-10

where:

q_{ij} = Water flux from compartment i to compartment j [m^3/year].

$Capacity_i$ = Capacity of compartment i [m^3].

A_i^n = Amount of nuclide n in compartment i [Bq].

Capacity is defined as:

$$Capacity = Volume\,(\phi + (1 - \phi)\,K_d\rho)$$ Equation 3-11

where:

ϕ = Porosity of material in compartment [–].

K_d = Partitioning coefficient [m^3/kg].

ρ = Particle density of the media in the compartment [kg/m^3].

Diffusive transport of dissolved species

Diffusive transfer is handled for all cementitious materials in the waste form and packaging. The input data include the media specific effective diffusivities and the porosities and geometries of the waste form and other cementitious materials in the waste domain. Diffusive resistance is neglected for bitumen stabilised wastes (a pessimistic assumption).

The diffusive transfer between compartments is expressed as a combination of two transfers, a forward diffusive transfer (Equation 3-12) and a backward diffusive transfer Equation 3-13).

$$Tr_{diff\_ij} = \frac{A_i^n}{0.5(res_i + res_j)Capacity_i}$$ Equation 3-12

$$Tr_{diff\_ji} = \frac{A_j^n}{0.5(res_i + res_j)Capacity_j}$$ Equation 3-13

where:

Tr_{diff_ij} = Diffusive transfer from compartment i to j [Bq/year].

res_i = Diffusive resistance of compartment i.

$Capacity_i$ = Capacity of compartment i.

A_i^n = Amount of nuclide n in compartment i [Bq].

Diffusive resistance for a compartment is defined as:

$$res = \frac{L}{AD_e}$$ Equation 3-14

where:

res = Diffusive resistance.

L = Length of compartment in direction of diffusion [m].

A = Cross sectional area of the compartment, perpendicular to direction of diffusion [m^2].

D_e = Effective diffusivity of material in compartment [m^2/year].

Sorption/uptake

Sorption/uptake has a retarding effect on both advective and diffusive transport of solutes. Sorption/uptake on cementitious waste and packaging materials is included in the radionuclide transport modelling using a linear approach, based on element (species) specific K_d values.

Solubility limitation

Solubility limitation is not considered in most calculation cases (a pessimistic approach). However, the effect of solubility limitation has been investigated in specific supporting calculation cases. The Ecolego model can account for solubility limitations by modifying the transfer expressions, see the Radionuclide transport report (SKB 2014j).

Corrosion

The reactor vessels contain radionuclides produced as a result of neutron activation of the steel, during the operation of the reactor. During this time the vessels are also contaminated on the surface by radionuclides present in the reactor water.

It is assumed that the fraction of the radionuclides that originates from neutron activation will be released as the steel corrodes. The slow corrosion rate of the reactor vessels will limit radionuclide release. The process is modelled as an approximately constant release of nuclides based on the corrosion rate for steel under repository conditions (i.e. the nuclides are released congruently with the corrosion products from the steel), see the Radionuclide transport report (SKB 2014j) for further details on the modelling.

Dependencies between processes and waste form variables

Table 3-23 shows both the influence of the defined waste form variables (defined in Section 2.1.2) on the process and the influence of the process on these variables.

Boundary conditions

The inner boundary for radionuclide transport processes is the initial inventory (or amount) of radionuclides in the waste. The outer boundary is the concentration in the packaging.

Model studies/experimental studies

Radionuclide transport from the waste in SFR has been studied in several previous safety assessments, most recently in SAFE (Lindgren et al. 2001) and SAR-08 (Thomson et al. 2008a, b). SR-PSU and these studies use a similar approach for handling radionuclide transport in the waste.

Natural analogues/observations from nature

No natural analogues have been identified for the transport of radionuclides in waste materials. However there exists natural analuoges that have been studied and have improved the knowledge about radionuclide transport in general (Chambers 1994, Steefel and Lichtner 1998).

Time perspective

Transport of radionuclides in the water phase is relevant throughout the period considered in the safety assessment.

Handling in the safety assessment

Radionuclide transport in the waste is calculated in the Ecolego radionuclide transport model. The Model summary report (SKB 2014i) describes the details of the Ecolego model.

Details of the radionuclide transport modelling can be found in the Radionuclide transport report (SKB 2014j).

Table 3-23. Direct dependencies between the processes "Transport of radionuclides in the water phase" and the defined waste form variables and a short note on the handling in SR-PSU.

Parameter	Variable influence on process		Process influence on variable	
	Influence present?	**Handling of influence**	**Influence present?**	**Handling of influence**
Geometry	Yes. Gives the volumes, transport length, porosity and areas available for transport.	Geometry variables are included in the RN-transport model.	No.	Not relevant.
Radiation intensity	No.	Not relevant.	Yes. The radiation intensity declines as nuclides are transported out.	Neglected. The effect on radiation intensity is assumed to be insignificant in the waste domain.
Temperature	Yes. Diffusivity and sorption/uptake will be affected.	Neglected due to the expected small temperature variations.	No.	Not relevant.
Hydrological variables	Yes. Water fluxes are very important for advective transport of RN.	Yes. Detailed flow parameters are included in the RN transport model.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes.	The radionuclide inventory is the source term for the radionuclide transport calculations.	Yes. The inventory declines as radionuclides are transported out.	Transport and decay processes are modelled.
Material composition	Yes. Sorption/uptake properties are highly dependent on material composition.	Yes. Material-specific K_d values are included in the RN transport model.	No.	Not relevant.
Water composition	Yes. Sorption/uptake properties are dependent on water composition.	Yes. Considered in the selection of K_d data.	Yes.	The porewater concentration of radionuclides in all parts of the system is calculated.
Gas variables	Yes. Build-up of gas pressure may expel water containing radionuclides.	Considered in a gas driven advection scenario.	No.	Not relevant.

Handling of uncertainties

Uncertainties in mechanistic understanding

The transport of radionuclides is dependent on several physical and chemical processes described elsewhere in this report. The uncertainties in the understanding of these processes affect the radionuclide transport calculations. However the processes expected to be of most significance for the radionuclide transport are well understood.

Model simplifications uncertainties

The following list contains some of the uncertainties related to the model simplifications:

- For practical reasons the different waste types in SFR have to be represented by a smaller number of "model waste types" (Radionuclide transport report (SKB 2014j)).
- The numerical dispersion introduced by the relatively coarse discretisation of the model is greater than the expected physical dispersion during transport. Therefore, the model generates results with a conservative estimate of dispersion, even without accounting for dispersion explicitly.
- Sorption/uptake properties are not represented in detail in the transport model. Instead a simplified methodology is applied, where retardation of nuclides is described with a linear K_d approach.
- The repository is assumed to be resaturated instantaneously; hence the initial transport of nuclides during resaturation is not represented in the modelling.
- Colloid transport is not included in the transport modelling. The effect of colloids on radionuclide transport is assumed to be negligible, due to the limited impact on radionuclide transport, see Section 3.5.4.

Input data and data uncertainties

Input data are described in detail in the Data report (SKB 2014c).

The uncertainties in parameter data are handled by means of probabilistic simulations and conservative assumptions. The uncertainties of the parameters are expressed with probability density functions, used in Monte Carlo simulations.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB.

3.6.3 Transport of radionuclides in the gas phase

Overview/general description

As described in Section 3.5.10 for the transport of gases in general, radioactive gases generated in SFR may be able to escape from the system. Since the waste forms will be water saturated, this process requires the creation of migration paths for a separate gas phase. This can occur when water is displaced from the saturated pore space of the waste form and/or through the creation of fractures. Once a gas path has been created and gas breakthrough has occurred, dissolved gaseous radionuclide species move into the gas phase to restore the equilibria. This enhances gas phase radionuclide transport out of the system.

Some of the factors affecting transport of radionuclides in gas phase are:

- Rate of gas generation.
- Saturation of the system.
- Solubility of the gas in the porewater.
- Permeability of the waste form.

Radionuclide transfer into the gas phase will depend on the relative concentrations of the radionuclides and their stable isotopes in the two phases and the rates of diffusion in the water phase.

Radionuclides, such as C-14, H-3 and Rn-222, can be transported as gases when a separate gas phase forms. The main factors that can affect the release of these gaseous radionuclides are:

C-14

The release of gaseous C-14 will be mainly controlled by the relative rates of CO_2 and methane generation and consumption. These two gases are mainly formed by microbial degradation of organic materials. It is generally assumed that CO_2 will be consumed by carbonation of cementitious materials in the matrix and therefore the amount of gaseous CO_2 will be negligible, although there are also zones in the SFR where conditions with lower alkalinity will develop and CO_2 can be more relevant. Additionally, methane formation has been shown to be out-competed as long as other electron acceptors are present (see Section 3.5.8).

H-3

H-3 can be present as H_2, the main gas generated in SFR, which is created during metallic corrosion and the degradation of some long chain organics. H_2 generation will start very soon after repository closure, due to the large amounts of metal present in the system. The release of tritium will depend on the migration of H_2 produced *in situ*. Tritium has a relatively short half-life (12.35 years) so will decay early in the lifetime of the repository.

Rn-222

Radon-222 is a very short-lived, gaseous daughter of the U-238 decay chain ($t_{½}$ = 3.8 days). Its transport in the gas phase is not expected to be relevant to the PSU, due to rapid decay. Approximate calculations have been performed for the spent fuel repository (SKB 2011, Section 13.8).

Other radionuclides in gas phase

The formation of volatile methylated compounds can increase the migration of radionuclides in the gas phase. Migration of I-129 is not affected by this type of formation in SFR due to the presence of hydroxyl ions ensuring that methyl iodide will undergo a nucleophilic substitution reaction forming methanol (Solomons 1996).

Iodine itself is volatile with a vapour pressure of about 1.3×10^{-4} atm. at 10°C, extrapolated from data in Green and Perry (2008). In a reducing environment it is reduced to I^-, which at high pH cannot form volatile HI. Paquette et al. (1986) analysed the volatilisation of iodine in the Three Mile Island accident. Their findings support that under reducing conditions iodine in water is in the form of iodide and is not volatile.

Volatile organic selenium compounds are known to exist (e.g. Evans et al. 1968). These are not expected to form in any major concentrations in the environment prevailing in SFR. Initially in the waste form Se are considered to be in either Se(IV) or Se(VI). Se(IV) and Se(VI) might slowly be reduced to Se(0) in a reducing environment either abiotically or catalysed by microbial activity (Yee et al. 2007). Possibly also Se(–II) could form in strongly reducing water. Such reducing conditions will exist at SFR1 after closure. Se(0) has a boiling point of 685°C and a negligible vapour pressure at ambient temperature. Se(–II), which can form H_2Se is dissociated to HSe^- at high pH in the waste and is not volatile. Therefore Se is considered to be a minor volatile compound under the conditions prevailing in SFR.

Theoretically, Cl-36 may also form gas, but the equilibrium favours dissolution and the amount in the gas phase is negligible.

Dependencies between process and waste form variables

Table 3-24 shows how the process influences, and is influenced by, all waste form variables defined in Section 2.1.2.

Geometry. The geometry can affect the access of water to the waste form and therefore gas transport of radionuclides due to the release of different gaseous radionuclides.

Radiation intensity. No direct influence is identified. Indirectly, radiation intensity affects gas phase transport through radiolytic gas generation (see Section 3.1.3 and Section 3.1.4).

Temperature. Temperature could affect gas phase transport of radionuclides. However, the low temperature variation expected in the repository means that it is not considered relevant for SFR.

Hydrological variables. Hydrological variables will affect the rate at which water is expelled from the system, and therefore affect the rate at which gas leaves the system including gas phase radionuclides.

Mechanical stresses. Only indirectly, stresses may create preferential paths for water transport and affect gas migration processes.

Radionuclide inventory. The radionuclide inventory will affect the type and amount of gaseous radionuclides that can be generated and thus transported.

Material composition. The composition of the material determines the total amount of gas volume that can be generated as well as the radionuclides able to be transported as gases.

Water composition. Water composition can affect the partitioning of radionuclides between the gas and dissolved phases and indirectly also the rate and total amount of gas build-up.

Gas variables. Gas pressures and compositions will affect gaseous radionuclide transport. Gas build-up in the system may create overpressures and generate new water/gas pathways that can favour transport of gas phase radionuclides.

