KBS TEKNISK RAPPORT

90

Copper as canister material for unprocessed nuclear waste – evaluation with respect to corrosion

Final Report 1978-03-31

The Swedish Corrosion Institute and
its reference group

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COPPER AS CANISTER MATERIAL FOR UNREPROCESSED NUCLEAR WASTE - EVALUATION WITH RESPECT TO CORROSION

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THE SWEDISH CORROSION INSTITUTE
Einar Mattsson
1978-03-31

DOCUMENTS INCLUDED IN THE REPORT

Final report of the reference group:

COPPER AS CANISTER MATERIAL FOR UNREPROCESSED NUCLEAR WASTE - EVALUATION WITH RESPECT TO CORROSION

- Premises for estimating the service life of a copper canister for spent fuel. KBS. Appendix A
- Thermodynamic aspects of copper encapsulation and the corrosion environment in a waste repository. I Grenthe. Appendix B
- Known geological processes for the reduction of sulphate to sulphide. R Hallberg. Appendix C
- Calculation of the amount of oxidants present in a waste repository with copper canisters. L Ekbom. Appendix D
- Statistical evaluation of copper corrosion in soil from tests conducted by Denison and Romanoff. L Ekbom. Appendix E
- Special statement. G Wranglén.

THE SWEDISH CORROSION INSTITUTE
1978-03-30

COPPER AS CANISTER MATERIAL FOR UNREPROCESSED NUCLEAR WASTE - EVALUATION WITH RESPECT TO CORROSION

Summary

The Nuclear Fuel Safety Project (KBS) has proposed, to fulfil the requirements of the so-called "Conditions Act", that spent unreprocessed nuclear fuel shall be disposed of by encapsulation in copper canisters with 200 mm thick walls. The canisters are to be placed in vertical boreholes in rock, 500 m below the surface, and embedded in a buffer of compacted bentonite.

The Swedish Corrosion Institute has been assigned the task of evaluating this proposal from the viewpoint of corrosion and of estimating the life of the canisters under the given conditions. To do this work, the Corrosion Institute has appointed an expert group of 10 Swedish specialists, mainly from the fields of corrosion and materials technology.

The thermodynamic possibilities of various corrosion reactions on copper under the prevailing conditions were studied, whereby bacterial action was also taken into account. Oxygen entrapped in the buffer material at the time of the closing of the repository was found to be an important oxidant for corrosion. Sulphide in the groundwater was found to be another important reactant. The supply of oxygen and sulphide, mainly by diffusion, was calculated, and from this the maximum possible corrosion of copper. The morphology of the attack was also examined, the finding being that an attack which starts as pitting will penetrate into the metal at a decreasing rate, after which the continued attack will proceed mainly in the form of a widening of the pits or an initiation of new pits. So the corrosion of a very thick-walled canister will, in the long run, have the character of a more or less uneven attack over the entire surface, with heterogenities not exceeding a

pitting factor of 25. The expert group arrived at the conclusion that, under the given conditions, the canisters will last for hundreds of thousands of years.

The expert group was unanimous in its opinion, with the exception of Professor Gösta Wranglén, who has submitted a special statement of his own.

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COPPER AS CANISTER MATERIAL FOR UNREPROCESSED NUCLEAR WASTE - EVALUATION WITH RESPECT TO CORROSION

1. BACKGROUND

The "Conditions Act" passed by the Swedish Parliament declares that the Swedish power producers, before charging any nuclear reactor with fuel, will have to demonstrate:

- either how and where an absolutely safe final storage of reprocessed waste can be effected,
- or how and where an absolutely safe final storage of the unreprocessed spent nuclear fuel can be effected.

In order to gather material for the report on final storage, the four companies which build nuclear power installations in Sweden formed the "Nuclear Fuel Safety Project" (KBS) in December of 1976. Within the framework of this project, the Swedish Corrosion Institute has been commissioned to provide an evaluation of the corrosion resistance of the various encapsulation alternatives proposed by KBS. The present report concerns an evaluation of copper as an encapsulation material for unreprocessed waste.

To carry out its undertaking, the Swedish Corrosion Institute has appointed a reference group consisting of specialists, mainly from the field of corrosion and materials technology. The group also includes a representative from the Swedish Nuclear Power Inspection Board as an observer. The reference group has the following composition:

Professor E. Mattsson	Swedish Corrosion Inst.	Chairman
L. Ekbom, Lic. Eng.	" " "	Secretary
R. Carlsson, Lic. Eng.	Swedish Silicate Research Institute	
Chief engineer, T. Eckered	Swedish Nuclear Power Inspection Board	Observer

Dr. G. Eklund	Institute for Metals Research
Professor I. Grenthe	Royal Institute of Technology
Dr. R. Hallberg	University of Stockholm
S. Henrikson, M.A.	AB Atomenergi
Professor N-G. Vannerberg	Chalmers University of Technology
Professor G. Wranglén	Royal Institute of Technology

The reference group has based its evaluation on tests, studies and calculations carried out both within and outside the group as well as on statements from and discussions with various foreign experts, including Dr. T.P. Gilbert and Dr. V.F. Lucey, both well-known specialists on copper corrosion.

In its evaluation, the group has sought to determine, on the basis of present knowledge, the corrosion resistance which the canister would exhibit under given conditions. The estimate of the service life of the canisters has been based on calculations of thermodynamic possibilities for corrosion reactions with the canister and of mass transport through the surrounding buffer bed of species which limit the corrosion rate. The reference group is unanimous in its opinions as presented in this report, with the exception of Professor Gösta Wranglén, who has submitted a special statement of his own.

2. PREMISES FOR THE EVALUATION

KBS has specified the premises on which the evaluation is to be based as regards geological conditions, the environment surrounding the canister and the function of the buffer mass (Appendix A). These premises have been discussed within the reference group, especially the function of the buffer mass. But it has not been up to the reference group to judge whether or not these premises are correct.

2.1 Proposed method of storage

According to the proposal, unreprocessed waste in the form of fuel rods from the reactor shall be enclosed in a canister made of pure copper. The canister shall be fabricated from a commercially available standard grade of copper known as "Oxygen Free High Conductivity Copper"(OFHC), with Swedish designation SIS 5011. The material is used in large quantities within the electrical engineering industry.

The design of the canister is shown in Fig. 1. The minimum wall thickness is 200 mm. The outside diameter is 770 mm, but 800 mm at the top in order to provide a grip for lifting. The lid is composed of three consecutive parts, each welded to the canister by means of electron beam welding. The innermost lid is extra thick to withstand deformation due to external pressure. The outer lids are supported by the inner lid.

The fuel in the canister is surrounded by cast lead, preventing deformation of the canister due to external pressure.

The canisters are placed in vertical boreholes extending from horizontal tunnels in rock 500 m below the surface (fig. 2). The vertical holes are drilled with a diameter of 1.5 m and a depth of 7.7 m and spaced at intervals of 6.0 m. One canister is deposited in each borehole.

The space around the canisters is filled with a buffer mass. The aim of the described method of storage is, according to the proposal, to create a number of barriers which prevent radioactive substances from reaching the biosphere. The more or less slow dissolution of radioactive substances from the waste comprises an inner barrier, the canister itself and the buffer mass around the canister comprise one barrier each and the long transport path in the rock comprises a fourth external barrier. The present study deals with only one of these four barriers - the canister.

2.2 Composition of the groundwater

The canisters will be surrounded by groundwater. The composition of the groundwater at the depth in question is given in Table 1. Of particular importance in evaluating the corrosion resistance of a copper canister is the concentration of oxidants in the groundwater. The groundwater at the depth in question is assumed to have a very low oxygen content (0.1 mg/l), except during an initial period immediately following deposition, when a thin surface zone along the walls of the repository has an elevated oxygen content. The inflow of sulphide is also of importance in the evaluation. The sulphide content, in equilibrium with surrounding minerals, is very low (0.01 mg S/l) (Appendix B). Analyses of groundwater from the depth in question have revealed a maximum level of 5 mg/l sulphide in the groundwater. According to the specified premises, the groundwater around the repository has a sulphide content (measured as sulphur) of no more than $1.5 \cdot 10^{-4}$ moles/l (5 mg S/l).

The quantity of organic material in the groundwater is also of importance, since it can be used by bacteria which mediate the reduction of sulphate to sulphide. The level of organic material is assumed to be no more than 13 mg/l (determined on the basis of $KMnO_4$ consumption).

The pH of the groundwater can be assumed to fall within the range of pH 7-9, in view of the buffering effect of minerals in and around the tunnel system.

When the canisters are deposited and the buffer mass is filled in around them, air will fill pores and cavities in the buffer mass and the tunnels up to the time of the final filling-up of the deposition gallery. After the repository has been closed, the atmospheric oxygen will dissolve in the inflowing groundwater. The oxygen content of the water will therefore be relatively high initially. The atmospheric oxygen in the buffer mass in the tunnels will, however, be bound relatively quickly by reaction with iron(II) phosphate (cf. section 2.4).

2.3 Groundwater flow

According to the premises, the waste will be placed in selected rock with low permeability, i.e. with few and narrow fissures. This means that the flow of water through the rock will not exceed a deciliter or so per m^2 cross-section of rock and year. The flow of water will be localized to thin fissures, generally spaced at intervals of a metre or so. Significantly greater flow of water in the rock can only occur as a result of extensive disturbances in the rock, e.g. due to tectonic movements. It is assumed that water flow which is so strong that the buffer material could be washed away cannot occur.

The buffer mass of compacted bentonite which surrounds the waste canisters is plastic and possesses very low permeability (10^{-12} m/s), much lower than the rock. The buffer material is homogeneous. The high swelling capacity of bentonite, combined with its plasticity, make the risk of fissure formation in the buffer mass negligible. These properties also enable the bentonite to penetrate into and seal fissures in the rock. The water flow through the buffer mass can be neglected and only diffusion through the water in the buffer mass need be taken into consideration.

2.4 The buffer

The canister is surrounded by a buffer mass consisting of compacted bentonite. This buffer is said to have several functions. It comprises a soft, formable bed with good bearing capacity for the canister to rest upon. It inhibits groundwater penetration and distributes the groundwater uniformly over the surface of the canister. It serves as a chemical buffer against the groundwater and thereby regulates the pH of the water to be between 8.5 and 9. Finally, the buffer retards the transport of corrosive reactants to and radioactive substances away from the canister.

A buffer of the specified composition is said to possess high plasticity and durability. Upon contact with water, the bentonite swells. This swelling capacity is assumed to provide a guarantee against the formation of water-bearing fissures in the material. The plasticity of bentonite is documented, even over geological periods of time.

The buffer is obtained by precompacting sodium bentonite, which has been subjected to oxidation treatment to reduce the sulphide level. The remaining sulphide is said to exist in the form of pyrite (FeS_2). The level of sulphide after oxidation treatment is said to be no more than 200 mg/kg. The level of organic material is said to be 200 mg/kg, consisting primarily of poorly biodegradable material. After oxidation treatment, the levels of iron compounds were determined to be: Fe(II) 0.12% and Fe(III) 2.72%. After the buffer mass has been placed in the repository, it will slowly be filled with groundwater, which takes hundreds of years.

A mixture of quartz sand (90 - 80%) and bentonite (10 - 20%) is used to fill up the tunnels (fig. 2).

