Forsmark site investigation

Study of U oxidation states in groundwater with high U concentrations

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SKB

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

Abstract

Redox speciation of U in groundwater, i.e. occurrence of U in its oxidation states U(IV) and U(VI), was studied in groundwater samples from Forsmark with high U concentrations. U(IV) and U(VI) fractions were separated from groundwater during sampling using a U(IV) specific co-precipitation technique which keeps U(VI) in solution. The precipitate was separated by filtering and the filter and filtrate water analysed for U. The U concentrations show how much occurs as U(IV) relative to U(VI). Results show that U occurs in the groundwater mainly in the U(VI) oxidation state. The isotopic activity ratio $^{234}U/^{238}U$ is similar in U(IV) and U(VI) which suggests that both fractions represent the same U inventory.

Sammanfattning

Uranets redoxstatus i grundvatten, dvs om uranet företrädesvis föreligger som U(IV) eller U(VI), undersöktes i grundvatten med hög uranhalt. Uran som U(IV) respektive U(VI) separerades från varandra i samband med provtagningen av grundvattnet. Separeringen skedde med en metod som innebär specifik utfällning av U(IV) medan U(VI) hålls i lösning. Fällningen avlägsnades genom filtrering. Filter och filtrat analyserades med avseende på uran. Urankoncentrationerna visar hur stor andel av uranet som föreligger som U(IV) respektive U(VI). Resultaten indikerar att uranet i grundvattenproverna i huvudsak föreligger som U(VI). Isotopkvoten $^{234}U/^{238}U$ är den samma i båda fraktionerna, dvs U(IV) i filtret och U(VI) i filtratet, vilket tyder på att de representerar samma uran inventarium.

Contents

1   Introduction

This document reports the results gained by an investigation of uranium (U) and its oxidation states in groundwater. The special activity was performed within the site investigation at Forsmark /SKB 2001ab, 2006/ due to the observed high U concentration in some of the groundwaters /Wacker et al. 2004ab/. The work was carried out in accordance with activity plan AP PF 400-06-039. Uranium oxidation states have not been determined before in Forsmark.

Several tens of µg/L of U have been repeatedly measured in reducing groundwaters from borehole KFM02A, section 491–515 m. Such high U concentrations under reducing conditions are difficult to explain unless U occurs in the U(VI) oxidation state.

Uranium occurs in groundwaters in two stable oxidation states, U(IV) and U(VI), with U(IV) concentrations in groundwater at low Eh levels, usually less than 10^{-8} M (< 2.4 µg/L) because of the very low solubility of U(IV) minerals.

The U(IV) and U(VI) fractions were separated from groundwater during sampling using a U(IV) specific co-precipitation technique followed by U analysis of the precipitate and filtrate.

Original data from the reported activity are stored in the primary database SICADA where they are traceable by the activity plan number (AP PF 400-06-039). Only data in databases are accepted for further interpretation and modelling. The data presented in this report are regarded as copies of the original data. Data in the databases may be revised, if needed. Such revisions will not necessarily result in a revision of the P-report. Minor revisions are normally presented as supplements, available at www.skb.se.
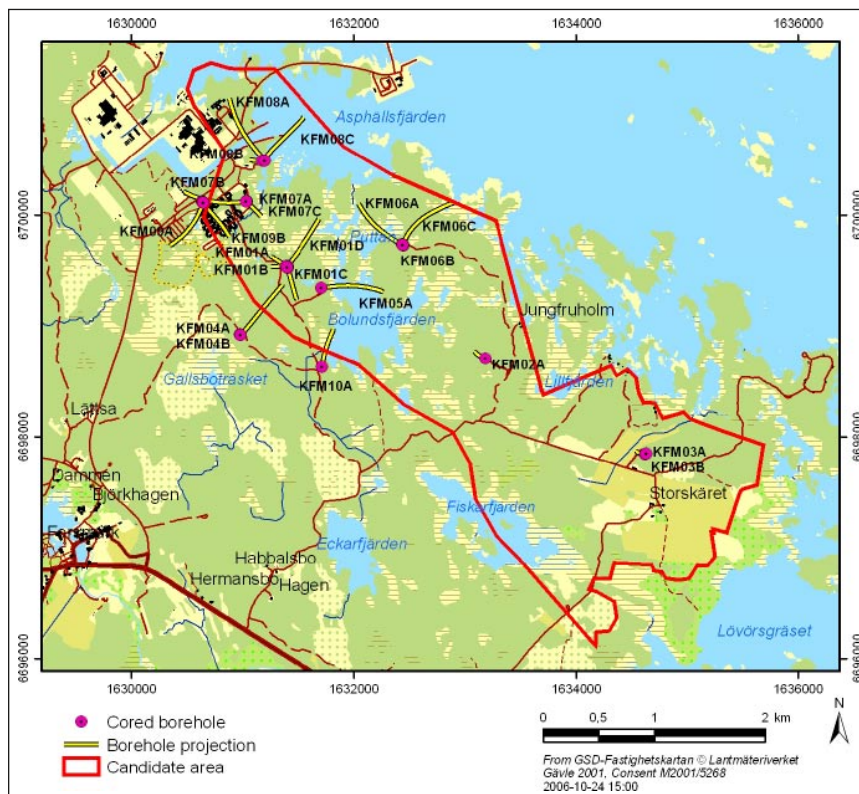