Table 3-24. Direct dependencies between the process "Transport of radionuclides in the gas phase" and the defined waste form variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry may affect gas-phase transport.	Neglected. The waste is considered to offer no resistance to gas transport.	No.	Not relevant.
Radiation intensity	No. Gas phase transport is influenced indirectly, since radiation intensity affects gas generation through radiolysis.	Neglected. Not considered sufficiently relevant.	No.	Not relevant.
Temperature	Yes. Temperature can affect gas streams, but the temperature range is very narrow in the repository.	Not considered sufficiently relevant.	No.	Not relevant.
Hydrological variables	Yes. Hydrological variables will determine the rate at which water is expelled from the system, thus the initial rate of gas-mediated phase transport.	Neglected. The waste is considered to offer no resistance to gas transport.	No.	Not relevant.
Mechanical stresses	No. However an indirect effect via geometry, since stresses may create preferential paths for water and affect gas migration.	Not relevant.	No.	Not relevant.
Radionuclide inventory	Yes. It will affect the amount of gaseous, and potentially gaseous radionuclides.	It is assessed through bounding calculations.	Yes.	Decay considered.
Material composition	Yes. The composition of the material determines the amount of radionuclides able to form a gas phase.	Through assessment of the waste inventory. The waste is considered to offer no resistance to gas transport.	No.	Not relevant.
Water composition	Yes. Water composition can affect the partitioning of gaseous radionuclides between the gas and dissolved phases.	Neglected. The waste is considered to offer no resistance to gas transport. Gasses dissolved in water are assumed to be transported out with the waterflow.	No.	Not relevant.
Gas variables	Yes. Gas pressures and composition will effect the transport of gaseous radionuclides.	Neglected. The waste is considered to offer no resistance to gas transport.	No.	Not relevant.

Boundary conditions

Boundary conditions defining the role of the gas phase in radionuclide transport are given by the pressures and fugacities of the gases produced, since these will determine the creation of gas migration paths. The sources of radionuclides to be transported must also be defined as inner boundaries, in this case only the migration of C-14, H-3 and Rn-222 are considered relevant. Temperature should also be defined in the boundary conditions given that it controls the solubility of a gas in water as well as the pressure of the gas phase (SKB 2008a).

Model studies/experimental studies

No direct studies of radionuclide transport in the gas phase are known for the conditions expected in the waste.

Natural analogues/observation from nature

Upreti et al. (2002) provide observations of the migration of CO_2, methane and ethane through Athabasca Bitumen that are useful analogues for the migration of C-14 in bituminised wastes.

Etiope and Martinelli (2002 and references therein) provide a good overview of the migration of carrier and trace gases in the geosphere that is helpful for putting the transport of gases through porous media in the context of the SFR repository. According to these authors, bubble movement in fissured rock material seems to be an effective way of rapid and long-distance gas migration.

Time perspective

Transport of radionuclides in the gas phase may occur from the moment that a gas pathway is created, which will occur when gas is generated in sufficient amounts to produce a gas escape route from the repository. The main gas generated in the repository is hydrogen, due to the anoxic corrosion of steel-based materials and the degradation of organic materials. Therefore, the rate of hydrogen generation and accumulation can be compared with the pressure of the repository to provide a rough estimation of the time for the onset of gas migration.

Handling in the safety assessment SR-PSU

Even though methane formation has been shown to be out competed as long as other electron acceptors are present (see Section 3.5.8), the release of C-14 as methane is handled by approximate calculations.

Handling of uncertainties the safety assessment SR-PSU

Uncertainties in mechanistic understanding

All uncertainties affecting the processes of gas generation will also affect the transport of radionuclides in the gas phase. The route by which the gases formed leave the repository can be considered to be another mechanistic uncertainty.

Model simplification uncertainty

Most uncertainties in the model simplification relate to gas formation, which are discussed in detail in Section 3.5.10. Additional model uncertainties relate to the conceptualisation of gas escape from the repository.

Input data and data uncertainty

The main uncertainties, besides those associated with gas formation, are related to the waste inventory of radionuclides likely to be incorporated into gaseous species.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

4 Steel and concrete packaging

4.1 Thermal processes

4.1.1 Heat transport

Overview/general description

The processes of heat transport are described in detail in Section 3.2.1. For this process, there is no difference between the waste form and packaging.

Dependencies between process and packaging variables

See Table 3-5 in Section 3.2.1.

Boundary conditions

See Section 3.2.1.

Model studies/experimental studies

See Section 3.2.1.

Natural analogues/observations from nature

See Section 3.2.1.

Time perspective

See Section 3.2.1.

Handling in the safety assessment SR-PSU

See Section 3.2.1.

Handling of uncertainties in SR-PSU

See Section 3.2.1.

4.1.2 Phase changes/freezing

Overview/general description

The process of freezing in concrete packaging components is covered by the general description in Section 3.2.2. The process of freezing is not relevant for steel packaging.

Dependencies between process and packaging variables

See Table 3-6 in Section 3.2.2.

Boundary conditions

See Section 3.2.2.

Model studies/experimental studies

See Section 3.2.2.

Natural analogues/observations from nature

See Section 3.2.2.

Time perspective

See Section 3.2.2.

Handling in the safety assessment SR-PSU

See Section 3.2.2.

Handling of uncertainties in SR-PSU

See Section 3.2.2.

Adequacy of references supporting the handling in SR-PSU

See Section 3.2.2.

4.2 Hydraulic processes

4.2.1 Water uptake and transport during unsaturated conditions

This process description is focussed on the concrete packaging. Water uptake and transport in steel packaging during unsaturated conditions is not judged to be relevant.

Overview/general description

In many respects, the processes are similar to those described for the waste form. Therefore, the overview and general description of the processes of water uptake and transport in waste forms during unsaturated conditions given in Section 3.3.1 are also valid for the packaging. The processes are therefore not described in this section, and the focus here is on significant deviations from the description of the processes for the waste forms.

Dependencies between process and packaging variables

Table 4-1 shows how the process water uptake and transport during unsaturated conditions influences, and is influenced by, all packaging variables defined in Section 2.2.2.

Influence by Geometry. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1. The time to reach full water saturation in the concrete packaging is likely to be short and determined by the rate of water penetration of surrounding constructions and/or the rock.

Influence on Geometry. No direct influence has been identified. The packaging geometry can be indirectly influenced by swelling of waste contained in the packaging, see Section 3.5.7. Concrete packaging may also swell to some small degree in response to resaturation, which reduces the drag force caused by capillary forces (reverse of shrink-drying).

Influence by Temperature. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1. The overall judgement is that temperature and temperature variability would have insignificant impact on the rate of water uptake.

Influence on Temperature. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1. The overall judgement is that water uptake would have insignificant impact on the temperature.

Table 4-1. Direct dependencies between the process "Water uptake and transport during unsaturated conditions" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Dimensions define the volume of voids to resaturate. Fractures constitute short-cuts for flow. Controlled by geosphere or barrier materials.	Geometry included in the models.	No. Indirectly via swelling of contained waste. see Section 3.5.7.	The swelling pressure is calculated, see Section 3.5.7.
Temperature	Yes. Effects viscosity and surface tension of water.	Reflected in the selection of hydraulic conductivities for model calculations. Effects of spatial temperature variability are judged negligible.	Yes. The water uptake redistributes heat. Indirectly the resaturation affects the thermal properties see Section 4.1.1 and Section 4.4.5.	The temperature is calculated.
Hydrological variables	Yes. Pressure is driving force for water uptake.	Included variables in water saturation calculations.	Yes. Water uptake will influence pressure and flow.	The pressure and suction are considered.
Mechanical stresses	No. Only indirectly via mechanical stesses affecting the geometry.	Not relevant.	No. Only indirectly via swelling of contained waste, see Section 3.5.7.	Not relevant.
Material composition	Yes. Material properties determine the waterflow and capillary suction.	The material composition is reflected in the selection of material data for calculation of water uptake.	No. Indirectly via water mineral reactions, see Section 4.4.5.	Not relevant.
Water composition	Yes. Salinity will influence density, viscosity and surface tension.	Reflected in the selection of viscosities, densities and surface tension used in water uptake calculations.	No. Indirectly via water mineral reactions, see Section 4.4.5.	Not relevant.
Gas variables	Yes. Gas solubility and reactivity will influence possibility to dissipate entrapped gases.	Considered in the calculations of water uptake.	Yes. Water uptake will influence the equilibria with gases.	Considered in the calculations of water uptake.

Influence by Hydrological variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1.

Influence on Hydrological variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1.

Influence by Mechanical stresses. No direct influence has been identified. Mechanical stresses may cause fracture formation in the concrete packaging, which may indirectly influence water uptake by creating shortcuts for water flow.

Mechanical stresses will also indirectly, via geometry, influence the water uptake in any material that is compressible or prone to swelling (see further the corresponding waste form variable in Section 3.3.1). However, the compressibility of the concrete packaging is judged to be very small. The impact by compressive stresses on the water uptake in concrete packaging is therefore assumed negligible.

Influence on Mechanical stresses. No direct influence has been identified. Concrete packaging containing waste form materials/compounds with swelling properties would indirectly increase the mechanical stresses in the concrete packaging as a result of water uptake.

Influence by Material composition. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1. The influence of material composition is reflected in the selection of material data for the model calculations of water uptake.

Influence on Material composition. No direct influence has been identified. Indirectly, the uptake of water may influence the material composition by allowing continued hydration of any reactive mineral phases in the concrete package; this may create new hydrated mineral surfaces, see Section 4.4.5.

Influence by Water composition. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1. Input data for the calculation of water uptake reflect the influence of water composition. Colloids, particulate matter and humic/fulvic substances in the water may have an influence on the water uptake and transport in materials with narrow capillaries due to possible precipitation/filtering/clogging effects, however judged to be negligible for the water uptake.

Influence on Water composition. No direct influence has been identified. For a description of indirect influence, see corresponding waste form variable in Section 3.3.1.

Influence by Gas variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1.

Influence on Gas variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable described in Section 3.3.1.

Boundary conditions

The relevant boundary conditions are different for different parts of the SFR repository. The boundaries are set by the conditions and physical components surrounding the individual waste package. Dissipation of any gases entrapped or formed in the concrete packaging, or the contained waste, also constitutes a boundary condition. Boundary conditions include the pressure and flow pattern of groundwater, temperature, mechanical stresses, composition of water and gas.

Water uptake in outer concrete packaging serves as a boundary condition for the water uptake in waste contained in concrete or steel packaging.

For concrete containers disposed in the silo, water uptake will be governed by the water penetration of the bentonite and concrete barriers of the silo. This may in turn be influenced by the inflow of water through the surrounding rock. These boundary conditions are described in the Barrier process report (SKB 2014a).

For concrete packaging stored in BMA, BTF and BLA, water transport is governed by the flow of water through the surrounding rock, and when present, through concrete structures and cement grouting. These boundary conditions are described in the Barrier process report (SKB 2014a) and Geosphere process report (SKB 2014e).

For waste stored in BMA, BTF and BLA, water uptake is governed by the inflow of water through the surrounding rock, and when present, through concrete structures and cement grouting. These boundary conditions are described in the Barrier process report (SKB 2014a) and Geosphere process report (SKB 2014e).

Model studies/experimental studies

See corresponding heading in Section 3.3.1.

Natural analogues/observations from nature

See corresponding heading in Section 3.3.1.

Time perspective

See corresponding heading in Section 3.3.1.

Handling in the safety assessment SR-PSU

The handling of the processes of water uptake and transport in the packaging during unsaturated conditions is the same as for the corresponding processes occurring in the waste forms described in Section 3.3.1.

Handling of uncertainties in SR-PSU

For a description of the handling of uncertainties within the safety assessment, see the corresponding heading in Section 3.3.1.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

4.2.2 Water transport under saturated conditions

This process description focuses on concrete packaging. Steel packaging is not considered to have any barrier properties with respect to water transport and is not treated here.

Overview/general description

In many respects, the process is similar to that described for the waste form. Therefore, the overview and general description of the process of water transport in waste forms under saturated conditions given in Section 3.3.2 is also valid for the packaging. Therefore, the focus here is on significant deviations from the description of the process for the waste forms.

Dependencies between process and packaging variables

The following table shows how the process water uptake and transport during unsaturated conditions influences, and is influenced by, all packaging variables defined in Section 2.2.2.

Influence by Geometry. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2.

Influence on Geometry. No direct influence has been identified. The concrete packaging geometry can be influenced indirectly by the swelling of the waste, see Section 3.5.7. The porosity and hydraulic conductivity of the concrete packaging may also change over time to a small degree in response to chemical degradation processes, see Section 4.4.5, governed by the supply of reactants carried by the groundwater flow, see Section 4.4.1.

Influence by Temperature. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2. The overall judgement is that temperature and temperature variability will have an insignificant impact on water transport under saturated conditions.

In the long-term, the occurrence of permafrost and glaciations will change the temperature in the repository, which will introduce major changes in the water flow, see Section 4.1.2.