Prior to the addition of bentonite, a deoxidation agent is added to the quartz sand to reduce the atmospheric oxygen which remains in the pores of the filler material after filling and sealing of the tunnel. This deoxidation agent consists of iron(II) phosphate, known in mineral form as vivianite. Through suitable heat treatment and grain size distribution, the reactivity of the deoxidation agent with oxygen is adjusted so that it is not consumed by reaction in open air during the filling of the tunnel, but is still reactive enough to reduce the oxygen in a year or two.

The diffusion of initial oxygen from the tunnel to the canister can also be limited by placing a copper lid in the deposition hole above the copper canister.

The air volume remaining in the tunnel after filling is estimated to be a maximum of 25 m^3 (at 1 atm, 0^oC) per deposition hole. An additional m^3 or so is present in the deposition hole.

2.5 Canister temperature

Due to its radioactivity, the waste generates heat which raises the temperature of the waste and thereby of the canister and its immediate surroundings. Heat generation is relatively high at the start, but declines rapidly after the first 100 years. The temperature of the canister at the time of deposition can be controlled by the adjustment of various parameters at the time of deposition.

In the case of unreprocessed waste, the maximum temperature at the outer surface of the canister is stated to be 80^oC; after 1000 years, the temperature has dropped to 50^oC. Thanks to the thickness and high thermal conductivity of the canister material, the temperature can be regarded as being equal over the entire surface of the canister.

2.6 Radiolysis

If the groundwater around the canister is subjected to nuclear radiation, radiolysis of the water may occur. This can lead to the formation of, i.e., oxygen and hydrogen. Radiolysis of water around the canister can influence the corrosion of the canister and thereby the canister's service life. Radiolysis is dependent upon the nature and the intensity of the radiation.

The quantity of copper which could theoretically be oxidized by the oxygen and by other oxidants (Fe^{3+},Cu^{2+}) resulting from radiolysis has been calculated to be in the present case 0.4 kg copper per canister over 10^6 years, of which about 20 g is oxidized during the first 10 000 years.

2.7 Canister life

The reference group has not received any specified requirements from KBS with regard to the service life of the canister.

Most of the radioactivity in the nuclear waste, namely that portion which derives from cesium 137 and strontium 90 (1), decays during the first 600 years. The remaining radioactivity decays at a considerably slower rate, and a small portion lasts millions of years. Some of the radioactivity derives from transuranium elements.

3 CORROSION - GENERAL

If, as in the present case, a canister made of a certain material surrounded by groundwater of a certain composition is postulated, it is possible to determine whether the system is thermodynamically stable or not. A stable system is in equilibrium, i.e. no net chemical reactions occur. A canister which is thermodynamically stable (immune) in surrounding groundwater has, theoretically, an infinite service life.

If, on the other hand, the canister is not thermodynamically stable in the surrounding groundwater, corrosion is possible, but the rate of corrosion can vary within wide limits. In some cases, a protective coating forms on the surface of the material and prevents corrosion to a greater or a lesser degree. It is then said that the surface has been passivated. In other cases, on the other hand, corrosion barriers are lacking, and the rate of corrosion can be high. Even on a passivated surface, the rate of corrosion can reach high values locally, e.g. due to pitting. Any estimate of the service life of a canister made of a material which is not thermodynamically stable must therefore be based on a determination or estimate of the rate of corrosion.

4 CORROSION OF THE COPPER CANISTER

Copper is a relatively noble metal, which means that it is not normally attacked by oxygen-free water. It usually possesses good corrosion resistance in different environments. Copper is therefore used to advantage as a material in such applications as hot water lines. The normally good corrosion resistance of copper does not, however, prevent rapid corrosion attacks from occurring under unfavourable circumstances, such as pitting in water lines.

4.1 Possibilities of attack on the copper canister

A calculation of the thermodynamic equilibria which prevail between copper and water is reported in Appendix B. The calculation shows that the solubility of copper as Cu(I) in oxygenfree pure water is less than $10^{-7.5}$M, which means that the corrosion attack at the rates of diffusion in question will be negligible, even after long periods of time.

In the presence of oxidants, however, copper can be oxidized and thereby attacked. The influence of various possible oxidants is dealt with in Appendix B. The oxidant which is of greatest interest here is oxygen dissolved in the groundwater. Other possible oxidants are e.g. sulphur(VI) in sulphate, hydrogen(I) in water + sulphide, sulphur(-I) in pyrite, nitrogen(V) in nitrate or iron(III) in various minerals. The two first-named oxidants are particularly important, since their concentrations are relatively high in the canister's environment.

4.1.1 Oxidation of copper by oxygen

Oxygen is an oxidant which can attack the copper during the introductory phase of the deposition, provided that a relatively high redox potential is prevailing (fig 3). The attack can occur in accordance with the following reaction formulae:

$$4Cu + O_2 = 2Cu_2O$$
$$2Cu + O_2 = 2CuO.$$

Oxygen can come from various sources:

- Oxygen is present in the buffer bed at the time of deposition, partially dissolved in the water in the buffer material and partially in the form of entrapped air. This oxygen can be bound by the addition of Fe(II) phosphate to the buffer material, which, according to the premises, is mixed with the buffer material in the horizontal tunnels, but not in the vertical boreholes.

- Oxygen is supplied with the surrounding groundwater. Owing to the fact that the rock below the groundwater table has a buffering effect, the oxygen content of the groundwater is very low, <0.1 mg/l.

- Oxygen is formed due to radiolysis caused by radiation from the canister.

The rate of attack is limited by the supply of oxygen to the surface of the canister. The supply of oxygen from various sources has been calculated as a function of time (Appendix D). The results are given in Table 2, expressed as an equivalent quantity of copper oxidized to Cu(I).

4.1.2 Oxidation of copper by sulphate or nitrate

The oxidation of copper by sulphate with the formation of sulphide is thermodynamically possible under the conditions which are expected to prevail in the waste depository. Geological and other chemical evidence indicates that the oxidation is negligibly low, even over geological periods of time (Appendix B3). The effects of sulphate in combination with sulphate-reducing bacteria are dealt with in section 4.1.3.

The oxidation of copper by nitrate is also thermodynamically possible. The rate of reaction is, as in the case of sulphate, extremely low. Nitrate (as well as nitrite) can therefore be disregarded as an oxidant for copper (Appendix B4).

4.1.3 Oxidation of copper in the presence of sulphide

Thermodynamic calculations show that copper can be oxidized by water and hydrogen sulphide at a relatively low redox potential (cf. fig. 3), e.g. according to the following reaction formula:

$$2Cu(s) + HS^-(aq) + H_2O(l) \rightarrow Cu_2S(s) + H_2(g) + OH^-(aq)$$

The upper potential limit for the stability range of Cu_2S is shifted downwards when the temperature is raised (fig. 3).

The oxidation rate is limited by the rate at which hydrogen sulphide is transported to the copper canister.

There are a number of sulphide sources in this case:

- Sulphide in the form of pyrite (FeS_2) is present in the buffer bed at the time of deposition. Due to the oxidation treatment of the bentonite, this sulphide level is low, no more than 200 mg S/kg. Owing to the low solubility of the pyrite, however, this sulphide source will not contribute towards an attack on the copper.
- Sulphide is supplied with the groundwater. But the content of sulphur as sulphide is, according to the premises, less than 5 mg S/l, usually considerably less.
- Sulphide is formed by the reduction of sulphate in the buffer bed mediated by bacterial action (cf. Appendix C) e.g. according to the following formula:

$$2CH_3 \cdot CHOH \cdot COOH + HSO_4^- \rightarrow 2CH_3 \cdot COOH + HS^- + 2CO_2 + 2H_2O.$$

The bacteria, however, for their life processes, require organic material , represented in the above formula by lactic acid. In the presence of a surplus of sulphate, the supply of organic material (OM) is determining for the sulphide formation. In this case, the groundwater is assumed to have an OM content of 13 mg/l, which is theoretically equivalent to a sulphide content increase of approx. 2 mg/l.

The supply of sulphide from various sources has been calculated as a function of time (Appendix D). The results (Table 2) are expressed as an equivalent amount of copper converted to Cu(I).

4.1.4 Attack by thermal diffusion

Another possibility for corrosion is associated with the temperature gradient which exists around the canister during the first few hundred years. This could give rise to a dissolution of copper from the canister and a reprecipitation of the metal, for example on the rock wall. But calculations show that material loss due to such dissolution is insignificant, less than 1 µm per 10^6 years (Appendix D).

4.2 Nature and rate of attack

The corrosion attack which can occur on the copper canister due to the action of oxidants is only of importance if it has the character of local corrosion. Our prime concern here is for pitting; the risk of stress corrosion cracking is considered to be eliminated when OFHC copper is selected.

Pitting in copper water supply lines is, as was mentioned above, a widespread corrosion phenomenon. Experts in the field are agreed that the rate of growth of the pits in depth decreases with time, due partly to the fact that the active surface in the pit grows and partly to the fact that the paths of transport in the pit and its mouth are blocked by the precipitation of corrosion products. The correlation between pit depth (P) and time (t) is usually expressed empirically by means of the equation

$$P = A\ t^{n} \qquad (1)$$

where A and n are constants (2). n has a value of between 0 and 1.

A statistical treatment (Appendix E) of the results of the Denison-Romanoff study of copper corrosion in various types of soil in the USA over a period of 14 years of exposure (2) has shown that the correlation between pit depth and time can better be expressed by means of the equation:

$$P = A(t - t_{o})^{n} \qquad (2)$$

where t_o is the incubation time before pitting starts.

The results of the Denison-Romanoff study show that n decreases with time (Appendix E).

In agreement with formula (1), the life of a copper water pipe increases sharply with wall thickness. If the wall is sufficiently thick, the growth of the pit in depth ceases practically altogether with time. The continued attack takes the form of a widening of existing pits and an initiation of new pits. At extremely great wall thicknesses - as in this case, 200 mm - the attack assumes, after a very long period of time, the character of a corroded surface zone with local variations in depth.

Table 3 gives the average penetration, i.e. the depth of the surface zone which can be attacked due to the rate of supply of reactants in question. Then a uniform attack is assumed over the entire surface. In this calculation of the average penetration, the attack caused by oxygen supplied with the groundwater and formed through radiolysis has been disregarded, since such oxygen cannot cause corrosion attack at the same time as sulphide in the groundwater attacks the copper; the two reactions take place at different electrode potentials, whereby the oxygen would be consumed by reaction with the sulphide. Furthermore, the attack caused by sulphide supplied with the groundwater via the tunnel is assumed to be concentrated to the top end of the canister (nearest the tunnel) over 1/10th of the canister surface.

The risk of local variations can be taken into account by calculating a maximum pit depth, which can be obtained by multiplying the average penetration by a pitting factor. Table 3 gives the maximum pit depths for a pitting factor of 25, the highest value which was observed in the Denison-Romanoff study. This value for the pitting factor can be regarded to be conservative, since theoretical analyses have indicated that the pitting factor decreases with time, as was also confirmed by the results of the Denison-Romanoff study (Appendix E).

5 CONCLUSIONS

Copper is a relatively noble metal and is therefore thermodynamically stable in oxygen-free pure water. In the case in question, however, some corrosion can occur due to the presence of oxygen or sulphide in the water which comes into contact with the canister. It is assumed that the oxygen in the buffer material in the tunnels can be eliminated by the addition of deoxidation agents. However, oxygen is present in the buffer material which is added to the deposition holes, and sulphide is supplied with the groundwater.