Figure 1-1. *The investigation area at Forsmark (approximately the area shown) with the candidate area outlined in red selected for more detailed investigation. The current telescopic and conventional core drilled boreholes are marked with pink infilled circles.*

2 Objective and scope

The objective of this study was to determine the U oxidation states U(IV) and U(VI) in groundwater samples in order to explain the anomalously high U concentrations present. Since U oxidation states have not been analysed before in Forsmark, an additional objective was also to test the methodology in order to use it in future studies.

Since U(IV) and U(VI) inventories in groundwater can originate from different sources and reflect different processes, important information for their interpretation can be obtained by studying the $^{234}U/^{238}U$ activity ratio (AR) in both oxidation states.

In this study the U concentrations and $^{234}U/^{238}U$ activity ratios were measured in the filtrate water and filtered NdF_3-precipitate, representing U(VI) and U(IV) respectively.
The U concentration was measured using standard ICP-MS and α-spectrometric techniques.

3 Equipment

3.1 Apparatus for U(IV) and U(VI) separation in the field

Separation of U(IV) and U(VI) from groundwater in the field was carried out using the apparatus shown in Figure 3-1. The equipment consisted of two plastic containers (HDPE), one constituting the reactor vessel where precipitation takes place and the other for collecting the filtrate. A Nucleopore polycarbonate filter (Θ 47 mm, 0.40 µm) placed in a plastic filter holder was used for filtration, and a peristaltic pump served to pump the solution through the filter. Groundwater was continuously pumped from the borehole section /Berg 2007/ during the experiment, and included 4 repeated runs (under Ar atmosphere) of groundwater collection, NdF_3-precipitation and filtration. A bypass was arranged to accommodate disposal of the water between each filling of the reactor vessel.

3.2 Measurement of U

The U concentration was measured using standard ICP-MS (Agillent 7500 CE) and α-spectrometry whereupon U is determined by the isotope dilution technique using ^{232}U as an isotopic tracer (14.12 dpm/ml; ref. date 21.7.2006).
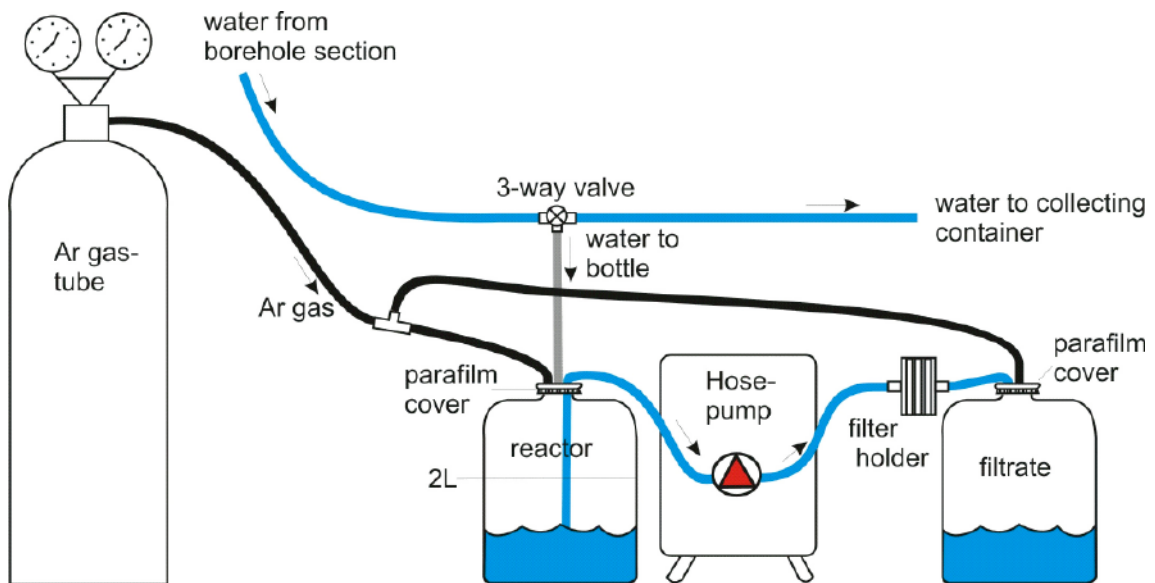

Figure 3-1. *Equipment setup for field separation of U(IV) and U(VI).*

4 Execution

4.1 General

The work was carried out in two stages: 1) separation of U(IV) and U(VI) was conducted in the field during groundwater sampling, and 2) separates, filter and filtrate water were sent for laboratory determination of U (Analytica and HYRL).