Influence on Temperature. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2.

Influence by Hydrological variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2.

Influence on Hydrological variables. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2.

Table 4-2. Direct dependencies between the process "Water transport under saturated conditions" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Water transport is controlled by the geosphere and barrier conditions. The flow resistance is proportional to dimensions. Fractures and voids constitute short-cuts for flow.	Geometry included in the models.	No.	Not relevant.
Temperature	Yes. Temperature will influence the density and viscosity of water and hence the hydraulic conductivity.	Reflected in the selection of hydraulic conductivities and densities and viscosities of water for use in the calculations.	Yes. Temperature is influenced by the redistribution of heat caused by the water transport, see Section 4.1.1.	The temperature is set by outer boundary conditions.
Hydrological variables	Yes. Water pressures constitute the driving force for water transport.	Input data in calculations of water transport.	Yes. Transport of water will define the pressure and flow distribution.	The pressure and flow are calculated.
Mechanical stresses	No. Indirectly via fracturing and geometry, see Section 4.3.1, reflected in the selection of hydraulic conductivities for calculations.	Not relevant.	No. Indirectly via the swelling of contained waste, see Section 3.5.7.	Not relevant.
Material composition	Yes. The material composition determines the hydraulic properties.	Relevant material data are selected for the water transport calculations.	No. Indirectly via dissolution–precipitation processes, see Section 4.4.5.	Not relevant.
Water composition	Yes. Water composition, e.g. salinity, influences the viscosity and density of water.	Relevant viscosities and densities are selected for the water transport calculations.	No. Indirectly via mixing/dissolution–precipitation, see Section 4.4.5.	Not relevant.
Gas variables	Yes. Reappearance of a gas phase, e.g. due to corrosion of steel components in the waste and packaging influences the water flow.	Effect of gas is considered in water flow calculations.	No. Indirectly water transport will influence the equilibria with gases by changing the water composition. Partitioning of gases according to Henry's and Raoult's laws.	Not relevant.

Influence by Mechanical stresses. No direct influence has been identified. Indirectly, mechanical stresses may cause fracture formation in the concrete packaging, see Section 4.3.1, which would enhance water transport.

Mechanical stresses will also indirectly, via geometry, influence the water flow in any material that is compressible or swelling (see further the corresponding waste form variable in Section 3.3.2). However, the compressibility of the concrete packaging is judged to be very small. The impact of compressive stresses on the water flow in concrete packaging is therefore assumed to be negligible.

Influence on Mechanical stresses. No direct influence has been identified. Concrete packaging containing waste form materials/compounds with swelling properties would indirectly increase the mechanical stresses in the concrete packaging as a result of water uptake.

Influence by Material composition. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2.

Influence on Material composition. No direct influence has been identified. The transport of water does not influence the material composition. Indirectly, the material composition may be influenced via dissolution–precipitation processes (see Section 4.4.5) and advection (see Section 4.4.1).

Influence by Water composition. A direct influence has been identified based on the reasoning used for the corresponding waste form variable, described in Section 3.3.2. Input data for the calculation of water transport reflect the influence of water composition.

Influence on Water composition. No direct influence has been identified. The water composition can be influenced indirectly by water uptake via dissolution–precipitation, see Section 4.4.5.

Influence by Gas variables. A direct influence has been identified. Any initial presence of a gas phase is treated in Section 4.2.1. The dissipation of dissolved gases is treated in Section 4.4.8. However, the reappearance of a gas phase due to e.g. corrosion of steel components in the waste or in the packaging forming gas will influence the water transport by blocking water conductive pores, and may also cause increased pressure and water flow. This is considered in the modelling of water flow.

Influence on Gas variables. No direct influence has been identified. Water transport will influence the composition of any gas phase present indirectly by removing the dissolved gas, which promotes further gas dissolution according to Henry's law and Raoult's law for each of the different gases.

Boundary conditions

The relevant boundary conditions for concrete packaging is different for different parts of the SFR repository. The boundaries are set by the conditions and physical components surrounding the individual waste package. Boundary conditions include the pressure and flow of groundwater, temperature, mechanical stresses and the composition of water.

The water transport in concrete packaging will also serve as boundary conditions for the water transport in waste contained in concrete packaging.

For concrete packaging disposed in the silo, water transport will be governed by the water penetration of the bentonite and concrete barriers of the silo. This may in turn be influenced by the inflow of water through the surrounding rock. These boundary conditions are described in the Barrier process report (SKB 2014a).

For concrete packaging stored in BMA, BTF and BLA, water transport is governed by the flow of water through the surrounding rock and, when present, through concrete structures and cement grouting. These boundary conditions are described in the Barrier process report (SKB 2014a) and Geosphere process report (SKB 2014e).

Model studies/experimental studies

Specific model studies or experimental studies on water transport in concrete packaging is generally not available due to the diverse nature of the different packaging/packages.

Natural analogues/observations from nature

Although water transport during saturated conditions is well observed and documented in natural materials, water transport in concrete packaging has not been studied or observed in nature *per se*. However, the seepage of water into the excavated drifts and vaults have been observed and monitored during the construction and operational phases in SFR (SKB 2008b). Numerous archaeological sites may offer opportunities for studies if desired.

Time perspective

See corresponding heading in Section 3.3.2.

Handling in the safety assessment SR-PSU

The handling of the process of water transport in the packaging under saturated conditions is the same as for the corresponding processes in the waste form, described in Section 3.3.2.

Handling of uncertainties in SR-PSU

For a description of the handling of uncertainties within the safety assessment, see the corresponding heading in Section 3.3.2.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in the SR-PSU. All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

4.3 Mechanical processes

4.3.1 Fracturing/deformation

Overview/general description

The general description of the mechanical response of cement-encapsulated waste to volume changes given in corresponding process for the waste form (see Section 3.4.1) is also of relevance for the concrete packaging. Additional processes comprise stresses arising from volume expansion of the waste form and volume expansion of the reinforcement bars in the concrete packaging due to corrosion and Alkali–Aggregate Reaction (AAR).

Corrosion of steel reinforcement

The corrosion of steel reinforcement bars is generally considered to be inhibited by the high pH maintained by the cement. However, the presence of chlorides, pH reduction due to carbonation or stray currents may depassify the steel. Thus, the corrosion rate will depend on the pH and composition of the pore water and will increase slightly with the intrusion of chlorides and/or reduction of pH. The significant difference in volume between uncorroded steel and the reaction products will create a pressure within the concrete. After a period of time, the pressure may exceed the tensile strength of the material and cause fractures and spalling. Fractures will subsequently increase the penetration of chlorides and further accelerate the corrosion rate.

Alkali–Aggregate Reaction (AAR) Alkali–Aggregate reactions result in the formation of a gel, which increases in volume by absorbing water and thereby exerting an expansive pressure. As described for the formation of steel corrosion products, the pressure will build up over time and finally exceed the tensile strength of concrete, causing fractures in the surrounding concrete. In the long term, the gel may take up calcium and eventually become similar to a CSH-gel (West 1996).

Although steel packaging is not credited as a barrier, changes in the volume of encapsulated waste forms and extreme mechanical loads will affect its structural integrity and could lead to fracturing. However, since steel is a ductile material, fractures are expected to be less important than the effects of corrosion.

Dependencies between process and packaging variables

The interaction between the process and packaging variables (defined in Section 2.2.2) are summarised in Table 4-3. Many of these interactions are also applicable for the corresponding waste form process, Section 3.4.1.

Geometry. All volume changes will influence the integrity of the packaging. However, pre-existing voids in the packaging will reduce the effects of swelling bituminised waste.

Table 4-3. Direct dependencies between the process "Fracturing/deformation" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry changes may result in fractures.	Porosity and micro fractures are included in calculations.	Yes. Fracturing will create fractures and thus affect the geometry.	Variations in hydraulic conductivity is accounted for.
Temperature	No.	Not relevant.	No.	Not relevant.
Hydrological variables	Yes.	Freezing is deemed to cause severe damage.	No. Fractures will affect the hydraulic conductivity. Indirectly influenced by geometry.	Not relevant.
Mechanical stresses	Yes.	Concidered in the selection of hydraulic conductivity.	Yes.	Neglected. Not important compared to other influences.
Material composition	Yes.	Concidered in the selection of hydraulic conductivity.	No.	Not relevant.
Water composition	No.	Not relevant.	No.	Not relevant.
Gas variables	No. Indirectly via mechanical stresses.	Not relevant.	No.	Not relevant.

Boundary conditions

The physical boundaries of the packaging is expected to be in contact with water early post-closure. The concentrations/gradients of anions in the waste will affect the release from the waste form and the subsequent evolution of the concrete packaging. Gas formation in the waste form will exert a pressure on the surrounding packaging. Freezing and mechanical load will also have a strong influence on the structural evolution.

Also see Section 3.4.1.

Model studies/experimental studies

Also see Section 3.4.1. No long-term safety function is assigned to steel packaging.

Natural analogues/observation from nature

Natural analogues are not relevant for steel packaging. For concrete packaging see Section 3.4.1.

Time perspective

Steel packaging is not considered as a barrier. For concrete packaging see Section 3.4.1.

Handling in the safety assessment SR-PSU

There are no requirements for the long-term function of the steel packaging. For concrete packaging see Section 3.4.1.

Handling of uncertainties the safety assessment SR-PSU

See Section 3.4.1.

4.4 Chemical processes

4.4.1 Advective transport of dissolved species

Overview/general description

The various types of packaging considered within SR-PSU are described in Section 2.2. The packaging materials are either concrete or steel. The key generic concepts and general descriptions of advection and dispersion in concrete packaging is very similar to those in cement stabilised waste forms, described in Section 3.5.1. Therefore, the discussion will not be repeated here. Advective transport does not occur through intact steel packaging. However, heterogeneities in the steel packaging such as faulty welds or other defects may provide pathways for solute transport, by either diffusion or advection depending on the local hydraulic conditions and the extent of deficiency. Furthermore, steel is vulnerable to corrosion and will degrade over time. Therefore, the retaining property of the steel packaging is expected to be lost completely as extensive penetrating corrosion drastically increases the permeability of the material.

Dependencies between process and packaging variables

See Section 3.5.1.

Boundary conditions

The boundary conditions for the processes of advection and dispersion in the packaging is the groundwater composition and the extent and direction of water flow at the physical boundaries to the surrounding barriers, and the waste form.

Model studies/experimental studies

See Section 3.5.1 for a description of relevant model and experimental studies.

Time perspective

Advective transport by flowing groundwater will occur within some parts of SFR, at least, over its lifetime. The current state of the steel packaging and the degree of deterioration at repository closure are uncertain. Furthermore, with extensive penetrative corrosion, steel will lose much of its transport restricting properties. For safety assessment purposes, the steel packaging must therefore be assumed to offer no retaining capability throughout the lifespan of the repository.

Dynamic changes are also expected in the hydraulic properties of the concrete packaging, particularly from freeze damage (fractures and fractures) during periglacial permafrost. Solute transport in the pores of the concrete packaging, which is initially diffusion-controlled, may therefore become advection-dominated as a result of dissolution reactions and freezing.

Natural analogues/observations from nature

See Section 3.5.1.

Handling in the safety assessment

See Section 3.5.1.

Handling of uncertainties

See Section 3.5.1.

4.4.2 Diffusive transport of dissolved species

Overview/general description

Various types of packaging is considered within SR-PSU. These are further described in Section 2.2. The materials used for the different types of packaging is either concrete or steel. The general description of the process of diffusion in concrete packaging is very similar to that for cement stabilised waste forms described in Section 3.5.2. That section also introduces key generic concepts of diffusion in porous media which will not be further discussed here. Diffusion through intact steel packaging may be regarded to be negligible. However, heterogeneities in the steel packaging, such as faulty welds or other defects may provide pathways for solute transport, by either diffusion or advection depending on the local hydraulic conditions. Furthermore, steel is vulnerable to corrosion and will be degraded over time, thus diffusion may occur through brittle layers of rust and corrosion products. Eventually, all retaining properties of the steel packaging will be completely lost, as extensive penetrating corrosion drastically increases the permeability of the material.

Dependencies between process and packaging variables

The following table (Table 4-4) shows how the process of diffusive transport of dissolved species influences and is influenced by the packaging variables defined in Section 2.2.2.