Even when these reactants are taken into consideration, however, it is considered realistic to anticipate a service life of hundreds of thousands of years for a copper canister with a wall thickness of 200 mm.

6. REFERENCES

1. Kjellbert, N: Källstyrkor i utbränt bränsle och högaktivt avfall från en PWR beräknade med ORIGEN.

   ("Emission rates in spent fuel and high-level waste from a PWR, calculated using ORIGEN") KBS Technical Report 01 (1977-04-05).

2. Denison, J.A. and Romanoff, M: Soil corrosion studies, 1946 and 1948: Copper alloys, lead and zinc. J. Res. NBS 44 (1950) p 259.

(1978-03-30)

Table 1. Groundwater composition at the repository site according to Appendix A

Analysis	Units	Probable interval	Min. value[x)]	Max. value[x)]
Conductivity	µS/cm	400-600		1100
pH		7.2-8.5		9.0
$KMnO_4$ cons.	mg/l	20-40		50
COD_{Mn}	"	5-10		12.5
Ca^{2+}	"	25-50	10	60
Mg^{2+}	"	5-20		30
Na^+	"	10-100		100
K^+	"	1-5		10
Fe-tot		1-20		30
Fe^{2+}	"	0.5-15		30
Mn^{2+}	"	0.1-0.5		3
HCO_3^-	"	60-400		500
CO_2	"	0-25		35
Cl^-	"	5-50		100[xx)]
SO_4^{2-}	"	1-15		50
NO_3^-	"	0.1-0.5		2
PO_4^{3-}	"	0.01-0.1		0.5
F^-	"	0.5-2		8
SiO_2	"	5-30		40
HS^-	"	< 0.1-1		5
NH_4^+	"	0.1-0.4		2
NO_2^-	"	< 0.01-0.1		0.5
O_2	"	< 0.01-0.07		0.1

[x)] The estimated probability that a value will fall between the min. value and the max. value is 95%.

[xx)] During the phase for drainage and filling, max. 400 mg/l.

Table 2. The greatest quantity of copper per canister which can react with supplied quantities of oxygen and sulphide. The amount is given in kg Cu as a function of time.

Reaction-determining reactant		Maximum amount of copper which can react with supplied reactant, kg			
		10^3 years	10^4 years	10^5 years	10^6 years
Oxygen:					
Initially	in deposition holes	2.4	2.4	2.4	2.4
	from tunnel	0	0	0	0
In ground-water	via fissures	0	0	0.09	0.9
	via tunnel	0	0	0.06	0.6
Formed by radiolysis		0	0	0.1	0.4
Total oxygen reaction		2.4	2.4	2.7	4.3
Sulphide:					
Initially	in deposition holes	0	2.6	2.6	2.6
	from tunnel	0	0.3	2.8	2.8
In ground-water	via fissures	0	0.3	3.1	31
	via tunnel	0	0.2	1.9	19
Total sulphide reaction		0	3.4	10.4	55.4

Table 3. Depth of attack on upper parts of copper canister as a function of time, assuming active deoxidation agent in tunnel buffer

	10^3 years	10^4 years	10^5 years	10^6 years
Average penetration, mm	0.02	0.1	0.5	2.4
Max. pit depth, 25 x average penetration, mm	0.5	2.3	13	60

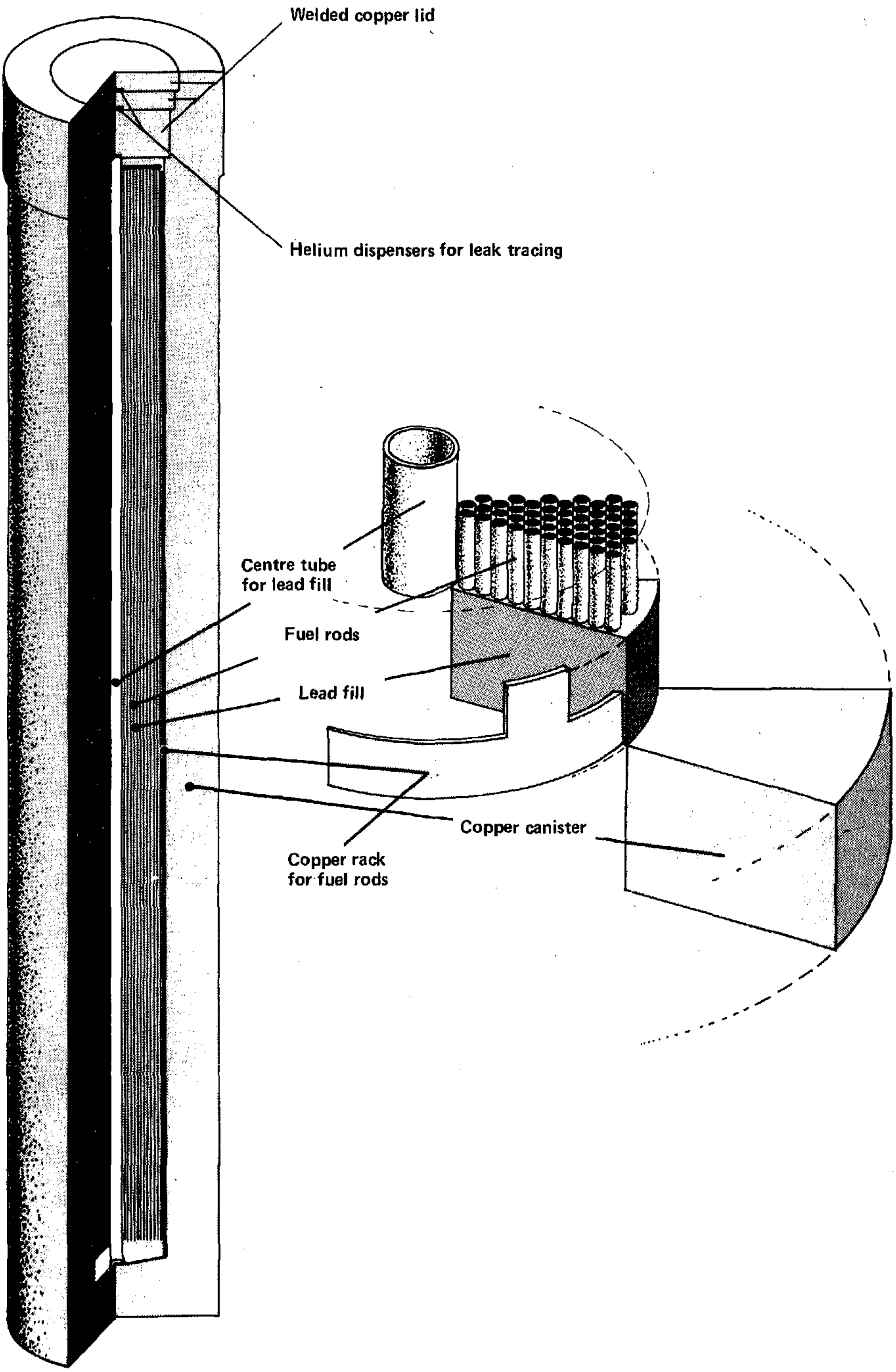


Fig. 1. Design of copper canister (in accordance with Appendix A).

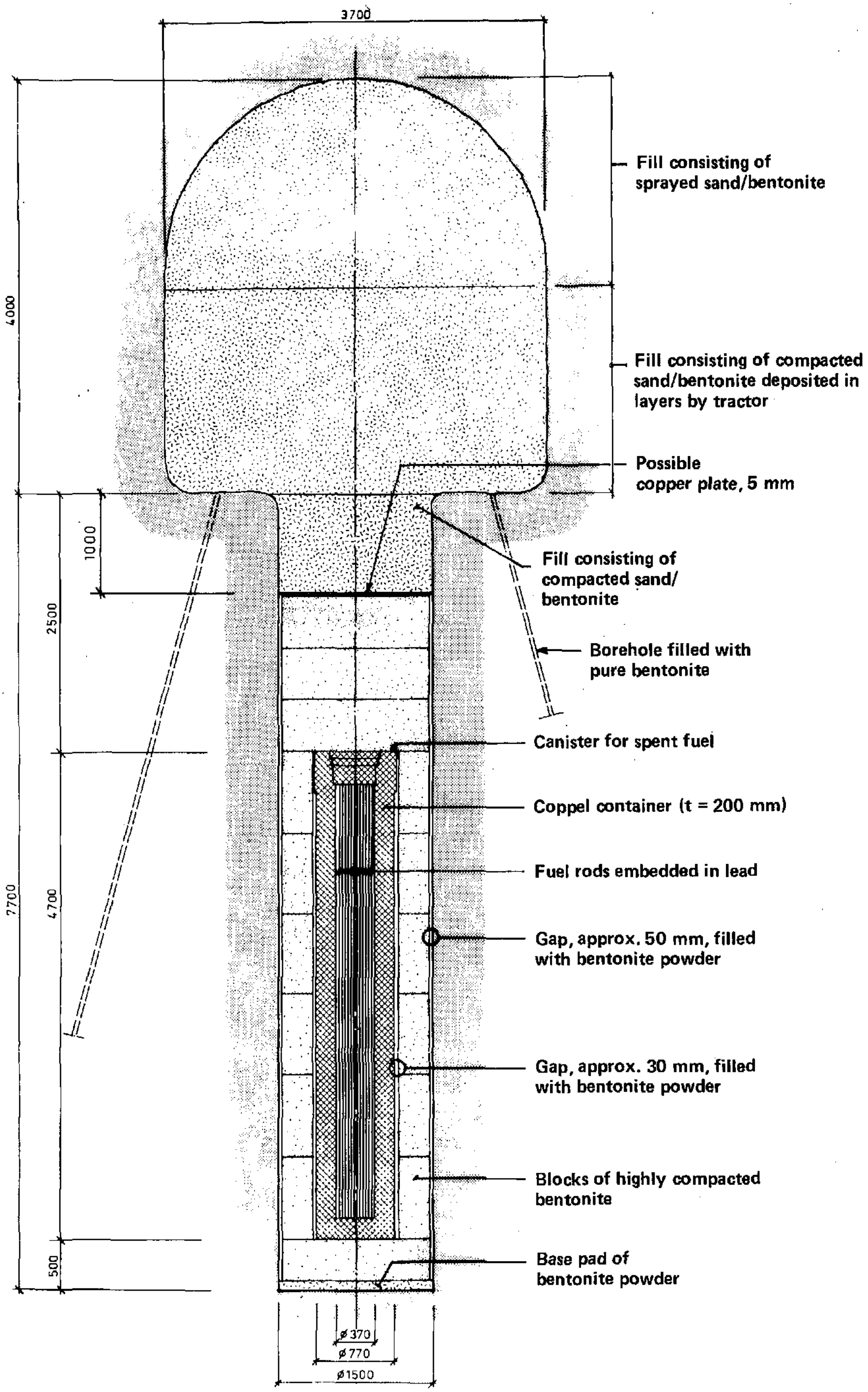


Fig. 2. Section through horizontal tunnel and vertical borehole with copper canister (in accordance with Appendix A).