4.2 Execution of field work

Separation of U oxidation states was carried out by applying the technique described in /Anderson et al. 1984/. In this procedure groundwater is collected on line in a reactor vessel containing precipitation reagents $Nd(NO_3)_3 \times 6H_2O$ and HCl. The reactor vessel is first filled with groundwater to 1/3 volume, followed by the addition of concentrated HF. The rest of the groundwater is added to achieve a final volume of ~ 2 L and then left to stand for 30–60 min. The precipitate obtained is separated by filtering and the filtrate water stored in a plastic can. Groundwater collection, NdF_3-precipitation and filtering are all performed under an Ar atmosphere, see Figure 3-1. Precipitation was repeated several times to check the reproducibility.

4.3 Preparation of samples

The filtrate water, contained in 2 L plastic cans, was stored in a refrigerator. After a few days a white precipitate appeared. The precipitate was assumed to be SiO_2 because of some Si dissolution during the short-term contact between glass and concentrated HF (cf Si concentration in filtrates and natural groundwater). Because the filtrates were acidic U(VI) was not expected to adsorb or precipitate.

Samples for ICP-MS were filtered and diluted 1/50 in 2% HNO_3 for analysis. For α-spectrometry the filtrate was centrifuged and filtered and 100 mL taken for analysis.

Precipitates (+ filter) were weighed to check the efficiency of precipitations (Table 4-1). Because all precipitations in the field were performed similarly and approximately from the same groundwater volume, it was expected that the precipitates would have the same weight. However a loss of precipitate was observed in sample 12323_U1, but the other three precipitates were close to each other.

The filter with NdF_3-precipitate was dissolved in hot concentrated HNO_3. After a few hours dissolution the solution was evaporated to dryness and the residues then dissolved in 3M HCl. The sample solutions obtained were adjusted to 50 ml which thus represented the filtered groundwater volume (see Table 5-1) and from which an aliquot for U analyses was taken. Sample solution was analysed using the same procedure as for the filtrate waters.

4.4 Nonconformities

The activity was conducted in compliance with the activity plan without deviations.

Table 4-1. Weights of filters with NdF_3-precipitates.

Sample	Filter + precipitate (g)
12323_U1	0.1219
12323_U2	0.3889
12323_U3	0.322
12323_U4	0.3692

5   Results

5.1   Filtrate water

The filtrates were first analysed for U to determine how much was removed from the natural groundwater by NdF_3-precipitation, and thus to get an estimate of the U(IV) concentration (Table 5-1).

The results show that NdF_3-precipitation removed 27%–39% of U from the natural groundwater. According to the method this U, corresponding to 34–54 µg/L, can be considered U(IV). The U(IV) concentrations, obtained by subtracting U concentration in filtrate water from U concentration in groundwater, appear much higher than published values in the literature (< 3µg/L). Results from the Laboratory of Radiochemistry are presented in Tables 5-2 and 5-3.

The results in Tables 5-2 and 5-3 show systematically lower U concentrations for filtrates when compared to Table 5-1. This may be explained by a small U adsorption on the massive white precipitate which appeared during the storage of filtrates in the refrigerator. A systematic difference in the U concentrations may also be explained by standardisation of the measurement systems in the respective laboratories.

The $^{234}U/^{238}U$ activity ratio (AR) was similar in all filtrates (2.04 ± 0.05). Since filtrates represent the same groundwater, this result was expected and can be taken to demonstrate good reproducibility of measurements.

Table 5-1. U concentrations in natural groundwater and filtrate water after NdF_3-precipitation (Analytica).

Sample	*) Filtered groundwater volume (mL)	U (µg/L)	± (µg/L)	^{238}U (µg/L)	^{238}U (µg/L)	$^{235}U/^{238}U$ ratio
Natural gw		129	21	128	1	0.00732
Filtrates						
12323_U1	1,891	83.1	13.3	82.5	0.600	0.000729
12323_U2	1,922	80.8	13.4	80.2	0.600	0.00729
12323_U3	1,881.5	77.9	14.0	77.3	0.600	0.00730
12323_U4	1,897.5	94.1	15	93.4	0.700	0.00729

*) Added reagent volumes and rinses of precipitate have been subtracted.