Table 4-4. Direct dependencies between the process "Diffusive transport of dissolved species" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Diffusion is proportional to packaging dimensions and is significantly affected by heterogeneities and pore geometry.	Included in the transport modelling.	No.	Not relevant.
Temperature	Yes. Affects diffusivity. At high temperature gradients even Soret effects may occur.	Neglected due to the largely isothermal conditions in SFR.	No.	Not relevant.
Hydrological variables	Yes. The aggregation state of water directly influences the extent of diffusion.	Changes in effective diffusivity due to water freezing will be included in the transport modelling.	No.	Not relevant.
Mechanical stresses	No. Mechanical stresses affect porosity and pore geometry, and therefore indirectly the effective diffusivity of species.	Not relevant.	No.	Not relevant.
Material composition	No. Material composition indirectly determines the porosity and the pore geometry in the packaging.	Not relevant.	No.	Not relevant.
Water composition	Yes. A major control of diffusion in the packaging.	Included in the transport models	Yes. Affect the water composition through the movement of dissolved chemical species, colloids, particles and dissolved gases in stagnant systems.	Included in the transport models
Gas variables	No. Diffusion is influenced by the dissolved concentration and thus indirectly affected by the gas variables within the packaging.	Not relevant.	No. Indirectly diffusion of dissolved gases will influence their aqueous concentration which affects the gas composition.	Not relevant.

Influence by geometry. Yes, a direct influence has been identified. Diffusion will be affected significantly by the geometric dimensions, porosity and pore characteristics of the packaging, as well as the frequency and size of fractures, fractures and defects. The cross-sectional area affects the extent of diffusion, while the thickness of the packaging influences the diffusion path length, and the porosity affects constrictivity and tortuosity of the path, thus the effective diffusivity of species. Narrow pores may also lead to surface-ion effects, i.e. anion exclusion and enhanced cation diffusion.

Dynamic changes such as chemical degradation of the concrete will influence the geometric parameters, i.e. porosity and pore characteristics, which will in turn influence diffusion (see further discussion in Section 4.4.5). Corrosion will eventually affect the ability of the steel packaging to prevent diffusion by creating brittle layers of rust and corrosion products and ultimately penetrating deficiencies which drastically increase the permeability of the material. Corrosion is further treated in Section 4.4.7.

Influence on geometry. No direct influence has been identified. Diffusion will not have a direct effect on geometry. Indirect effects due to diffusion-induced changes in the water composition that may influence dissolution, precipitation and recrystallisation reactions within concrete packaging and corrosion of steel packaging is addressed in Section 4.4.5 and 4.4.7 respectively.

Influence by temperature. Yes, a direct influence has been identified. Temperature will affect the rate of diffusion, with higher temperatures increasing the rate of diffusion due to increased Brownian motion. The Stokes–Einstein relationship explains how the diffusion coefficient varies with temperature and viscosity. This shows that the product of the diffusion coefficient and viscosity of the solution divided by the temperature is constant. However, this simple relationship does not hold true for ionic species. At low concentrations of ionic species, the diffusivity increases by approximately a factor of two between 0 and 25°C (Lerman 1988).

Temperature gradients may also induce changes in chemical potential, creating diffusional gradients (Lerman 1988). This is known as thermal diffusion or the Soret effect. The buffer, backfill and closure process report for SR-Site (SKB 2010a) suggests that a change from ambient temperature to 50–60°C doubles the effective diffusivity of species. This sensitivity to temperature was considered to be too small to be included in the model. The impact of thermal diffusion is judged to be negligible due to the practically isothermal conditions in the SFR repository, at any given time.

Influence on temperature. No direct influence has been identified. Diffusion of dissolved species will not have any direct effect on temperature.

Influence by hydrological variables. Yes, a direct influence has been identified. Diffusion is dependent on the concentration gradient and the pore characteristics of the packaging, thus hydrological variables directly affect diffusion when there is a change in aggregation state. The freezing of water during glaciation periods will clearly slow the rate of diffusion.

Other hydrological variables have indirect influences on diffusion. The total diffusive transport through the solution phase will be affected by the amount of water and degree of saturation, when dissolution is solubility-controlled. Lower amounts of water lead to dissolution of less solid material and therefore diffusion of a smaller amount of dissolved species. Water pressure may affect the equilibrium position of dissolution reactions, in particular of gases, thereby altering the concentration gradients in the packaging. If large amounts of water flow through the repository, e.g. during post glacial ice melting, the relative importance of diffusion may decrease as advective transport becomes more prominent, an effect that may be quantified using the Péclet number. Therefore, the relative importance of diffusion is dependent on the magnitude, direction and distribution of water flow.

Influence on hydrological variables. No direct influence has been identified. Diffusion will not affect hydrological variables directly. Indirect effects due to changes in the water composition that influence the freezing point of water are addressed in Section 4.1.2. Indirect effects due to changes in the water composition that result in dissolution or precipitation within concrete packaging, which may affect the amount of water and degree of saturation are addressed in Section 4.4.5.

Influence by mechanical stresses. No direct influence has been identified. Mechanical stresses may influence diffusion indirectly through changes in the porosity and pore geometry of the packaging resulting from elastic compression and compaction. The degree of this impact depends on the strength and compaction of the packaging material, the mechanical stress applied, etc. This may change over time due to interactions with other processes, such as degradation caused by dissolution, precipitation and recrystallisation (Section 4.4.5) , deterioration due to corrosion (Section 4.4.7) and different external load scenarios, e.g. rock fallout (see the Geosphere process report (SKB 2014e)) and the possible mechanical consequences for the packaging (see Section 4.3.1). Except for extreme conditions, which are handled by scenario analyses, the impact of mechanical stresses on diffusion is judged negligible.

Influence on mechanical stresses. No direct influence has been identified. Diffusion will not affect mechanical stresses directly. Indirect effects on concrete packaging is addressed in dissolution, precipitation and recrystallisation (Section 4.4.5).

Influence by material composition. No direct influence has been identified. The material composition will significantly influence the porosity and pore geometry of the concrete packaging and therefore has an indirect influence on diffusion. The material composition in steel packaging may also affect diffusion indirectly through porosity changes upon corrosion of the metal (Section 4.4.7). Material composition may also indirectly affect diffusion as a result of sorption (Section 4.4.3), dissolution, precipitation and recrystallisation reactions (Section 4.4.5) and their influence on the aqueous concentration gradients.

Influence on material composition. No direct influence has been identified.

Diffusion will only affect material composition indirectly due to sorption (Section 4.4.3), dissolution, precipitation and recrystallisation reactions (Section 4.4.5) resulting from diffusion-induced changes in the water composition.

Influence by water composition. Yes, a direct influence has been identified. The water composition is a major control of diffusive transport in the packaging. Diffusion will occur simultaneously in different directions for different dissolved chemical species, colloids, particles, and dissolved gases, according to the individual concentration gradients. Spatial variations in pH and Eh will determine the diffusion of protons, hydroxyl ions, and pH and Eh-sensitive chemical species. The water composition will also influence the diffusivity of individual ionic species due to the constraints of electroneutrality and interdiffusion between the diffusing species. Diffusivity is also related to the viscosity of the solution, which in turn is controlled to a significant extent by the water composition.

Influence on water composition. Yes, a direct influence has been identified. Diffusion affects the water composition through the movement of dissolved chemical species, colloids, particles and dissolved gases in stagnant systems. It also influences the pH, redox conditions, water density and viscosity along their respective gradients. Under advective conditions, determined by the local Péclet number, the influence by diffusion may be negligible.

Influence by gas variables. No direct influence has been identified. The presence of gas in the pores of the concrete packaging will indirectly influence diffusion by limiting the accessible pore volume for diffusion of dissolved species. The occurrence of any connected gas-filled porosity in the packaging would allow for diffusive or advective transport of gaseous compounds handled in Section 4.4.8 and Section 4.5.3.

The amount, composition, volume and pressure degree of saturation of gases in different parts of the packaging may indirectly influence diffusion by gas dissolving into the aqueous phase creating concentration gradients of dissolved species. The magnitude, direction and distribution of gas flow will affect the extent to which dissolved gas concentrations vary within the packaging.

Influence on gas variables. No direct influence has been identified. The diffusion of dissolved gases away from the source will influence gas composition and pressure indirectly by promoting further gas dissolution.

Boundary conditions

The boundaries of this process are the geometric boundaries of the packaging itself with exchange of mass and heat with the waste form and the surrounding barriers or geosphere.

Model studies/experimental studies

See Section 3.5.2 for a description of relevant model and experimental studies.

Time perspective

Molecular diffusion processes will take place throughout the lifetime of the repository. Possible degradation/dissolution/corrosion of the packaging might also impact the long term evolution of diffusion in the packaging.

Natural analogues/observations from nature

See Section 3.5.2.

Handling in the safety assessment

See under the corresponding heading in Section 3.5.2 for diffusion in concrete packaging. In the case of steel packaging, no transport retention is accounted for in the modelling due to uncertainties in the current state of deterioration of the packaging material as well as the degree of deficiency at the time for repository closure.

Handling of uncertainties

See under the corresponding heading in Section 3.5.2.

4.4.3 Sorption/uptake

Overview/general description

Sorption processes in the packaging is essentially the same as in the waste form, and these are described in detail in Section 3.5.3. In the cement waste form and the concrete packaging, the hydrated cement paste (HCP) contains all of the relevant solid phases for sorption.

Dependencies between process and packaging variables

The following table (Table 4-5) shows how the process of sorption influences and is influenced by the packaging variables defined in Section 2.2.2.

Geometry. Sorption (incorporation) of major elements or ions in the HCP structure can indirectly lead to mineral expansion and fracturing. This mostly concerns processes that occur in the presence of relatively high concentrations of chloride, sulphate and carbonate.

Temperature will influence sorption processes in several ways. First, the stability of the various HCP mineral phases is a function of temperature, and a change in temperature will indirectly influence the material composition (mineralogy) and therefore sorption. Second, it is known that temperature can have an effect on sorption processes such as ion exchange, surface complexation, and solid solution formation. While the latter effect can be predicted within reasonable certainty, the influence of temperature on sorption and also on mineralogy in the complex HCP system is not known. Based on the (overall) low crystallinity and high reactivity of HCP, as well as on the narrow temperature range expected for SFR, it is assumed that chemical effects will be dominating in comparison to temperature.

Table 4-5. Direct dependencies between the process "Sorption/uptake" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No. Sorption is a molecular-level chemical process that is not influenced by macroscopic geometry.	Not relevant.	No. Sorption of certain ions (e.g. sulphate) can lead to mineral alteration, which could create fractures.	Not relevant.
Temperature	Yes. Temperature will effect sorption equilibrium. Indirectly temperature will have an effect on the solids involved in sorption processes.	Neglected. Expected to be of minor relevance or, at least, the uncertainty on the effect of temperature will be lower than the uncertainty in other parameters.	No.	Not relevant.
Hydrological variables	Yes. The contact time between between solid and solution can be affected.	Yes. Indirectly included by the selection of K_d values.	No. There is an indirect effect since incorporation of major ions in HCP may cause mineral expansion and alter flowpaths.	Not relevant.
Mechanical stresses	No.	Not relevant.	No. See hydrological variables	Not relevant.
Material composition	Yes. The composition of the material influences its sorption properties.	Included in K_d where relevant	Yes. Incorporation of major ions in HCP may cause mineral alteration.	Considered in the context of cement degradation.
Water composition	Yes. Water composition can affect sorption.	Included in K_d where relevant.	Yes. Sorption on HCP influences dissolved concentration.	Included in K_d where relevant.
Gas variables	No. CO_2 can influence mineralogy. Indirectly through water composition.	Not relevant.	No. However, there is an indirect effect through the influence on dissolved concentrations. No significant effects expected.	Not relevant.

Hydrological variables. Waterflow can change the concentration of dissolved species hence reequilibrate the initial equilibrium, this has a direct influence on sorption. An indirect influence via flow-induced changes in porewater composition is not likely, as the porewater composition is well buffered. Changes in pressure of CO_2 should also have no (indirect) influence because the dissolved carbonate concentration is controlled by solubility equilibrium with calcite or other solids. On the other hand, incorporation of major ions present at relatively high concentrations in HCP minerals (and precipitation from homogeneous solution) may lead to an increase in volume and pore clogging, thus decreasing flow (and diffusion).

Mechanical stresses. Flowpaths may indirectly be influenced, see hydrological variables.

Material composition. Sorption is dependent on the composition of HCP and possibly on the aggregate composition. The composition of HCP is partly determined by the clinker composition and grout/concrete formulation, and partly by the extent and type of degradation, which occurs through contact with groundwater.