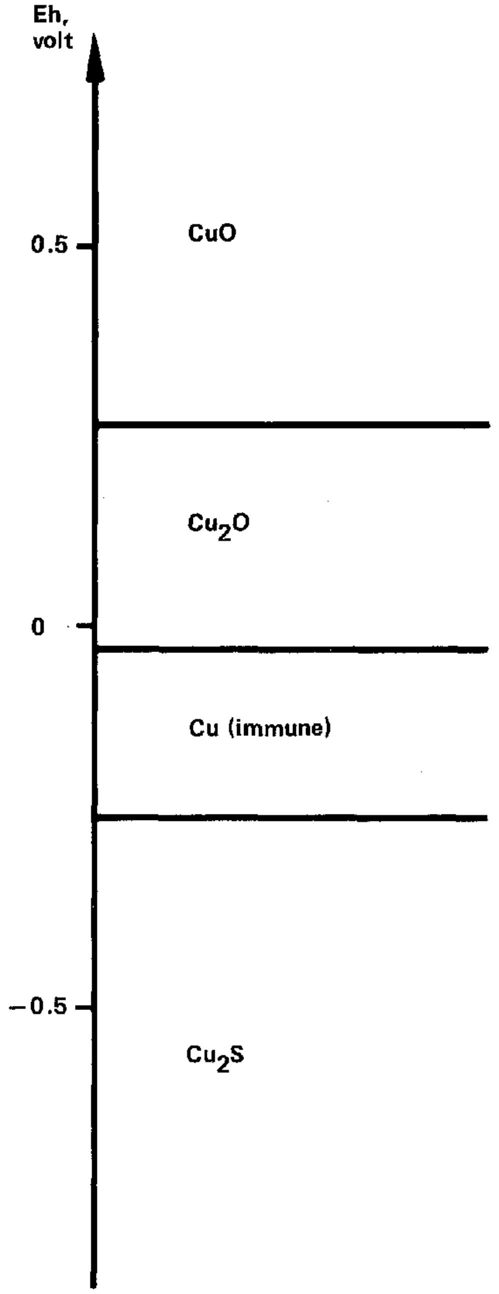


Fig. 3. Approximate diagram of state for copper in contact with water at pH 8.5 in the presence of oxygen (at high redox potentials) or sulphide (at low redox potentials), 25°C. If the temperature is increased, the immunity range for Cu is broadened somewhat as a result of the fact that the Cu/Cu_2S line is shifted downwards while the Cu_2O/Cu line remains unchanged.

PREMISES FOR ESTIMATING THE SERVICE LIFE OF A COPPER CANISTER FOR SPENT FUEL

Specifications concerning the conditions in a final repository for unreprocessed spent nuclear fuel are presented below. They are intended to serve as a basis for the Swedish Corrosion Research Institute's assessment of the service life of the copper canister which is to be used for the long-term isolation of the fuel from the groundwater.

1 The final repository

The final repository is to be located in selected, low-permeable crystalline rock (granite or gneiss) at a depth of about 500 m.

A number of vertical shafts connect the storage level with the surface of the ground. At the storage level, approx. 1 km long tunnels with a cross-sectional area of about 15 m^2 are blasted at intervals of 25 m. Vertical holes with a diameter of 1.5 m and a depth of 7.7 m and spaced at intervals of 6.0 m are drilled in the bottom of the tunnels.

The design of the final repository is illustrated in figs. 1 and 2. It is planned that the repository will be kept open for a period of 30-40 years before final backfilling. For a number of years during the operational period of the repository, waste will be deposited at the same time as new storage space is opened up. But these activities will be carried out in such a manner that they will not affect each other.

The procedure which will be followed for a given storage tunnel is basically as follows. The tunnel is blasted out of the rock using a method which produces minimal fissuring in the surrounding rock. Before the storage holes are drilled, smaller holes are made for the purposes of rock investigation and grouting both at the position of the planned storage hole and in two rows along the tunnel walls, see fig. 3. These latter holes will also be used for drainage during the filling phase of the repository.

On the basis of observations on the tunnel walls and in the test holes, a final decision will be made concerning which sections of rock are to be used for deposition and which are to be excluded due to unsatisfactory quality of the local rock mass.

Fissures in the rock which communicate with the storage hole will be sealed by grouting with bentonite. The increase in the resistance of the rock to diffusion achieved by grouting with bentonite is not, however, taken into consideration in the calculation of the service life of the copper canister.

The canisters are deposited one by one in the storage holes. After all of the storage holes have been filled, the tunnel can be backfilled, either immediately or at a later time.

Tunnel backfilling is carried out in a number of stages. The lower part of the tunnel is compacted by means of a technique developed for roadway embankments, earth dams etc. The upper part is filled by spraying using the same technique as is employed in concrete reinforcement work in rock tunnels. A more detailed description is provided in (1). Before the tunnel is filled, the test holes are first filled with bentonite.

After all of the storage tunnels have been filled, the vertical shafts are also backfilled with the same material as that which is used in the tunnel. The repository can then be abandoned for all time.

2 Geo-hydrological conditions in the repository

2.1 Permeability of the rock, groundwater flow.

Test drillings and measurements at three different locations in Sweden to a depth of about 500 m (a total of 7 boreholes) have demonstrated that rock with the permeability of about 10^{-9} m/s is available at the intended depth (2).

The hydraulic gradient (i.e. the slope of an isobar surface) is only one or a few promille at the depth in question. At a hydraulic gradient of $3\,^{o}/_{oo}$ and a permeability of 10^{-9} m/s, a flow of 0.1 litre per year and per square metre of cross-sectional area of the rock is obtained.

The above conditions apply to the period before the repository has been blasted out of the rock and the period after the groundwater table has been re-established after the repository has been sealed. During the intervening period, an inflow of groundwater into the repository will take place which will compensate for drainage pumping and eventually recharge the groundwater storage. The regional flow pattern of the groundwater should be restored 100 years after the sealing of the repository. Disturbances in the groundwater flow due to heating of the repository are largely negligible.

The repository's storage holes will not, as has already been indicated, be located in or immediately adjacent to existing zones of weakness in the bedrock in which future rock movements will be concentrated. Stress changes of tectonic origin, e.g. caused by a glaciation, may, however, give rise to fractures and minor displacements in the rock around the repository. Such movements will be minor and the buffer material will, by virtue of its swelling capacity, seal the small fractures which may open around the storage holes. But fractures will not be opened to such an extent that the buffer material will be carried away with the groundwater. The canisters will therefore always be located in an environment of unchanging low water permeability.

2.2 Composition of the groundwater

The chemical composition of groundwater at great depths in the bedrock, which is of special interest from the viewpoint of corrosion, has been studied by means of analyses of samples taken from 500 m deep boreholes at Forsmark and in the Finnsjö district in northern Uppland County. Together with the results of other analyses of groundwater in bedrock, the probable composition of groundwater in the bedrock at the assumed site of the final repository has been obtained (see subappendix A:1).

If relict salt water is present near the repository, the Cl^- level during the repository's drainage and recharging phase may increase to about 300-400 mg/l. In later phases, the Cl^- level will be lower.

3 Buffer material and tunnel fill

The canister is surrounded in its storage hole by a buffer material, which fills up the space between the canister and the rock wall. The most important function of the buffer material is to limit the inflow of such substances (oxidants) which could react with the canister material and cause corrosion. The buffer material should therefore:

1 minimize the groundwater flow in the immediate environment of the canister

2 be free of water-bearing fissures

3 have a low diffusion coefficient for the oxidants in question

The active substance in the buffer material is sodium bentonite. The buffer material in the storage holes and the backfill in the overlying tunnel are of different composition, as described below.

3.1 Properties of the bentonite

A suitable bentonite which has been closely studied is mined in an area of Wyoming and South Dakota in the United States. It originates from a volcanic ash. The main constituent of bentonite is montmorillonite, also called smectite. It is a layer-lattice mineral of the three-layer type, where the layers are negatively charged owing to the fact that atoms of lower valence have taken the place of silicon and aluminium. Positive counterions between the silicate layers compensate for the negative charge of the layers. In the material used here, these ions consist largely of sodium.

Upon contact with water, the bentonite swells as the water is absorbed between the silicate layers. If swelling is prevented by the material being constrained in a closed volume, a swelling pressure arises which can amount to tens of MPa at a low moisture ratio and approaches zero at a sufficiently high moisture ratio.

The swelling capacity of the material provides a guarantee against the formation of water-bearing fissures in the material.

At the moisture ratios in question here, the permeability of the material is extremely low, so low that liquid flow through the material can be completely disregarded when considering the transport of substances through the material. Only diffusion phenomena need be taken into consideration.

Owing to its swelling capacity, the bentonite can penetrate into and close water-filled fissures which form in the rock around the storage hole (3). This also counteracts any increase in the supply rate of oxidants in the very unlikely event that new water-bearing fissures should form subsequent to deposition.

In the calculation of the oxidant supply rate, the diffusion-impeding properties of the clay filling in the fissures has not been taken into account.

Geological evidence proves that the bentonite will remain stable over millions of years at the temperatures in question (4).

Subappendix A:2 gives the chemical composition of the bentonite. The pH of water in contact with the bentonite lies within the range 8.5-9.

Prior to use in the repository, the bentonite is subjected to heat treatment in air at approximately 425°C for 15 hours. According to the results of tests and analyses, most of the sulphidic sulphur in the bentonite is hereby oxidized to sulphate. Only 0.02% S remains in the form of pyrite. The properties of the active silicate mineral are not altered by this treatment. Organic material which could serve as a nutrient for sulphate-reducing bacteria is also eliminated by this treatment, so the bentonite does not have a potential for the production of sulphidic sulphur. Some organic material (approx. 150 ppm), has, however, been found in heat-treated bentonite. To be on the safe side, it should therefore be assumed that this content is available as nutrition for sulphate-reducing bacteria.

For a fuller description of the function of the bentonite, see reference (5).

3.2 Buffer material in the storage holes

Pure bentonite in highly compacted form is used in the storage holes.

After heat treatment and dampening to a moisture ratio of about 10%, the bentonite is compressed into cylindrical and annular bodies with a bulk density of 2.3 t/m^3. Isostatic compaction by means of ASEA's Quintus technique is employed.

These blocks are positioned so that they surround the canister in the storage hole, fig. 4.

The spaces between the bentonite blocks and the rock wall and between the blocks and the canister are filled with bentonite powder.

Water absorption in the bentonite and the establishment of the swelling pressure (whereby all gaps such as joints between blocks and cracks disappear) takes a very long time, hundreds of thousands of years (5). In its final state, the compacted bentonite has expanded slightly upwards in the hole, compressing the looser tunnel fill (section 3.3). Its final bulk density is about 2.1 t/m^3. The material is then solid, completely fissureless, impermeable to waterflow and exerts a swelling pressure on the canister and the rock wall of about 8 MPa. The diffusion coefficient for dissolved gases is estimated to be 8 x 10^{-11}m^2/s, for anions 8 x 10^{-11}m^2/s and for cations 4 x 10^{-11}m^2/s at 50°C (6). At 25°C, half these values are expected.

3.3 Buffer material in tunnels

The tunnel fill consists of a mixture of 10-20% bentonite and 90-80% quartz sand (so-called "silver sand"). The chemical analysis of the quartz sand is given in sub-appendix A:3.

Prior to its mixture with the bentonite, a deoxidizer is added to the quartz sand to reduce the oxygen in the air which remains in the pores in the filler material after filling and sealing of the tunnel. This deoxidizer consists of 0.5% iron(II) phosphate, in mineral form known as vivianite. It is prepared by the dissolution of iron powder in phosphoric acid, followed by precipitation.