Table 5-2. U concentrations in filtrate water measured by α-Spectrometry.

Sample	U (µg/L)	± δ	$^{234}U/^{238}U$	± δ
12323_U1	66.0	1.7	2.04	0.05
12323_U2	68.8	1.7	2.04	0.05
12323_U3	63.4	1.7	2.07	0.05
12323_U4	77.0	2.3	2.03	0.05

Table 5-3. U concentrations of filtrates measured by ICP-MS.

Sample	U (µg/L)	± δ
12323_U1	65.6	0.7
12323_U2	69.8	1.0
12323_U3	62.1	2.4
12323_U4	71.5	0.2

5.2   Precipitate

Based on the results in Table 5-1 the NdF_3-precipitates were expected to contain significant amounts of U. Precipitation data show some variability. One of the precipitates (+ filter) was clearly lighter than others, indicating loss of precipitate or variable precipitation of NdF_3 (and possibly SiO_2). The efficiency of U co-precipitation with NdF_3 was checked by calculating the U concentration in weighed precipitation (+ filter) (Table 5-4). This indicates equal values for the first two samples but a loss of U in the last two samples.

The total U (µg) of the NdF_3-precipitates was proportioned to respective groundwater volumes shown in Table 5-1. Total U in sample 12323_U2 (9 µg) was used to calculate U(IV) concentration in groundwater, i.e. 4.7 µg/L, see Table 5-5. Sample 12323_U1 would have yielded the same U(IV) concentration without obvious loss of precipitate (see Table 4-1).

The activity ratio (AR) in precipitates is slightly higher than in filtrates but is the same within the margin of error, i.e. U(IV) and U(VI) have the same AR. This finding is interesting and two alternative explanations can be put forward: 1) oxidised U(VI) has entered the reducing groundwater environment and part of it was reduced to U(IV), or 2) a solid U(IV) compound with AR ~ 2 has been oxidised in situ and mobilised resulting in the observed U distribution. The problem could be solved by analysing the respective U sources for U(IV)/U(VI) and AR, if the source could be identified.

5.3   Redox state of U

Based on the results of both natural groundwater and filtrates (Table 5-1), and the results from the Laboratory of Radiochemistry, it is clear that the U in the studied groundwater samples occurs mainly in the U(VI) state. Based on measured ARs in the filtrate water and NdF_3-precipitate, both U(IV) and U(VI) most probably represent the same U inventory.

The origin of U(VI), whether it has been introduced into the sampling section (anthropogenic drilling source) or formed in situ by dissolution of a U-bearing mineral phase(s), remains unsolved.

Table 5-4. U in NdF_3-precipitates. Values represent averages from α-spectrometric and ICP-MS measurements. Error margin has been calculated applying max-min technique.

Sample	Total U of precipitate (+ filter) (µg)	U in precipitate (+ filter) (µg/g)
12323_U1	2.6 ± 0.2	21.5 ± 1.9
12323_U2	9.0 ± 1.4	23.2 ± 3.5
12323_U3	5.3 ± 0.6	16.5 ± 2.0
12323_U4	4.3 ± 0.4	11.6 ± 1.1

Table 5-5. U(IV) concentrations in the groundwater calculated from the total U (µg) in precipitates.

Sample	U (µg/L)	± δ	AR	± δ
12323_U1	1.4	0.1	2.06	0.05
12323_U2	4.7	0.7	2.06	0.05
12323_U3	2.8	0.3	2.10	0.05
12323_U4	2.3	0.2	2.11	0.05

6   Summary and discussions

The results unequivocally show that U in the studied groundwater occurs mainly in the U(VI) oxidation state. This result was expected and explains the measured high U concentrations in groundwater. The U(IV) concentration of 4.7 µg/L obtained by analysing the NdF_3-precipitates represents ~ 5% of the total U in groundwater and is in agreement with data for U(IV) published in the literature.

An interesting finding was that both oxidation states have the same $^{234}U/^{238}U$ activity ratio which suggests that U(IV) and U(VI) represent the same U inventory. Some ideas of the possible age of U(VI) inventory and reduction kinetics can be deduced using ^{14}C concentrations in the groundwater which are around 17% modern carbon. If the half-life of ^{14}C (5730 a) and radioactive decay are used, a simple calculation yields groundwater residence times of ~ 14,000 a. It is possible, however, that the measured ^{14}C contains some old carbon which dilutes the ^{14}C concentration, shifting the groundwater residence time to an apparent older age, when in reality the residence time is shorter and may suggest an overlap with the deglaciation period.

Whether the U(VI) inventory is the same age as the estimated groundwater residence time is an interesting matter of discussion. Fracture surface samples from the groundwater sampling depth could help further interpretation.

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