Water composition can have an important direct influence on sorption. In some cases, the dissolved concentration of radionuclides can influence the type and magnitude of sorption processes (see discussion of individual radionuclides further below). Elevated concentrations of ions such as (stable) chloride or sulphate in the wastes will lead to elevated concentrations in the pore solution, although the pore solution in HCP is well buffered with respect to pH and the concentration of some typical groundwater constituents. The same is true for organic complexing agents such as EDTA. Whether this will have a significant effect on sorption depends on the sorption process involved and needs to be evaluated for each element (or group of elements). Additionally, the water composition has an indirect influence on sorption by affecting cement degradation and the resulting mineral composition of HCP. Sorption can also influence the composition of incoming groundwater by incorporation of major ions into HCP. Most of the solid–liquid equilibria important for determining the water composition can be handled by using thermodynamic solubility products.

Gas variables. Certain gases can indirectly influence the material composition (mineralogy of HCP) which could affect sorption properties. However, no major effect is expected in comparison to mineral alteration through contact with water. Indirectly, gas composition can influence sorption through aqueous speciation (e.g. by changing the oxidation state of radionuclides).

Boundary conditions

Boundary conditions concerning sorption within the concrete packaging is

- Those of the transport processes that control the exchange of solutes between the surrounding water and the cementitious waste form compartments; i.e. those of the processes diffusion and advection/dispersion.
- All boundary conditions relevant for assessing cement/concrete degradation, as this process will partly determine the properties of the sorbing solid.

Further boundary conditions include the radionuclide concentration and distribution in the waste, as well as the temperature.

Model studies/experimental studies (including time perspective)

See Section 3.5.3.

Natural analogues/observations from nature

See Section 3.5.3.

Handling in the safety assessment in PSU

See Section 3.5.3.

Handling of uncertainties in PSU

See Section 3.5.3.

4.4.4 Colloid transport and filtering

Overview/general description

The general processes of colloid transport and filtering are introduced in Section 3.5.4, and these are also relevant to the packaging. The similar water chemistry in the waste and packaging mean that colloid concentrations are likely to be similar, i.e. low. Colloids may form within the cement or steel packaging materials but, perhaps more importantly, the packaging may filter colloids or prevent colloid transport between the waste form and the vault. Fractures in the concrete packaging will enhance the likelihood of colloidal transport through the packaging, as discussed in Section 3.5.4. In the steel packaging, the frequency and size of pores/fractures resulting from faults and/or corrosion will also affect the transport of colloids, and the corrosion products formed may affect the degree of filtering. However, the steel packaging is not considered to offer any resistance to transport in the safety case.

Dependencies between process and packaging variables

The dependencies between the process and packaging variables are adequately described by Table 3-13, for the waste form. The main differences arise from the steel packaging material and the lack of bitumen. Since steel packaging is not considered to offer any resistance to transport, the only difference from the dependencies in Table 3-13 is that the indirect influence on colloid formation due to radiolytic decomposition of organic material will not be relevant here, as bitumen is absent in the packaging.

Boundary conditions

See Section 3.5.4.

Model studies/experimental studies

See Section 3.5.4.

Natural analogues/observation from nature

See Section 3.5.4.

Time perspective

See Section 3.5.4.

Handling in the safety assessment SR-PSU

Low concentrations of colloids are expected and hence the influence of colloids on radionuclide transport has been neglected in the main scenario. Also, the cautiously neglected inherent physical and electrostatic filtering capacity in the stabilising matrices and concrete packaging, would restrict the transport of any colloids to and from the waste packages, and therefore further support this handling.

The impacts of bitumen colloids are neglected as discussed in Section 3.5.4.

Handling of uncertainties the safety assessment SR-PSU

See Section 3.5.4.

4.4.5 Dissolution, precipitation and recrystallisation

This section focuses on dissolution, precipitation and recrystallisation processes in concrete packaging. The dissolution−precipitation processes in steel packaging are described in Section 4.4.7. A general description of the fundamental processes of dissolution, precipitation and recrystallisation in cement is given in Section 3.5.5, and the processes in the concrete packaging are similar to those described for the cement waste matrices; therefore Section 3.5.5 is referred to where relevant.

Conditions for processes to occur

The rate and extent of dissolution–precipitation processes in the concrete packaging is determined by:

- The rate of advective water transport carrying dissolved species (see Section 4.4.1).
- The rate of diffusive transport of dissolved species (see Section 4.4.2).
- The composition of the concrete, including the assembly of hydrated cement clinker minerals.
- Any changes in the chemical composition of the concrete induced by chemical reactions with surrounding materials and porewater. This may in turn influence the microstructure of the concrete which would affect the transport properties.
- The composition of concrete packaging pore water, which is in turn, determined by local thermodynamic equilibria between the pore water and the solid hydrated cement minerals.
- Kinetic factors causing metastable equilibria or slow establishment of equilibria.
- The composition of the groundwater and the pore water of adjacent materials (rock, other barriers, waste).

Concrete packaging

Concrete packaging consists of hydrated cement clinker minerals and different filler and ballast materials.

Composition of concrete

Concrete is manufactured from anhydrous cement clinker materials, sand and gravel/crushed rock, and water. The water initiates the hydration of the cement clinker minerals, and the reaction products. During hydration, the anhydrous cement clinker minerals react with water and form new hydrated solid compounds that give the cement its mechanical strength. For certain purposes, different additives can be used in concrete, e.g. to improve flow properties and workability of the freshly mixed concrete slurry. In some cases significant amounts of filler materials such as slags or fly ashes are added to change the mechanical or chemical properties of the concrete.

Construction concrete mixtures commonly have a high amount of ballast material (75–80 wt-%), about 15 wt-% cement and 7–8 wt-% water. Details on the actual composition of concrete packaging in the SFR repository are presented in the Data report (SKB 2014c).

Composition of cement clinker minerals

Unhydrated cement clinker minerals are formed at high temperature in cement kilns. Typical unhydrated cement clinker minerals and components are given in Section 3.5.5.

Details on the actual composition of cement clinker minerals used for the manufacture of the concrete packaging in the SFR repository are presented in the Data report (SKB 2014c).

Hydration processes in cement

The unhydrated cement clinker minerals are highly reactive in contact with water. The hydration processes of relevance are described in detail in Section 3.5.5.

Chemical interactions with the waste

The concrete packaging is in direct contact with the waste, therefore, exchange of dissolved chemical species between the porewater of the waste and the concrete packaging may initiate chemical reactions that could affect the integrity of the concrete packaging. A thorough description of possible chemical interactions between the concrete packaging and species originating from the waste is provided in Section 3.5.5 and therefore not further described here.

The concrete packaging will act as a buffer for the surrounding concrete barriers against attack by deleterious species in the waste.

Chemical interactions with the other barriers and the groundwater

The presence of other concrete barriers around the concrete packaging, such as the silo wall and concrete walls in BMA, will protect the concrete packaging from direct attack by deleterious species in the groundwater. The chemical conditions at the surface of the concrete packaging may therefore remain fairly constant, characterised by a high pH, as long as the other barriers can withstand the action of the groundwater. Over time the effect of the groundwater will become increasingly important as the buffering components of the other concrete barriers become depleted.

Dependencies between process and packaging variables

The following table shows how dissolution, precipitation and recrystallisation processes in cement/concrete influences, and is influenced by, all concrete packaging variables defined in Section 2.2.2.

Influence by Geometry. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Table 4-6. Direct dependencies between the process "Dissolution, precipitation and recrystallisation" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Packaging dimensions and porosity (solid to liquid ratio) directly influence the process.	The packaging dimensions are considered. The solid-to-liquid ratio is considered.	Yes. Dissolution, precipitation and recrystallisation of solid phases can modify the porosity of the system.	Porosity changes due to dissolution–precipitation reactions are considered. Changes of the gross volume of the packaging due to internal chemical reactions with components released from the waste are considered.
Temperature	Yes. Temperature affects thermodynamic constants.	Constant reference temperature assumed over long periods.	Yes. Heat effect of initial hydration is expected to take place before disposal in SFR. Long term heat effect expected negligible.	Considered insignificant.
Hydrological variables	Yes. The amount of water has a direct influence on the process.	The water consumption during cement hydration is calculated.	No. Indirectly via changes of porosity and pore geometry that effects advection and diffusion.	Not relevant.
Mechanical stresses	Yes. In general, mechanical stresses may affect chemical equilibria where volume changes of solid phases are involved. Indirect influence may occur via stresses causing fracture formation, see Section 4.3.1, which may enhance dissolution.	The direct impact is judged insignificant for the safety analysis of SFR.	Yes. The formation of expansive solid phases, e.g. ettringite, may cause mechanical stresses. Indirect influence may occur via changes in the material composition causing reduction of strength possibly leading to fracture formation, see Section 4.3.1, or ultimately collapse.	Mechanical stresses is handelled by assigning appropiate hydraulic conductivity.
Material composition	Yes. Cement mass and mineralogy and amount and composition of waste material determines the reactions that may occur.	Included in modelling.	Yes. Modification of mineral composition and changes in mass due to degradation processes.	Included in modelling.
Water composition	Yes. Affects the reactions within the concrete packaging. Influences the rate of solute exchange with the surroundings.	Included in modelling.	Yes. Reaction with minerals results in changes in porewater composition.	Included in modelling.
Gas variables	Yes. Release of CO_2 from the waste could effect dissolution–precipitation.	Considered in calculations of gas generation.	Yes. CO_2 will be consumed by reaction with alkaline minerals and form e.g. calcite.	Included in modelling.

Influence on Geometry. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5. However, the gross volume of the concrete packaging is not expected to increase significantly, as the cement waste matrix is expected to buffer the impact of deleterious species released from the waste to a large extent.

Influence by Temperature. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Influence on Temperature. No direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Influence by Hydrological variables. Yes, a direct influence has been identified. The amount of water influences the extent of cement hydration during the early stage. This is accounted for in cement hydration modelling.

Using the reasoning given for the cement waste matrix, an indirect influence via the water composition is valid also here. The cement waste matrix is expected to buffer the impact of deleterious species released from waste to a large extent.

Influence on Hydrological variables. No direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5. However, the formation of expansive mineral phases as a result of sulphate release from certain waste materials is not expected in the concrete packaging since the waste matrix is expected to buffer the impact of deleterious species released from the waste to a large extent.

Influence by Mechanical stresses. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5. The influence is neglected within SR-PSU.

Influence on Mechanical stresses. Yes, a direct influence has been identified. Leakage of sulphate, which may result in the formation of the expanding mineral ettringite could create mechanical stresses in the concrete packaging. Therefore, the dissolution, precipitation and recrystallisation processes in the concrete packaging may affect the mechanical stresses in the repository. However, the cement waste matrix is expected to protect the cement packaging from the impact of deleterious species released from the waste to a large extent, such as sulphate. Indirectly, dissolution–precipitation processes, and to lesser extent the recrystallisation processes lead to reduced strength which could result in fracture formation, see Section 4.3.1, and eventually collapse. Dissolution of portlandite is reported to be the main cause for loss of strength in leached concrete (Carde et al. 1996). The formation of minerals with larger molar volumes, such as ettringite, within the cement waste matrix will also have an indirect effect on the mechanical stresses in the concrete packaging.

Influence by Material composition. Yes, a direct influence has been identified, using the reasoning given for the cement waste matrix, see Section 3.5.5. This variable has a very significant influence on this process.

Influence on Material composition. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Influence by Water composition. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Influence on Water composition. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Influence by Gas variables. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5. As discussed for the waste matrix, no significant gas formation is expected in the concrete packaging.

Any presence of a gas phase is treated in Section 4.2.1. The dissipation of dissolved gases is treated in Section 4.4.8.

Influence on Gas variables. Yes, a direct influence has been identified using the reasoning given for the cement waste matrix, see Section 3.5.5.

Boundary conditions

There are no particular boundary conditions to discuss for these processes. The relevant boundary conditions in order to treat the processes quantitatively are those of the transport processes that control the solutes transport between the concrete packaging, the waste, the surrounding barriers and the groundwater as adjacent system components, i.e. the boundary conditions of the processes diffusion (see Section 4.4.2) and advection (see Section 4.4.1).

Model studies/experimental studies

A large amount of research that is relevant for the processes of dissolution, precipitation, and recrystallisation in cementitious packaging has been reported in the scientific literature. A comprehensive list of studies is provided in Section 3.5.5, which describes these processes in the waste form, and most of these studies are equally relevant for the packaging. However, the studies focusing on the possible influence of salts from evaporator concentrates on cement and concrete (SKBdoc 1417785, 1032170) and the chemical degradation of cement conditioned ion exchange resins (Allard et al. 2002) are of less importance for the packaging.

Natural analogues/observations from nature

Natural analogues of relevance for dissolution, precipitation and recrystallisation processes in the cementitious waste forms are presented in Section 3.5.5. These studies are of equal relevance for the processes occurring in the packaging.