By means of a suitable heat treatment and particle size distribution, the reactivity of the deoxidizer with oxygen is adjusted so that it is not consumed by reaction in open air during the tunnel filling phase, but is still reactive enough to absorb the oxygen in one or a few years time. Laboratory tests have shown that heat treatment at 200°C for 2 hours is a suitable pretreatment in order to obtain the desired reaction rates. See further subappendices A:5 and A:6.

The diffusion of initial oxygen from the tunnel to the canister can also be restricted by placing a copper lid in the storage hole above the copper canister.

After the quartz sand is mixed with the bentonite, the mixture is given a 10-15% moisture content in order to prevent dusting in connection with application.

The air volume remaining in the tunnel after filling is estimated to be a maximum of 25 Nm^3 per storage hole. Another Nm^3 or so remains in the storage hole.

4 The copper canister

4.1 Material

The canister is fabricated from a commercially available standard grade of copper known as "Oxygen Free High Conductivity Grade" (OFHC), with Swedish designation SIS 5011. The material is used in large quantities within the electrical industry.

4.2 Design

The design of the canister is shown in fig. 5. The minimum wall thickness is 200 mm. The outside diameter is 770 mm, 800 mm at the top end in order to provide a grip for lifting. The lid is composed of three parts placed on top of each other, each welded to the canister by means of electron beam welding.

The innermost lid is extra thick to withstand deformation due to external pressure. The outer lids are supported against the inner lid.

The fuel in the canister is surrounded by cast lead, preventing deformation of the canister due to external pressure.

4.3 Fabrication

Fabrication has been discussed with a number of manufacturers with suitable experience. Even though the canister as a component will be larger than any objects previously made of copper, it should be possible to employ existing technology.

The most suitable fabrication process is as follows:

a) Casting of a solid blank under vacuum

b) Cold forging consisting of upsetting and flattening with intervening annealing in a protective atmosphere.

c) Finish turning

d) Drilling of cavity

e) Ultrasonic inspection

A bundle of dried fuel rods (498 BWR rods or an equivalent quantity of PWR rods) is inserted into the canister, which is then placed in a vacuum furnace and heated to about 400°C. Lead is then pumped into the canister to fill up the space between the fuel rods completely. After cooling and solidification, which is done in a controlled manner in order to avoid "pipes", the cast surface is machined and the joint surfaces which are to be welded are cleaned. The three lids are then electron beam welded one at a time with helium leakage tracing after each welding operation. The welds are also tested ultrasonically. The canister is then ready for deposition in the repository. The operations in the encapsulation station are illustrated by fig. 6.

4.4 Mechanical stresses on the copper canister

The canister will be subjected to an external pressure of roughly 10 MPa in the repository. This pressure will remain indefinitely, although it may vary slightly in magnitude. Stresses in the canister caused by this pressure are extremely small. The lead filling prevents a long-term tendency towards "waist formation" due to compression, which is otherwise a possibility due to the low creep resistance of copper. The empty space inside the fuel rod cladding has no effect, since the zircaloy cladding is not deformed, even over long periods of time and even if the external pressure is transmitted completely to the fuel rods through the copper and lead. The copper material will therefore remain in an isostatic state for a very long period of time.

Shear forces on the canister will be insignificant. Uneven swelling of the buffer material during the water absorption phase is prevented by the fact that the incoming water is distributed evenly in the annular gaps by material of higher permeability (section 3.2). Movements in the rock are not expected to occur to an extent which would lead to stresses of any appreciable magnitude.

5 Temperature of the canister

Owing to the moderate heat output of the waste (0.8 kW per canister at deposition) and the thicknesses and high thermal conductivity of the canister material, the temperature can be considered to be the same everywhere on the canister surface. But the temperature will differ somewhat between different canisters, partly due to variations in the degree of burnup of the fuel, and partly depending on where in the repository the canister is located. Canisters located in the centre of the repository with maximum fuel burnup will have the highest temperature. Canister temperature as a function of time for such a canister is illustrated in subappendix A:4. These curves are based on three-dimensional calculations carried out by means of a computer program, based on the measured thermal conductivity of compacted bentonite and an average value for the thermal conductivity and heat capacity of the bedrock (8).

6 The transport of oxidants to the copper canister

Oxidants which can cause corrosion on the copper canister can be divided into three categories:

a) Material which has been introduced into the final repository (buffer material) at the time of deposition

b) Material which enters the final repository with the groundwater

c) Material which is formed through radiolysis after the final repository has been sealed.

The composition of the buffer material (incl. air-filled pores) and the groundwater was described in sections 3 and 2, respectively.

6.1 Transport of oxidants present in the buffer material

Oxidants present in the buffer material are transported to the canister surface solely by means of diffusion. Pore water flow can be excluded as a transport mechanism and fissures cannot exist in the bentonite when it is in contact with water (3, 5, 6).

The diffusion coefficients required for the calculations are given in section 3.2.

6.2 Transport of oxidants present in the groundwater

Three consecutive transport processes are required for the transport of oxidants present in the groundwater to the canister surface:

1. Diffusion through a slow-flowing laminar water layer up to the bentonite fill in fissures which communicate with the storage hole
2. Diffusion in the fissures through the bentonite fill
3. Diffusion in the bentonite fill in the storage hole

The fissures which are found when the repository is built are injected with bentonite, which actually increases their resistance to diffusion considerably. As was mentioned above, however, this is not taken into account in the transport calculations. Due to the small width of the fissures (approx. 0.1 mm), a very important contribution to the diffusion resistance is provided by the water film.

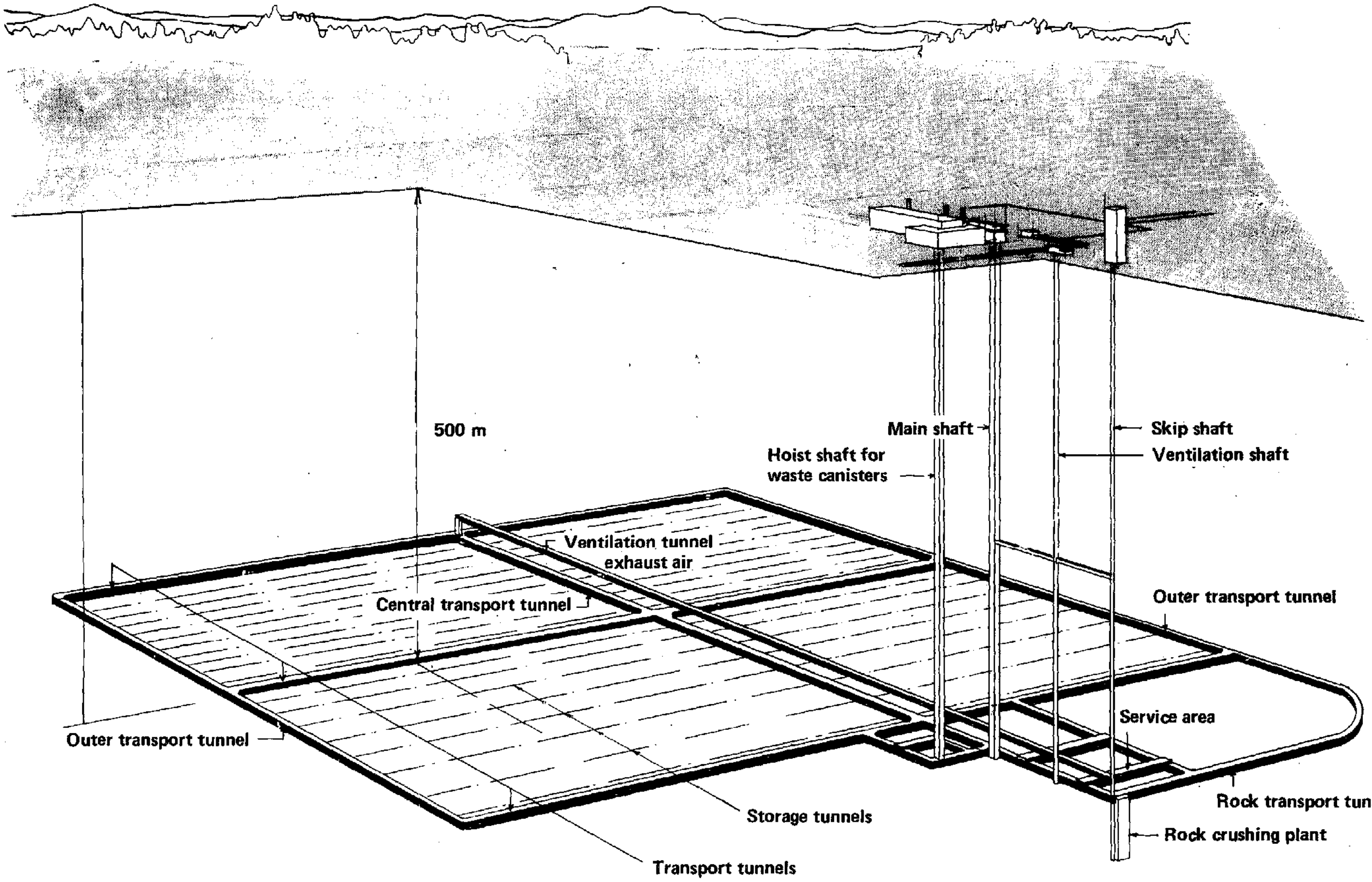
The method used to calculate the transport of oxidants into the canister is described in reference 6. The amount of sulphide transported with the regional groundwater flow to the copper canister calculated by means of this method, expressed as the amount of copper per canister converted to Cu_2S, amounts to about 22 kg over a period of 10^6 years, assuming a sulphide content in the groundwater of 5 mg/l and assuming that each mole of sulphide produces one mole of Cu_2S. This is based on the premises that the average permeability of the rock mass is 10^{-9} m/s and that the hydraulic gradient is 3 ‰. It is also based on the premise that rock fissures with a width of 0.1 mm and spaced at a distance of 1 m are present next to the storage hole, which is assumed to give rise to a local increase of the water flow by a factor of 2 in relation to the flow in the surrounding rock. These premises, which are considered to be realistic but conservative, correspond to "case 5" in table 3 in (6). This table illustrates the effects of varying flow (U_o), fissure width (2d), fissure spacing (S) and clay fill in fissures (Z_o), with slightly different premises regarding sulphide content and stoichiometry.

6.3 Radiolysis

Due to the great thickness of the copper canister walls, the effects of radiolysis in its immediate environment will be largely negligible. Very conservative calculations (7) show that, assuming that all oxygen produced by the decomposition of water is converted to Cu_2O, radiolysis will cause a metal loss rate of only 0.5 kg over a period of 10^6 years.