Time perspective

The time perspective considerations in Section 3.5.5 for the dissolution, precipitation and recrystallisation processes in cementitious waste forms are equally relevant for the concrete packaging.

Handling in the safety assessment SR-PSU

The durability of the concrete packaging is important as its degradation can affect the pH in the near field of the repository. The rate of degradation will also affect the geochemical conditions in the contained waste and nearby concrete barriers.

The concrete packaging is evaluated as a part of the waste domain in the long-term reactive transport modelling, hence it is not treated explicitly.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

A major uncertainty is related to the complex solubility of CSH phases, which has been represented by increasingly complex modeling approaches as compared to previous studies of cement degradation, see Model studies in Section 3.5.5.

Uncertainties also concern the fate and properties of different calcium sulpho-aluminates, calcium sulpho-ferrites (AF_m and AF_t), and similar calcium alumino- and calcium ferrite- mineral phases formed by reactions with chloride and carbonate. The volume change of the solid phases involved in these reactions is of particular interest, as this could result in the clogging of pores, or the formation of expanding minerals causing fracture formation.

Other uncertainties are associated with the long-term evolution of the pore network and the diffusivity in the cement paste. The diffusivity depends strongly on the porosity values, and the coupling between the dissolution processes and the resulting micro-structural changes are not fully understood.

Model simplification uncertainty in SR-PSU

The solid phases considered are a simplification of the CSH-phases that form during cement hydration. In addition, the representation of the AF_m and AF_t and similar compounds that may form as a result of reactions with sulphate, chloride and carbonate is also simplified.

Input data and data uncertainty in SR-PSU

The main uncertainties concern the composition of the concrete packaging, the thermodynamic stability of CSH gels, as well as AF_m and AF_t and similar compounds that may form as a result of reactions with sulphate, chloride and carbonate. In these calculations, data on and the uncertainties related to the content of soluble and/or degradable components of the waste that may result in exposure to sulphate, chloride and carbonate in increased concentrations are of particular concern.

Adequacy of references supporting the handling in SR-PSU

All supporting references have undergone a documented factual and quality review by SKB or have been published by refereed scientific journals.

4.4.6 Microbal processes

Overview/general description

A general description of microbial processes is given in Section 3.5.8.

Dependencies between microbial processes and packaging variables

Table 4-7 shows how microbial processes are influenced by and influence the packaging variables defined in Section 2.2.2. The handling in SR-PSU is indicated in the table and further described below.

Alkaline conditions are assumed to persist throughout the life time of SFR. Therefore, the microbial activity is expected to be very low.

For detailed description see Section 3.5.8.

Table 4-7. Direct dependencies between the processes "Microbial processes" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes.	Neglected as the microbial activity will be low under alkaline conditions.	Yes.	Neglected as the microbial activity will be low under alkaline conditions.
Temperature	Yes.	Neglected. Negligible effect in expected temperature interval.	Yes. In cases with high microbial activity, heat is generated.	Neglected as the microbial activity will be low under alkaline conditions.
Hydrological variables	Yes. The extent of microbial processes increases with increasing flow.	Neglected as the microbial activity will be low under alkaline conditions.	No. Indirectly via geometry since, microbial biofilms may clog flow paths.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. Microbial process rates depend on the composition of materials.	Neglected as the microbial activity will be low under alkaline conditions.	Yes. Microbial processes will degrade packaging material.	Neglected as the microbial activity will be low under alkaline conditions.
Water composition	Yes. The content of carbon sources, electron donors and acceptors will influence microbial processes.	No. Negligible effect, in the expected high pH, low redox range of waters expected.	Yes. Microbial processes will influence concentrations of water components, dissolved gases, Eh and to some extent pH.	Neglected as the microbial activity will be low under alkaline conditions.
Gas variables	Yes. Hydrogen and methane in gas phases can be utilised by microbial processes.	Neglected as the microbial activity will be low under alkaline conditions.	Yes. Microbial processes generate gases, but they also consume gases.	Neglected. Expected to be of minor importance compared to the gas production in the waste form.

Boundary conditions

The same boundary conditions as in Section 3.5.8 apply.

Model studies/experimental studies

Cement and concrete waste packages: see corresponding in Section 3.5.8.

Natural analogues/observations from nature

See Section 3.5.8, as the same analogues apply.

Time perspective

The time scale or time scales on which microbial processes occurs is related to the available nutrients and energy sources in the system, but in order to understand this in detail more research is needed. Access to electron acceptors and, under fermenting conditions, also removal of waste products are important factors affecting microbial activities.

Handling in the safety assessment SR-PSU

Microbial processes are neglected in the packaging in the SR-PSU.

Handling of uncertainties in SR-PSU

Uncertainties in mechanistic understanding

See corresponding section in 3.5.8.

Model simplification uncertainty

Since modelling is not performed, no uncertainties apply.

Input data and data uncertainty

Input data are not required as the process is neglected. Microbial processes are not considered to be a radiological risk.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU.
All supporting references are either peer-reviewed articles or documents which have undergone factual review.

4.4.7 Metal corrosion

Overview/general description

A general description of metal corrosion is given in Section 3.5.9. Steel corrosion is generally considered to be inhibited at the high pH maintained by cement. However, the presence of aggressive ions such as chloride and pH reduction due to carbonation may increase corrosion rates.

During SFR's operational period, the metallic containers will be exposed to oxygen and water. They are therefore likely to corrode to some extent, forming iron(III) oxy-hydroxide rusts, through an overall reaction exemplified by:

$4\ Fe^0 + 3\ O_2 + 6\ H_2O = 4\ Fe(OH)_3(s)$

After repository closure, the oxygen trapped in the system will be depleted through redox reactions and anoxia will develop. The container walls will then corrode anoxically using water as the oxidant (see Section 3.5.9) to form a mixed Fe(II)/Fe(III) oxide such as magnetite and hydrogen gas, according to the following model reaction:

$$3\ Fe(s) + 4\ H_2O = Fe_3O_4(s) + 4\ H_2(g)$$

Steel reinforcement bars are embedded in the concrete packaging. An increase in the volume of the steel, due to the formation of corrosion products, could therefore create stresses and fractures in the concrete packaging. Additionally, many waste types are stabilised or solidified in cement and some repository parts, such as the silo, will be backfilled with cement. Here, corrosion of the steel packaging could create stresses and fractures in the surrounding cement backfill or enclosed waste form.

The presence of high concentrations of aggressive ions, such as nitrate and sulphate, in precipitated sludge wastes, may also accelerate the corrosion of the inner surface of the steel packages. These ions enhance the dissolution of corrosion products formed on the steel surface, thereby decreasing the protective effect of the passivating layer.

Although it is not considered directly in this assessment, it is worth mentioning the higher resistance of stainless steel to corrosion versus the widely used carbon-steel. Both types of steel are used in the construction of the drums and steel-containers. The reported corrosion rates are around 2 orders of magnitude lower for stainless steel (Kursten et al. 2004) and there is also evidence of its greater longevity as a concrete reinforcement material in civil construction (see for example Crossland 2006).

Dependencies between process and packaging variables

Table 4-8 shows how metal corrosion is influenced by and influence the packaging variables defined in Section 2.2.2. The handling in SR-PSU is indicated in the table and further described below.

Table 4-8. Direct dependencies between the process "Metal corrosion" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry and pore space will affect water access to the metal components.	Not considered explicitly. Incorporated within the uncertainties associated with the corrosion rates.	No. Indirectly, formation of secondary products may affect the pore space and create fractures.	Not relevant.
Temperature	Yes. Temperature affects corrosion rates and products.	Not considered due to the narrow temperature range expected. Uncertainties associated with the corrosion rates include the possible variations due to temperature.	Yes.	Neglected. Thermal effect due to steel oxidation predicted to be low, see Section 3.1.2.
Hydrological variables	Yes. Saturation degree affects metal corrosion.	The system is assumed to be saturated instantaneously.	No. Indirectly via geometry.	Not relevant.
Mechanical stresses	No. Indirectly via geometry.	Not relevant.	Yes. Formation of corrosion products with different molar volumes may create mechanical stress.	Considered in the selection of hydraulic conductivity.
Material composition	Yes. The composition of the material determines the corrosion rates and products.	Considered by taking into account a range of corrosion rates from the literature.	Yes. The composition of the material will change due to the formation of corrosion products.	Considered in the redox modelling.
Water composition	Yes. Water composition can affect corrosion rates and products.	Not specifically handled, included in the range of corrosion rates considered.	Yes. Corrosion will create more reducing conditions.	Considered in the Redox modelling.
Gas variables	No. Indirectly, affecting rates and corrosion products.	Not relevant.	Yes. Corrosion under anaerobic conditions will cause hydrogen build-up.	The gas production is treated in Section 3.5.10.

Geometry. Geometry affects corrosion processes as the dimensions of the steel packaging define the surface area to mass ratio.

Temperature. Temperature affects corrosion rates and the type of corrosion products formed. However, the temperature within SFR is only expected to vary by a few degrees prior to glaciation. Therefore, this effect can be neglected.

Hydrological variables. Hydrological variables only have an indirect effect on the corrosion of the steel packaging. The flow and saturation degree will affect corrosion in terms of the flux of water and other chemical species that can influence corrosion in and out of the system.

Mechanical stresses. Mechanical stresses can influence corrosion indirectly via fracturing, generating new water pathways and increasing the surface area exposed to water.

Material composition. The initial material composition will affect the rate and extent of the corrosion process.

Water composition. The water composition will affect the corrosion process, specifically the rate and the products formed. The presence of high concentrations of Cl^- favours localised steel corrosion under oxidising conditions. The presence of dissolved carbon dioxide increases the corrosion rate of iron in water by decreasing the pH of the water. The presence of complexing agents in the porewater may affect corrosion through re-dissolution of protective corrosion product layers on the steel surface. The presence of alkaline conditions may cause depassivation of metallic surfaces, as presented in Section 3.5.9.

Gas variables. The gas composition will affect the corrosion rate and the type of secondary products indirectly, via gas dissolution that affects the groundwater composition.

Boundary conditions

It is likely that some packaging will have corroded to an extent before repository closure, due to their exposure to air and water during the operational period.

Post closure boundary conditions are the amount of oxygen present, the composition of the water in contact with the packaging, and the water heads and pressures affecting the ingress of water, water flow rates.

Model studies/experimental studies

There are many model and experimental studies in the literature supporting the corrosion of steel and other metals. Kursten et al. (2004) provide a thorough review of the literature and more details and examples are given in Section 3.5.9.

Natural analogues/observation from nature

The corrosion of archaeological iron artefacts has been studied. A short review of these can be found in the SR-Site fuel and canister process report (SKB 2010b) as well as in Section 3.5.9.

Time perspective

When the repository is closed and pumping ceases, water will saturate the system. It has been estimated that it will take 25–100 years for the silo to saturate, and a few years for other parts of the repository. Following water saturation, trapped oxygen will be consumed by microbial activity and/or redox reactions, and reducing conditions will be established. From this point, metal corrosion will be an anaerobic process, generating hydrogen gas.

Handling in the safety assessment SR-PSU

The steel packaging is not considered to have a long-term barrier function in the safety assessment.

Metal corrosion is considered explicitly in terms of the generation of reducing conditions see Section 3.5.9.

Metal corrosion is also considered as one of the main gas producing processes in the repository see Section 3.5.10.

Handling of uncertainties the safety assessment SR-PSU

Conceptual uncertainties are discussed and numerical uncertainties are addressed through sensitivity analyses in the safety assessment.

Uncertainties in mechanistic understanding

Steel corrosion is a well characterised process. The main uncertainties in the mechanistic understanding relate to the corrosion rates and the corrosion products formed.

Model simplification uncertainty

Corrosion is one of the main processes driving the evolution of the redox conditions in the repository (Duro et al. 2012c). The main model simplification is the treatment of all metal in the waste and packaging as a single, homogeneous component. This means that the uncertainties described in Section 3.5.9 for metallic waste components apply here, in summary:

- Immediate contact of the bare metal surface with oxygen-equilibrated water.
- Immediate oxidation of the metal surface by the available oxygen.
- Onset of kinetically driven anaerobic corrosion once oxygen is depleted.
- Infinite water availability for anaerobic corrosion.
- Constant corrosion rate over time.

A more detailed description of the simplifications can be found in Section 3.5.9.

Input data and data uncertainty

A range of input data is required for this process, specifically:

- Inventory of metal in packaging.
- Extent to which the metals in packaging have corroded at the point of repository closure.
- Surface area and composition of exposed metal.
- Type of groundwater contacting the packaging.
- Groundwater flow through the repository, which may influence mass fluxes and the rate of corrosion at the exposed surfaces, and affect the uncertainties introduced by the assumption of infinite water availability for anoxic metal corrosion.

Most of the input data uncertainties can be addressed through sensitivity analyses of the corrosion rates and the groundwater flow rates.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU. All supporting references are either peer-reviewed articles or documents which have undergone factual review.

4.4.8 Gas formation and transport

Overview/general description

Gas formation

Metal corrosion is responsible for gas generation in the packaging. A general overview of metal corrosion processes is given in Section 3.5.9. The metallic packages are made of either carbon or stainless steel, thus the main component is iron. Steel containers are likely to corrode to some degree during the operational stage of SFR, due to the exposure to air and water. After closure, oxygen will become depleted in the system, thus the main gas generation process in the steel packaging will be anoxic corrosion by water, according to the following reaction:

$3\ Fe(s) + 4\ H_2O = Fe_3O_4(s) + 4\ H_2(g)$

Gas transport

The transport of gases across the packaging will involve gases dissolved in water and those present in the gas phase, once the solubility of the gas in water is exceeded (according to Henry's law).

Dependencies between process and packaging variables

The direct dependencies between the process and the defined packaging variables (defined in Section 2.2.2) are summarised in Table 4-9.

Table 4-9. Direct dependencies between the process "Gas formation and transport" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Gas formation is influenced, since the geometry may affect contact of water with the metal, and thus gas generation processes. Geometry can also affect gas transport.	Geometry is included in the gas generation calculations. The packaging is assumed to offer negligible resistance to gas transport.	No. Indirectly via mechanical stresses.	Not relevant.
Temperature	Yes. Temperature affects gas solubilities.	Neglected due to the limited variations in temperature.	Yes.	Neglected. Gas formation is expected to have a negligible effect on temperature.
Hydrological variables	Yes. The formation of a separate gas phase depends on pressure and flows, and this affects gas transport.	Discussed conceptually and bounding cases are modelled.	No.	Not relevant.
Mechanical stresses	No. Indirectly, since stresses may create preferential paths (geometry) for water and thereby affect gas generation and transport processes.	Not relevant.	Yes. Mechanical stresses created through the generation of a separated gas phase.	See fracturing processes, Section 3.4.1.
Material composition	Yes. The composition of the material determines the total amount of gas volume generated. The gas transport is also affected by the material composition.	The material composition is used as input data for the gas generation. The packaging is assumed to offer negligible resistance to gas transport.	No.	Not relevant.
Water composition	Yes. Water composition can affect gas/liquid equilibria and indirectly gas formation rates.	Gas solubilities are accounted for in the modelling of the redox evolution of the repository.	Yes. The gas generated can dissolve in water and change the water composition.	Neglected in gas transport calculations. The formed gas is assumed to remain in the gas phase. Included in the modelling of the redox evolution.
Gas variables	Yes.	Incorporated in the gas/liquid equilibria. The packaging is assumed to offer negligible resistance to gas transport.	Yes.	Neglected in gas transport calculations. The formed gas is assumed to remain in the gas phase. Included in the modelling of the redox evolution. The amount of generated gas is calculated.

Geometry. Geometry affects gas transport and indirectly also gas formation processes.

Temperature. Temperature can affect gas solubility in groundwater and therefore the composition of gas in equilibrium with water. The small temperature variations expected in the repository are not considered to have a significant effect on the assessment. Gas generation processes are also unlikely to influence the temperature of the waste.

Hydrological variables. Hydrological variables only exert an indirect influence on gas formation via metal corrosion (see Section 3.5.9). While gas transport is affected by the degree of saturation, this consideration is not of particular relevance to the steel packaging; the packaging is not taken into account in the safety assessment and is considered to exert no influence on gas migration.

Mechanical stresses. Stresses may result in container rupture and, thus, indirectly via geometry enhance gas transport processes.

Material composition. The composition of the packaging material determines the total amount of gas volume that can be generated and the rate at which it is generated.

Water composition. Water composition can affect gas/liquid equilibria and, indirectly, the rates and total amount of gas produced.

Gas variables. The composition of the gases will affect the process of gas transport and vice versa, through the displacement of gas/liquid equilibria and creating the necessary pressures for gas transport.

Boundary conditions

Boundary conditions include the generation of gases in the waste matrices and those relevant to advection and diffusion, i.e. pressures, heads, temperature and the hydrodynamic properties of the external backfilling of the vaults.

Model studies/experimental studies

See Section 3.5.10.

Natural analogues/observation from nature

No natural analogues for gas generation or migration are available.

Time perspective

Anoxic corrosion of the steel packaging material will begin once the oxygen trapped in the repository has been consumed, shortly after closure. Hydrogen generation will occur throughout the time of interest for the safety assessment (100,000 years in the PSU).

According to the calculations by Duro et al. (2012c), the most important hydrogen-generating process is anaerobic metal corrosion. The entire metal inventory in SFR was estimated to generate more than 1 million cubic meters of gas (calculated at standard T and P) over the assessment period.

The steel packaging is assumed to offer no resistance to gas transport. Therefore dissolved gas transport is considered to occur from the time the gas is generated and, gas phase transport will occur once its solubility in water is exceeded. The time at which gas is calculated to escape through preferential pathways due to fracturing is therefore not affected by the packaging.

Handling in the safety assessment SR-PSU

The amount of $H_2(g)$ from the corrosion of reinforcement bars and steel packaging is included in the gas calculations, see Section 3.5.10.

The gas is assumed to escape through the packaging without any delay or causing any damage.

Handling of uncertainties in the safety assessment SR-PSU

Uncertainties in mechanistic understanding

The uncertainties associated with the corrosion of steel, reported in Section 3.5.9, also affect the estimation of the amount of gas generated. The uncertainties related to the exposure of the metal surface to water and the protection offered by the passivating layer over time are quantified using sensitivity analysis on the corrosion rate.

Model simplification uncertainty

From the perspective of gas generation, the main model simplification is the assumption that the waste form and packaging comprise a single source of gas. However, this does not introduce notable uncertainties in the repository assessment.

From the perspective of gas transport, the packaging is considered transparent. The uncertainty lies in whether the packaging material could act as a barrier for gas transport.

Input data and data uncertainty

The final inventory of waste packages, and thus total steel surface area, is currently estimated, introducing significant uncertainties in the gas generation calculations. Other input data and uncertainties relate to the corrosion rates and initial condition of the steel at repository closure. These uncertainties are bound through sensitivity analyses of the corrosion rates.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU.
All supporting references are either peer-reviewed articles or documents which have undergone factual review.

4.5 Radionuclide transport

4.5.1 Speciation of radionuclides

The general description of the radionuclide speciation is given in Section 3.6.1.

This process is only relevant for the packaging that contains a pore system, i.e. concrete packaging. Speciation within the steel packaging material is not relevant.

Dependencies between processes and packaging variables

The following table (Table 4-10) shows how the process influences, and is influenced by, all packaging variables defined in Section 2.2.2.

Temperature. The effect of temperature on radionuclide aqueous speciation is relatively well understood and can be handled (within the relatively narrow range expected for the repository) by speciation models (Stumm and Morgan 1996, Puigdomenech et al. 1997). The effect on solubility can be more difficult to predict, especially in cases where the corresponding solid phases become relevant (Puigdomenech et al. 1997). For effects on sorption/uptake, see Section 3.5.3.

Water composition is the main factor influencing speciation. Therefore, other variables that influence water composition (such as the composition of solids and gas) will affect radionuclide speciation indirectly. Conversely, trace concentrations of radionuclides entering the waste form void volume will not have a notable effect on bulk water properties. Speciation affects the chemical form of the dissolved radionuclides, this is handled in the selection of K_d values see Section 3.5.3.

Table 4-10. Direct dependencies between the process "Speciation of radionuclides" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	No. Speciation is a molecular-level chemical process which is not influenced by macroscopic geometry.	Not relevant.	No.	Not relevant.
Temperature	Yes. Temperature will have effect on speciation.	Neglected. Thermodynamic data is used at the temperature given in the thermodynamic data set.	No.	Not relevant.
Hydrological variables	No. No direct influence on speciation.	Not relevant.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Material composition	No.Indirectly through porewater composition.	Not relevant.	No.	Not relevant.
Water composition	Yes. Water composition directly affects speciation.	Included in the speciation calculations and considered in the selection of K_d.	Yes. Speciation effects the chemical form of the dissolved radionuclides.	Included in the speciation calculations and considered in the selection of K_d.
Gas variables	No. Indirectly by influencing water composition.	Not relevant.	No.	Not relevant.

Boundary conditions

See Section 3.6.1.

Model studies/experimental studies

See Section 3.6.1.

Natural analogues/observations from nature

See Section 3.6.1.

Time perspective

See Section 3.6.1.

Handling in the safety assessment SR-PSU

See Section 3.6.1.

Handling of uncertainties in SR-PSU

See Section 3.6.1.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU. All supporting references are either peer-reviewed articles or documents which have undergone factual review.

4.5.2 Transport of radionuclides in the water phase

Overview/general description

The radionuclide transport processes for the concrete packaging is very similar to the corresponding processes for the cement based materials in the waste form (see Section 3.6.2).

The steel packaging have not been designed for a long-term containment function and therefore can not be considered to constitute any particular resistance to radionuclide transport. Hence, the steel packaging is not further treated in this section. Sorption onto corrosion products might be a relevant retardation process affecting the overall transport in the packaging.

Dependencies between processes and packaging variables

Table 4-11 shows the influences between the process and the defined packaging variables defined in Section 2.2.2.

Boundary conditions

The inner boundary for radionuclide transport processes in the packaging is the concentration of nuclides in the waste form. The outer boundary is the concentration in water in the compartment surrounding the waste packages.

Table 4-11. Direct dependencies between the processes "Transport of radionuclides in the water phase" and the defined packaging variables and a short note on the handling in SR-PSU.

Parameter	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Gives the volumes, transport length,porosity and areas available for transport.	Yes. Geometry variables are included in radionuclide transport model.	No.	Not relevant.
Temperature	Yes. Diffusivity and sorption/uptake will be affected.	Neglected due to the expected small temperature variations.	No.	Not relevant.
Hydrological variables	Yes. Water fluxes are very important for advective transport of radionuclides.	Yes. Detailed flow parameters are included in the radionuclide transport model.	No.	Not relevant.
Mechanical stresses	No.	Not relevant.	No.	Not relevant.
Material composition	Yes. Sorption/uptake properties are highly dependent on material composition.	Yes. Material-specific K_d values are included in the radionuclide transport model.	No.	Not relevant.
Water composition	Yes. Sorption/ uptake properties are dependent on water composition.	Yes. Considered in the selection of K_d data.	Yes.	The porewater concentration of radionuclides in all parts of the system is calculated.
Gas variables	Yes. Build-up of gas pressure may expel water containing radionuclides.	Considered in a gas driven advection scenario.	No.	Not relevant.

Model studies/experimental studies

In the most recent safety assessments of SFR, SAFE (Lindgren et al. 2001) and SAR-08 (Thomson et al. 2008b), the steel packaging was handled in the same way as in SR-PSU, i.e. the steel packaging was assumed to corrode to such an extent that the retention effect of the steel packaging could be neglected. Also, transport in cement based materials was handled using the same approach as in SR-PSU.

Time perspective

Transport of radionuclides through the concrete packaging will be relevant throughout the period considered in the safety assessment.

During a short initial phase, the steel packaging will inhibit all nuclide transport. However this effect is not accounted for in the calculations, due to the difficulty in predicting the time for steel packaging to degrade. Instead the steel packaging is not considered to act as a barrier.

Handling in the safety assessment

Radionuclide transport in the cement based packaging is handled in the same way as for cement based waste form materials (see Section 3.6.2).

The steel packaging is assumed to offer no retardation effect.

Handling of uncertainties

See Section 3.6.2.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU. All supporting references are either peer-reviewed articles or documents which have undergone factual review.

4.5.3 Transport of radionuclides in the gas phase

Overview/general description

For the gases generated in the waste form and packaging to migrate out of the repository, there must be gas pathways in the backfill, engineered barriers and/or the surrounding geosphere. Once a gas pathway has been created and gas breakthrough has occurred, radionuclides distributed in the gas phase will be transported out of the system.

Some of the factors affecting transport of radionuclides in gas phase are:

- Rate of gas generation.
- Generation of paths for gas migration into the surrounding environment.