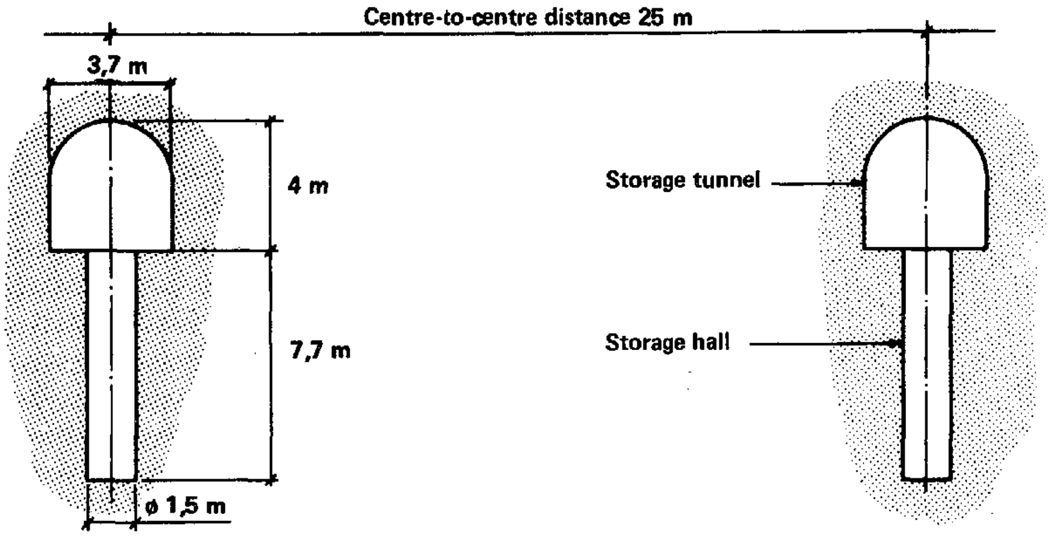
References

1	KBS	Handling of Spent Nuclear Fuel and Final Storage of Vitrified High Level Reprocessing Waste, Volume III, page 99
2	KBS	Handling of Spent Nuclear Fuel and Final Storage of Vitrified High Level Reprocessing Waste, Volume II, pages 29-31
3	KBS-TR-73	Selfinjection of highly compacted bentonite into rock joints, R Pusch
4	KBS-TR-32	Long term mineralogical properties of bentonite/quartz buffer substance, R Pusch, A Jacobsson
5	KBS-TR-74	Highly compacted Na-bentonite as buffer substance, R Pusch
6	KBS-TR-79	Transport of oxidants and radionuclides through a clay barrier, I Neretnieks
7	KBS-TR-106	Strålningsnivå och till vatten deponerad strålningsenergi utanför kapslar i slutförvaret. ("Radiation level and radiant energy imparted to water outside canisters in the final repository") Klas Lundgren, ASEA-ATOM
8	KBS-TR-46	Temperatur beräkningar för använt bränsle ("Temperature calculations for spent fuel") Taivo Tarandi, VBB.

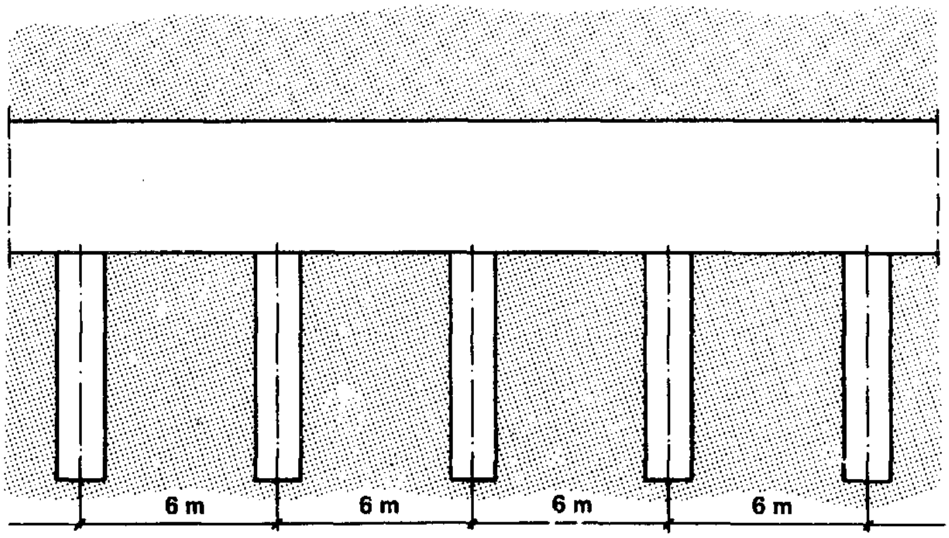

500 m
Main shaft
Skip shaft
Hoist shaft for waste canisters
Ventilation shaft
Ventilation tunnel exhaust air
Central transport tunnel
Outer transport tunnel
Outer transport tunnel
Service area
Rock transport tunnel
Rock crushing plant
Storage tunnels
Transport tunnels

A FIG. 1

A FIG 2

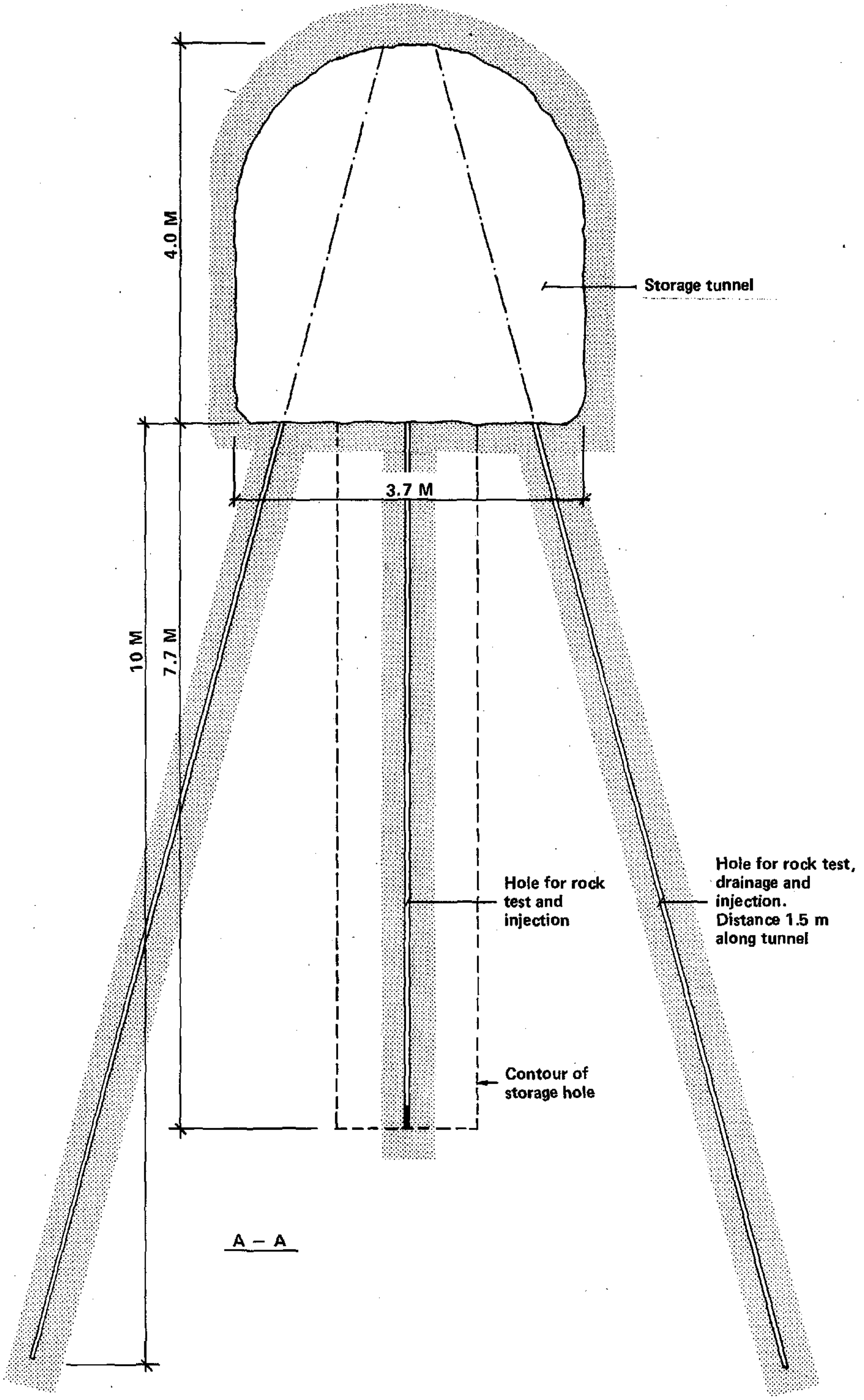


CROSS-SECTION

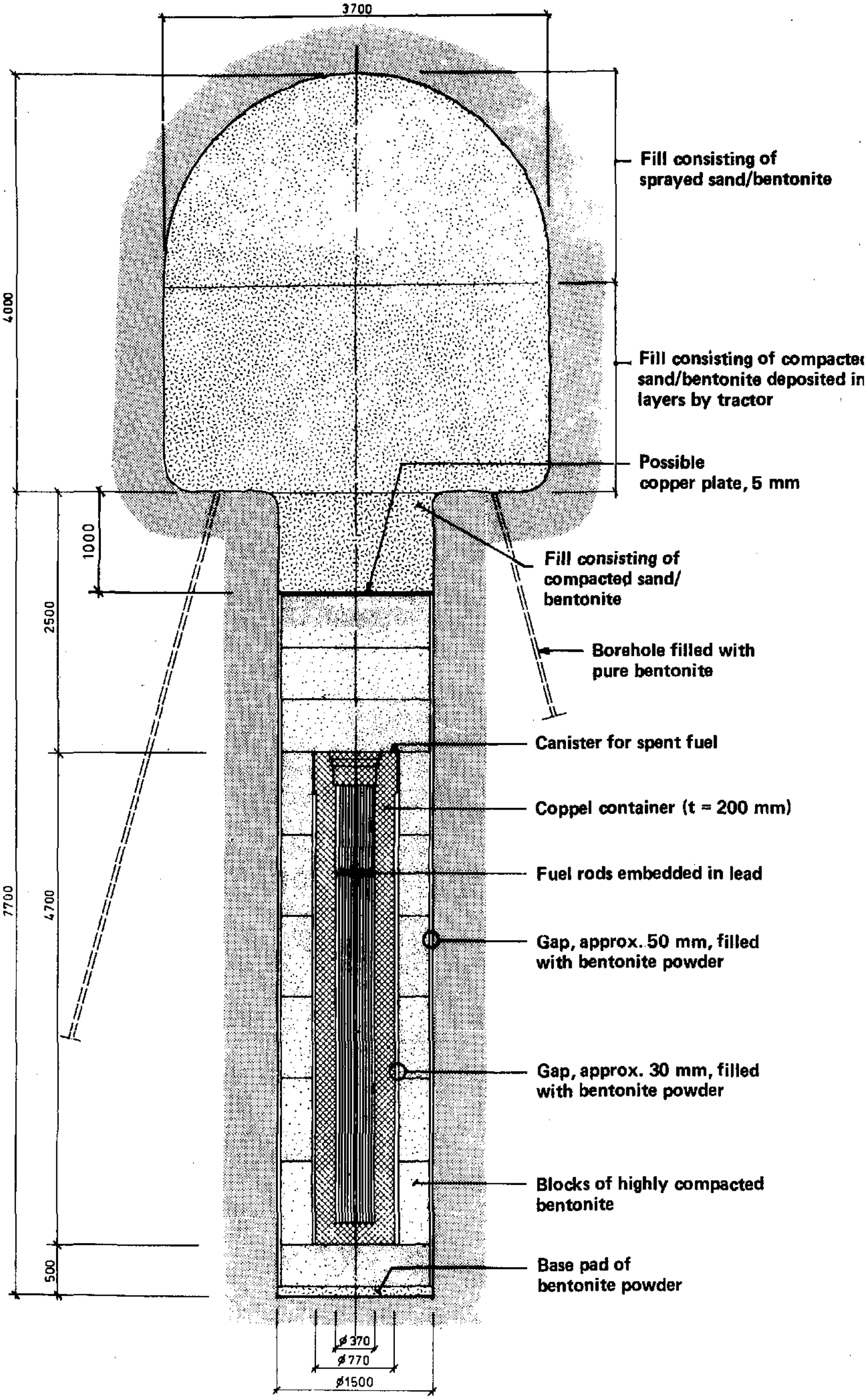


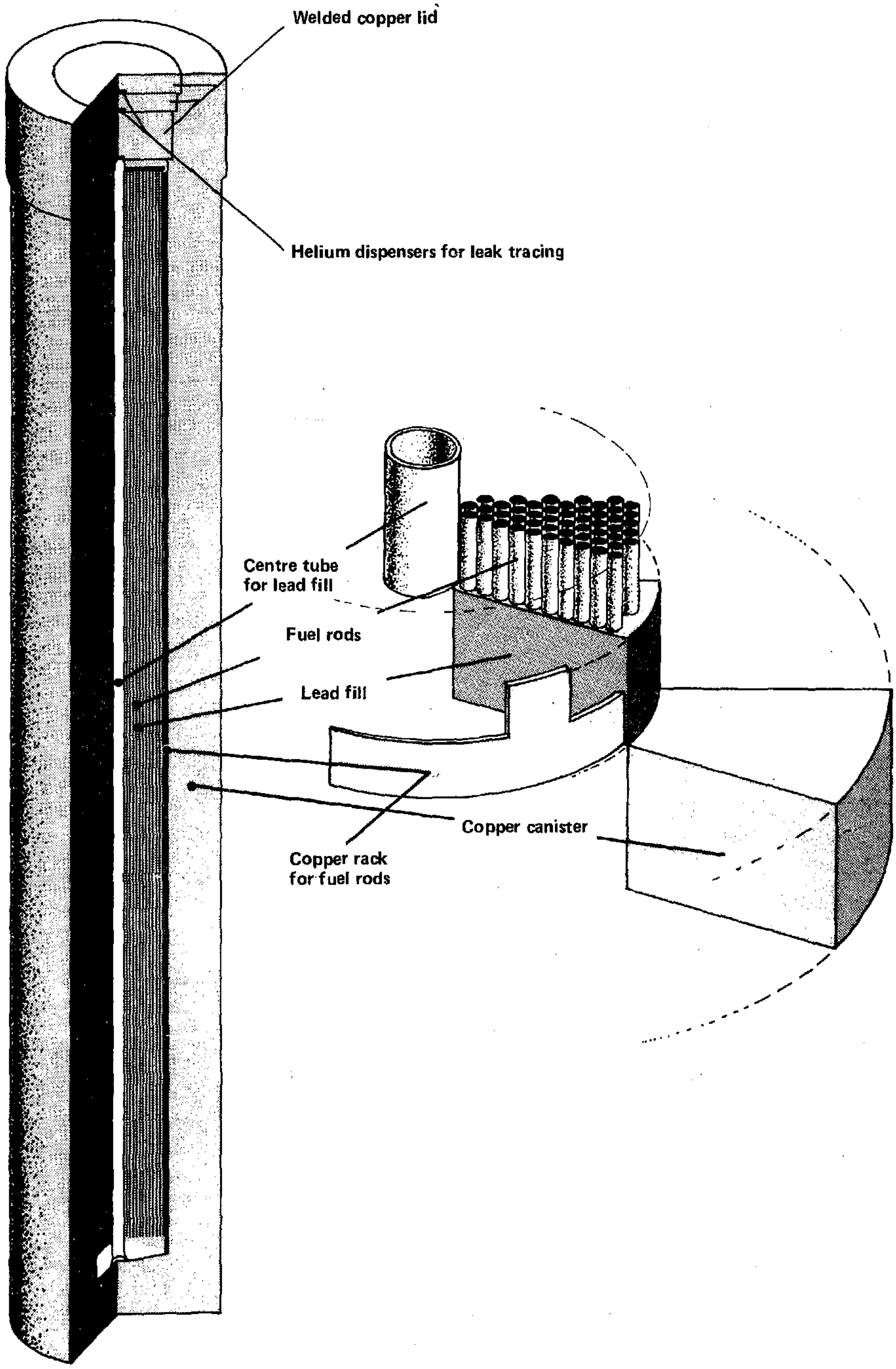
LONGITUDINAL SECTION

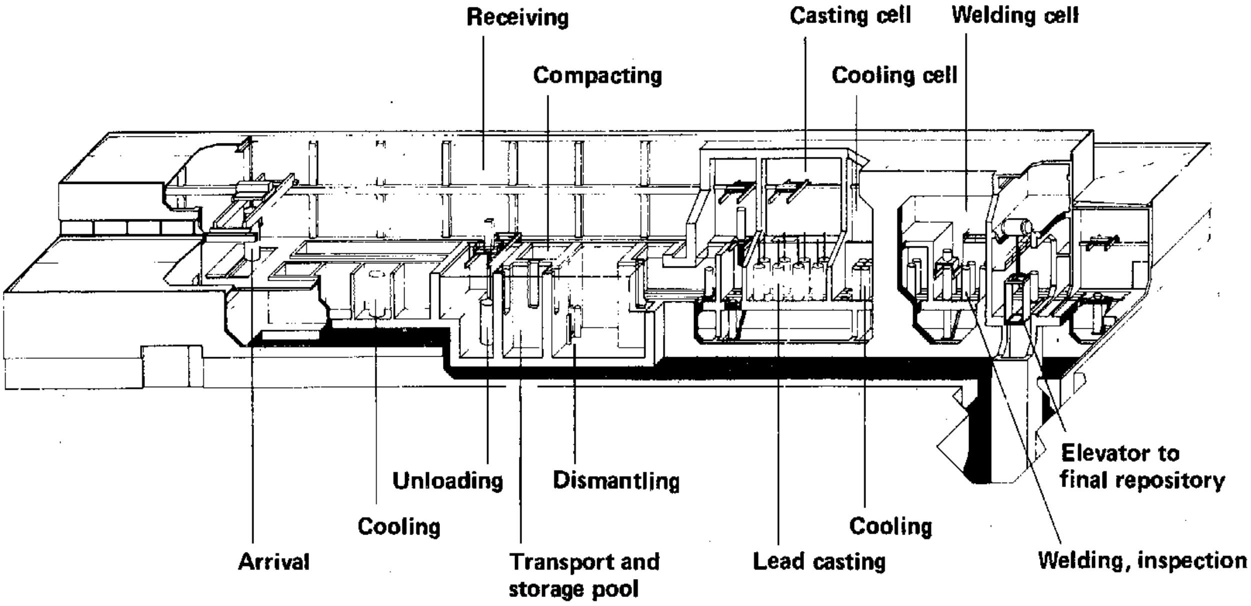
Cross-section and longitudinal section of storage tunnels in the final repository. Each storage hole is designed for one canister.


4.0 M
Storage tunnel
3.7 M
10 M
7.7 M
Hole for rock test and injection
Hole for rock test, drainage and injection. Distance 1.5 m along tunnel
Contour of storage hole
A – A

A FIG. 4


3700
4000
1000
2500
7700
4700
500
ø370
ø770
ø1500
Fill consisting of sprayed sand/bentonite
Fill consisting of compacte
sand/bentonite deposited in
layers by tractor
Possible copper plate, 5 mm
Fill consisting of compacted sand/ bentonite
Borehole filled with pure bentonite
Canister for spent fuel
Coppel container (t = 200 mm)
Fuel rods embedded in lead
Gap, approx. 50 mm, filled with bentonite powder
Gap, approx. 30 mm, filled with bentonite powder
Blocks of highly compacted bentonite
Base pad of bentonite powder


Welded copper lid
Helium dispensers for leak tracing
Centre tube
for lead fill
Fuel rods
Lead fill
Copper canister
Copper rack
for fuel rods


Receiving
Compacting
Casting cell
Welding cell
Cooling cell
Unloading
Dismantling
Cooling
Arrival
Transport and storage pool
Cooling
Lead casting
Elevator to final repository
Welding, inspection

1978-04-21
AWF/me

Enclosure A:1

PROBABLE COMPOSITION OF GROUND WATER IN CRYSTALLINE ROCK AT GREAT DEPTHS

1 Earlier investigations

In KBS Technical Report No 36 a probable composition of groundwater in crystalline rock at great depths was indicated.

The values were based on analyses made of groundwater from various parts of the country, at which values from wells drilled in rock in Uppland with a depth mostly less than 100 m were considered.

After that this table was prepared additional analyses have been made, e.g. at Finnsjön and Stripa, and analyzed at the department of agricultural hydrotechnics of the Royal Institute of Technology in Stockholm, by Gunnar Jacks.

2 Additional investigation

In this additional investigation the results from the new analyses made were considered. In particular it has been considered essential to give the analyses from greater depths a more dominant influence on the selection of a probable interval.

When it has been possible to do so the values have been confined within a more narrow interval than in report No 36.

The table reflects the composition of the groundwater in rock formations which from a geological and hydrological point of view are suitable for a final repository. Such areas can first of all be found under a local watershed.

The results of the analyses show that the intervals selected are realistic.

Of special interest from a corrosion point of view are the values for:

disolved oxygen
sulphides
sulphates
organic substances

At the assessment of the risk for corrosion due to microbacterial activity the content of nitrates and phosphates is also of interest.

The following general comments may be made on the analyses:

Oxygen

The oxygen content in the groundwater can be expected to be very low. The oxygen has been consumed through biological activity in the groundlayers through which the surface water passes on its way down to the groundwater area.

If Fe^{2+} and sulphides are present in the water, free oxygen will be consumed at the oxidation of these ions. The analyses confirm that the oxygen contents are very low, <0.01 - 0.07 mg/l.

Sulphides

Sulphides can be formed from sulphates through reduction caused by microbacterial activity during the passage of the water through the groundlayer and the rock.

When iron is present the sulphides should appear as iron sulphides with poor solubility.

Analyses made on water from Finnsjön and Stripa have shown contents <0.1 mg/l HS^-. One analysis from Forsmark has shown 5 mg/l but this value may possibly include sulphide present in Fe-sulphide form.

The contents of dissolved sulphides can be expected to be in the interval 0.1 - 1 mg/l.

Sulphate

G Jacks material from wells indicates sulphate contents in the order of magnitude of 15 mg/l, while materials from health authorities have shown contents in the order of 30-40 mg/l.

The analyses of water from great depths show considerably lower sulphate content, in most cases 6-12 mg/l and in some cases still lower values.

The most probable reason for the decrease of the sulphate content with the depth is that sulphate is reduced to sulphides which are then bound to iron as iron sulphide or pyrite. This process has been proved to occur in nature. In deep mines the sulphate content has been found to decrease very much with the depth.

Organic substances

The content of organic substances measured as $KMNO_4$ - consumption is 30-40 mg/l. This corresponds to a chemical oxygen consumption of 7.5 - 10 mg/l and an approximate organic content of about 10 mg/l. The organic substances may be expected to be resistant to biological decomposition

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The above is an English translation of a document in Swedish dated Stockholm March 7, 1978, by Jan Rennerfelt and Gunnar Jacks.