A fraction of the gaseous radionuclides present will be dissolved in the aqueous phase, in an equilibrium defined by Henry's law. When gas is transported away, dissolved gas will move into the gas phase to restore equilibrium. The extent to which this happens will depend on the relative concentrations of the radionuclides and stable isotopes in the two phases and the rates of diffusion in the water phase, as described for the waste form. Hydrogen will be the main gas generated due to the corrosion of steel packaging. As presented in Section 3.6.3, H-3 could be incorporated into H_2 that forms during corrosion of the steel packaging and be transported as a gas. However, formation of radioactive gases will occur predominately in the waste, and these will mix with gases produced in the packaging once a pathway is created.

Dependencies between process and packaging variables

Table 4-12 shows how the process influences, and is influenced by, all packaging variables defined in Section 2.2.2.

Table 4-12. Direct dependencies between the process "Transport of radionuclides in the gas phase" and the defined packaging variables and a short note on the handling in SR-PSU.

Variable	Variable influence on process		Process influence on variable	
	Influence present?	Handling of influence	Influence present?	Handling of influence
Geometry	Yes. Geometry may affect gas-phase transport.	Neglected. The packaging is considered to offer no resistance to gas transport.	No.	Not relevant.
Temperature	Yes.Temperature can affect gas streams, but the temperature range is very narrow in the repository.	Neglected. Not considered sufficiently relevant.	No.	Not relevant.
Hydrological variables	Yes. Hydrological variables will determine the rate at which water is expelled from the system thus the initial rate of gas-mediated transport.	Neglected. The packaging is considered to offer no resistance to gas transport.	No.	Not relevant.
Mechanical stresses	No. However an indirect effect via geometry, since stresses may create preferential paths for water and affect gas migration.	Not relevant.	No.	Not relevant.
Material composition	No. An indirect effect, since the composition of the packaging (steel or concrete) will determine whether gas is generated or not.	Not relevant.	No.	Not relevant.
Water composition	Yes. Water composition can affect the partitioning of gaseous radionuclides between the gas and dissolved phases.	Considered in radionuclide transport modelling.	No.	Not relevant.
Gas variables	Yes. Gas pressures and composition will effect the transport of gaseous radionuclides.	Considered in radionuclide transport modelling.	No.	Not relevant.

Geometry. The geometry of the packaging can affect gas transport and thus gas phase radionuclide transport.

Temperature. Temperature could affect gas phase transport of radionuclides due to its impact on the gas variables and thus on the formation of gaseous phases. However, the low temperature variation expected in the repository means that it is not considered relevant for SFR.

Hydrological variables. Hydrological variables will affect the rate at which water is expelled from the system to allow gas migration, and therefore affect the rate at which gas leaves the system including gas phase radionuclides.

Mechanical stresses. Only indirectly, stresses may create preferential paths for water transport and affect gas migration processes.

Material composition. The composition of the material determines the amount of gas volume generated as well as the radionuclides able to be transported as gases. In principle, only the steel packages will generate gas. Concrete degradation is not foreseen to create gases.

Water composition. Water composition can affect the partitioning of radionuclides between gas and dissolved phases and indirectly the rate and total amount of gas build-up.

Gas variables. Gas pressures and compositions will affect gaseous radionuclide transport. Gas build-up in the system may create overpressures and generate new water/gas pathways that can favour gas phase transport of radionuclides.

Boundary conditions

Boundary conditions will define the state of the packaging on disposal. The rate of gas generation will depend on the initial corrosion state of the steel packaging walls and reinforcement in concrete packaging. The H_2 generating processes of anaerobic steel corrosion will occur once the initial oxygen trapped in the repository is exhausted. The integrity of the barriers of the vaults will affect how readily pathways are created for gas escape. Temperature should also be defined in the boundary conditions given that it controls the solubility of a gas in water as well as the pressure associated with the gas phase (SKB 2008a).

Model studies/experimental studies

All studies relating to the generation of gases through anoxic steel corrosion are of interest in this section. These are reviewed in Section 3.5.9.

Natural analogues/observation from nature

Not applicable.

Time perspective

Transport of radionuclides in the gas phase may occur from the moment a gas pathway is created, which will occur when gas is generated in sufficient amounts to produce a gas escape route from the repository. The main gas generated from the packaging is hydrogen, due to the anoxic corrosion of steel. Therefore, the rate of hydrogen generation and accumulation can be compared with the pressure of the repository to provide a rough estimation of the time of the onset of gas migration.

Handling in the safety assessment SR-PSU

The packaging is assumed to offer no resistance to gas transport.

Handling of uncertainties the safety assessment SR-PSU

Uncertainties in mechanistic understanding

All uncertainties affecting the processes of gas formation, see Section 3.5.10, will also affect the transport of radionuclides in the gas phase.

Model simplification uncertainty

Most uncertainties in the model simplification relate to gas formation, which are discussed in detail in Section 3.5.10. Additional model uncertainties relate to the conceptualisation of gas escape from the repository.

Input data and data uncertainty

The main uncertainties, besides those associated with gas formation, are related to the waste inventory of radionuclides likely to form a gaseous species. The final number of different types of waste packaging is also uncertain.

Adequacy of references supporting the handling in SR-PSU

The references are judged to be adequate and sufficient to support the handling in SR-PSU. All supporting references are either peer-reviewed articles or documents which have undergone factual review.

5 Summary of handling of the processes in SR-PSU

5.1 Waste form processes

Table 5-1 summaries the handling of waste form processes in the safety assessment SR-PSU, as stated in this report. In the table, the process is associated with a brief verbal description of how it will be handled.

Table 5-1. Process table for the waste form describing how processes will be handled in the safety assessment SR-PSU.

Process	Handling
Radioactive decay	The process is included in the model calculations of radionuclide transport.
Radiation attenuation/heat generation	Radiation attenuation is neglected due to the low radioactivity. Heat generation caused by radiation in the waste has been shown to be negligible, as has heat generation from corrosion, due to the low radioactivity and limited quantities of aluminium in the waste.
Radiolytic decomposition of organic material	Swelling due to radiolytic decomposition of bitumen is neglected due to the low radioactivity of the waste and the fact that it is judged to be subordinate to swelling due to water uptake. Formation of complexing agents, i.e. oxalic acid, from degradation of bitumen is neglected due to negligible radiolytic degradation of bitumen under the conditions prevailing in the waste. Ettringite formation from release of sulphate is neglected due to the negligible radiolytic degradation rate of the ion exchange resins.
Water radiolysis	Water radiolysis in the waste has been shown to be negligible due to the low radioactivity of the waste.
Heat transport	The temperature evolution in SFR is controlled completely by the external conditions, i.e. the temperature is determined by the surrounding rock. The influence of the temperature evolution on radionuclide transport is neglected.
Phase changes/freezing	Freezing is expected to result in structural degradation (cracking) of cement, concrete and bitumen, materials that are present as a stabilising matrix in different waste packages. This is handled by choosing suitable values of hydraulic conductivity and diffusivity in the modelling of e.g. water flow, concrete degradation and radionuclide transport.
Water uptake and transport during unsaturated conditions	Water uptake and water transport during unsaturated conditions are only relevant during a short initial period. Water uptake defines the time when release of radionuclides begins. Due to the fact that unsaturated conditions prevail for a relatively short time, no further handling is deemed to be needed in the safety assessment.
Water transport under saturated conditions	The process “water flow under saturated conditions” will be crucial for the safety assessment. The water flow through the waste is estimated by numerical modelling. The time at which water saturation is reached in different parts of the repository is estimated by numerical modelling.
Fracturing	Fracturing is handled by choosing suitable values of hydraulic conductivity and diffusivity in the modelling of e.g. water flow, concrete degradation and radionuclide transport.
Advective transport of dissolved species	Advection plays a central role for the transport of dissolved species in all parts of SFR, including the waste. The advection process is included in the modelling of e.g. concrete degradation and radionuclide transport.
Diffusive transport of dissolved species	Diffusion plays a central role for the transport dissolved species in all parts of SFR, including the waste. The diffusion process is included in the modelling of e.g. concrete degradation and radionuclide transport.
Sorption/uptake	Sorption/uptake of radionuclides is included in the modelling of radionuclide transport. Sorption/uptake is quantified by using partitioning coefficient (K_d) values, which are dependent on element/oxidation state.
Colloid formation and transport	Low concentrations of colloids are expected in most parts of the repository, so the influence of colloids on radionuclide transport is neglected in the main scenario. Bitumen colloids are expected in high concentrations in those parts of the repository that contain bitumen. However, the degree of complexation with radionuclides is expected to be low, so the influence of bitumen colloids on radionuclide transport is neglected.
Dissolution, precipitation and recrystallisation	The durability of the cement matrix is important, since degradation can affect pH. The durability of the cement matrix is evaluated by reactive transport modelling.
Degradation of organic materials	Degradation of cellulose to ISA in an alkaline environment is the only chemical degradation process that is significant for safety. Other chemicals present in SFR have been judged to be stable under the conditions that prevail in SFR or to degrade to substances that are not expected to influence sorption. Their ability to influence the mobility of radionuclides is therefore judged in their original form.

Process	Handling
Water uptake/swelling	Knowledge of swelling pressure as a function of expansion volume is used to evaluate how much pressure structures and barriers surrounding bituminised waste will experience. The effect of water uptake on the subsequent release of radionuclides is handled by assigning appropriate release rates for the radionuclides from the bituminised waste.
Microbial processes	Due to the expected high pH, the effect of microbial processes on the function of the repository is neglected from a safety assessment perspective, with the exception of the gas formation process.
Metal corrosion	Formation of fractures due to less dense corrosion products is included qualitatively in the choice of hydraulic conductivities. Corrosion of metallic waste is taken into account as a contribution to the creation of reducing conditions. The evolution of redox conditions is modelled. The metal corrosion process is judged to be one of the main gas formation processes.
Gas formation and transport	The volume of gas that is formed is calculated. Gas transport in the waste is not treated specifically. The waste is considered only as a source of gas. Displacement of pore water containing radionuclides is modelled as a function of gas formation.
Speciation of radionuclides	Speciation of the redox-sensitive radionuclides Se, Tc, Np and Pu is calculated with thermodynamic data (i.e. assuming equilibrium). The radionuclide concentrations in the waste are estimated (based on the inventory and geometrical considerations) to be below all relevant solubility limits. Speciation of non-redox sensitive radionuclides is taken into account indirectly by the choice of K_d values.
Transport of radionuclides in the water phase	Radionuclide transport in the waste is included in the radionuclide transport model for the whole repository system.
Transport of radionuclides in the gas phase	Formation of methane due to microbial activity has been shown to be subordinate, as long as there are other electron acceptors present. Release of C-14 as methane is handled by scoping calculations.

5.2 Steel and concrete packaging processes

Table 5-2 summaries the handling of steel and concrete packaging processes in the safety assessment SR-PSU, as discussed in this report. In the table, the process is associated with a brief description of how it will be handled.

Table 5-2. Process table for the steel and concrete packaging describing how processes will be handled in the safety assessment SR-PSU.

Process	Handling
Heat transport	See waste form
Phase changes/freezing	See waste form
Water uptake and transport during unsaturated conditions	See waste form
Water transport under saturated conditions	See waste form
Fracturing/deformation	There are no requirements regarding the long-term function of steel packaging. For concrete packaging, see waste form.
Advective transport of dissolved species	See waste form
Diffusive transport of dissolved species	Diffusion in concrete packaging, see waste form. In the case of steel packaging, no credit is given for transport resistance in the modelling due to uncertainties in the scope of corrosion during the operating phase.
Sorption/uptake	See waste form
Colloid formation and transport	See waste form
Dissolution, precipitation and recrystallisation	The durability of the concrete packaging is important, since its degradation can affect the pH in the near-field of the repository. The degradation rate also affects the chemical conditions in the waste and nearby concrete barriers. Concrete packaging is evaluated as a part of the waste domain in the long-term reactive transport modelling, hence these processes are not treated separately.
Microbial processes	Microbial processes in the steel and concrete packaging are neglected.
Metal corrosion	Steel packaging is assumed not to have any long-term barrier function in the safety assessment. Metal corrosion is included explicitly since it contributes to reducing conditions. Metal corrosion is also included in the safety assessment as one of the dominant gas-generating processes.
Gas formation and transport	The quantity of $H_2(g)$ from corrosion of steel is included in the calculations of the amount of gas formed. The gas is assumed to be released from the packaging without delay and without causing any damage.
Speciation of radionuclides	See waste form
Transport of radionuclides in the water phase	For concrete packaging, see waste form. In the case of steel packaging, no credit is given for transport resistance in the modelling due to uncertainties in the extent of corrosion during the operating phase.
Transport of radionuclides in the gas phase	It is assumed that the packaging do not offer any transport resistance to gases.

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SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications. References to SKB's unpublished documents are listed separately at the end of the reference list. Unpublished documents will be submitted upon request to document@skb.se.

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