Analysis	Unit	Probable interval	Min.value x)	Max valu
Conductivity	S/cm	400-600		1100
pH		7,2-8,5		9,0
$KMnO_4$-consumption	mg/l	20-40		50
COD_{Mn}	"	5-10		12,5
Ca^{2+}	"	25-50	10	60
Mg^{2+}	"	5-20		30
Na^+	"	10-100		100
K^+	"	1-5		10
Fe-tot	"	1-20		30
Fe^{2+}	"	0,5-15		30
Mn^{2+}	"	0,1-0,5		3
HCO_3^-	"	60-400		500
CO_2	"	0-25		35
Cl^-	"	5-50		100
SO_4^{2-}	"	1-15		50
NO_3^-	"	0,1-0,5		2
PO_4^{3-}	"	0,01-0,1		0,5
F^-	"	0,5-2		8
SiO_2	"	5-30		40
HS^-	"	$<$0,1-1		5
NH_4	"	0,1-0,4		2
NO_2	"	$<$0,ol-0,1		0,5
O_2	"	$<$0,01-0,07		0,1

x) Estimated probability for that the values will not be lower than the minimum or higher than the maximum is 95%.

PROBABLE COMPOSOSITION OF GROUND WATER IN CRYSTALLINE ROCK AT GREAT DEPTHS

VOLCLAY

PHYSICAL CHARACTERISTICS OF VOLCLAY BENTONITE

The properties of Volclay are those of montmorillonite, a clay mineral of unique characteristics, which constitutes 90% of Volclay substance. Montmorillonite has the approximate chemical formula:

$$[(Al, Fe)_{1.67}Mg_{0.33}]\ Si_4O_{10}(OH)_2(Na, Ca_{0.33})$$

The other 10% consists of minute fragments of other minerals, the most abundant being feldspar. There are small fractions of gypsum, calcium carbonate, and quartz and traces of partially altered volcanic glass, biotite mica, magnetite, limonite, hematite, leucoxene, apatite, zircon, pyrite, titanite, and tremolite.

TYPICAL CHEMICAL ANALYSIS, MOISTURE FREE BASIS

	Percent by Wt. (Varies Between)	
Silica (SiO_2)	58.0	64.0
Alumina (Al_2O_3)	18.0	21.0
Ferric Oxide (Fe_2O_3)	2.5	2.8
Magnesia (MgO)	2.5	3.2
Lime (CaO)	0.1	1.0
Soda (Na_2O)	1.5	2.7
Potash (K_2O)	0.2	0.4
Ferrous Oxide (FeO)	0.2	0.4
Titanium Oxide (TiO_2)	0.1	0.2
Other minor constituents	0.5	0.8
Chemically-held water (H_2O)		5.64
Mechanically-held water (H_2O)		0.00

PARTICLE SIZE

When dispersed in water, Volclay separates into extremely fine particles, as follows:

96% to 97% finer than 44 microns (No. 325 Standard U.S. Sieve)
93% to 94% finer than 5 microns
87% to 89% finer than 0.5 micron
60% to 65% finer than 0.1 micron

One micron is about 1/25,000 inch. One cubic inch of dry Volclay, when disintegrated in water, is estimated to yield 9500 billion individual flakes, and the total surface area of these particles is about one acre in extent.

GENERAL

Specific gravity—2.7. Actual weight relative to volume depends on the degree of pulverization, the packing and settling of the sample.

pH value of water suspensions is 8.5 to 10.0.

Index of refraction—1.55.

Mohs Hardness—1 to 1.5. Slightly harder than talc.

BASE EXCHANGE

Volclay is noted for its base exchange properties; in a water solution, it gives up sodium and potassium ions and takes in calcium and magnesium ions, thus softening the water slightly. It also enters strongly into base exchange with organic bases, extracting them from solutions of their salts.

The exchangeable metallic bases of average Volclay, determined quantitatively by leaching with ammonium acetate are:

ELEMENT	meg./100 gms.
Sodium	60 to 65
Calcium	15 to 20
Magnesium	5 to 10
Potassium	1 to 5
Sum-corrected for sulphates	85 to 90

Because the exchange ions are affected by many factors, values are somewhat different in different shipments. These values are not guaranteed to exist in any lot or any one shipment.

SWELLING

The rate of swelling depends upon the fineness, grade and on how the bentonite is handled; all grades expand very slowly when water is poured on them, much faster when they are poured into water. Finely powdered Volclay grades absorb water slowly; MX-80 Volclay absorbs it intermediate and specially sized KWK Volclay absorbs water more rapidly.

Volclay absorbs nearly 5 times its weight of water and at full saturation it occupies a volume 12 to 15 times its dry bulk. On drying, it shrinks to its original volume. The swelling is reversible — it can be wetted (swelled) and dried (shrunk) an infinite number of times, if the water used is fairly pure.

It absorbs and swells faster in hot water than cold; it does not swell in alcohol, gasoline and similar liquids; it swells only slightly in solutions of strong chemicals, such as acids, alkalies or salts.

WATER SUSPENSIONS

When mixed with 7 to 10 parts water, it makes gelatinous pastes. With 15 to 20 parts water, it forms milkv, flowable sols.

Figures are given showing the consistency (viscosity) of two Volclay suspensions compared with clear water, mixed thoroughly:

	Centipoises
Clear Water	1
5% Volclay (1 Part Volclay to 19 Parts Water)	3 to 8
6-1/4% Volclay (1 Part Volclay to 15 Parts Water)	8 to 25

The sols were tested immediately after stirring; they show higher readings after standing a few hours.

In thinner dilutions — as 1 part Volclay to 99 distilled water — most of the Volclay remains suspended indefinitely. Even in dilutions as low as 1 to 5000, a considerable part does not settle. Distilled water must be used with low Volclay concentrations as the electrolytes in tap water might cause partial flocculation.

Dilute suspensions show Brownian movement — the particles are in motion, colliding and repulsing each other. Heavier slurries exhibit thixotropy, a kind of gelation that occurs when they stand quiescent, but which reverts to fluidity on being shaken or stirred.

EFFECT OF ELECTROLYTES

Particles of Volclay in water carry strong negative charges, causing them to attract and cling to positively charged particles of matter. When neutralized by oppositely charged substances, they floc together, forming spongelike aggregates, and if this occurs in dilute dispersions, the flocs settle. In thicker mixtures, however, as those containing 6% or more of Volclay, the effect of added electrolytes is to increase the viscosity.

Suspensions of Volclay are ordinarily difficult to filter, forming impenetrable cakes which seal off water. One of the effects of neutralizing or flocculating the particles is to make such suspensions more readily filterable.

It follows that all dispersions of Volclay are profoundly affected by electrolytes. The higher the valance of the latter the stronger the effect; monovalent cations are mildly active in causing flocculation, di-valent ones more so and tri-valent ones much more so.

The order of adding electrolytes is important. If an electrolyte is added to a thick slurry in which the Volclay has first been fully hydrated and swelled, the consistency of the slurry will be increased; but if the water is first treated with an electrolyte and the Volclay put in later, the dispersion will be thinner than a mixture of Volclay and clear water.

Temperature of water and time of standing also are factors. Some electrolytes stiffen the slurries temporarily, followed by thinning, after standing days or weeks; others reverse this action.

SORPTION

Montmorillonite unit cells, of the particular kind that constitute Volclay, have the outstanding peculiarity of expanding accordion-like in water. This enlarges the space between the sheets which form the structure and permits the free ingress and egress of ions of various kinds.

The mobility of the flakes when in suspension brings them in close contact with other dissolved and suspended substances. Particles of matter are not only adsorbed onto the surface of the bentonite molecule, but probably also absorbed within its lattice-like structure. The avid sorption of Volclay for other substances — both organic and inorganic — is therefore due to one or more of these factors: great surface area; spongy structure; mobility; base-exchange; strong negative polarity.

BOND STRENGTH

The maximum adherent powers of Volclay in moistened masses with other minerals is exerted when the added moisture is 50% of the weight of the Volclay.

EFFECT OF TEMPERATURE

The properties of Volclay are unaltered at temperatures below 204° C. The chemically held water is progressively driven off when exposed to higher heats for any length of time and is completely gone at 660° C. However, if heated to 537° C. and quickly cooled, its properties are unchanged.

Its swelling properties decrease progressively in the same ratio as the loss of chemically held water.

Softening begins about 1037° C. and fusion occurs at 1337° C.

Volclay imparts to masses of other minerals bonded with it an extraordinary "hot strength", i.e., resistance to load pressure while hot. In the range of temperatures just below the softening point, its "hot strength" far exceeds that of other clays.

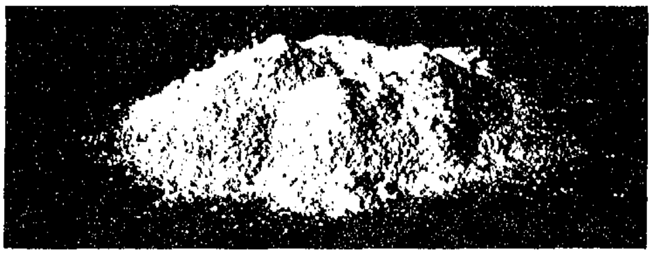
MECHANICALLY HELD MOISTURE

Volclay as shipped contains different moisture contents. When exposed to the atmosphere, it slowly gains or loses moisture according to the humidity.

It requires 2 hours at 105° C. to 110° C. to dry it to a moisture-free condition.

KWK VOLCLAY — *fine pellet-size bentonite. Disperses in water much quicker than powder and yields the same, smooth gel.*

SPV VOLCLAY — *powdered bentonite. Mainly for general industrial purposes where bentonite is not mixed with water.*



CHEMICAL COMPOSITION OF THE QUARTZ SAND

The chemical composition of the quartz sand to be used in the final repository appears from the enclosed records which refer to samples of the so called silver sand supplied from Bornholm, Denmark.

The sulfur content in the silver sand is only a few thousands of one percent in according to tests made on eight samples.

ANALYTICA AB

Ångsvägen 4 · Box 6 · 191 21 Sollentuna-Sweden
Telephone 08-96 03 60 · Telex 11285 ANA S

A:3.2

ANALYSINTYG nr 76-16951

KBS
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IR- INDUSTRIRÅVAROR

Uppdragsgivare

Ahlsell & Ågren AB
Sektion IR, IA, rib
Fack
104 60 STOCKHOLM

Datum 76-05-10

Ref.: I. Ahlandsberg

Prov märkt Silversand 95, provnr 1228.

Pb	<10	ppm
Cd	< 5	
As	< 300	
Hg	0.8	
Be	< 1	
Cu	5	
Cr	< 30	
Ni	< 10	
Zn	< 30	
Sn	< 10	
Co	<10	
Mo	<10	
Mn	15	
V	<10	
Fe tot	400	

ANALYTICA AB
M. Merseburg

A:3:3

Glasforskningsinstitutet i Växjö

Glasteknisk Utveckling AB

ATTEST 55 V

Ahlsell & Ågren A/S

3700 Rønne
Danmark

Kem analys

1 sand S-17. 4-1-78

SiO_2	98,8	%
Al_2O_3	0,23	
Fe_2O_3	0,20	
Cr_2O_3	0,0011	
CaO	0,04	
Na_2O	0,02	
K_2O	0,10	

1 sand S-36. 4-1-78

SiO_2	99,3	%
Al_2O_3	0,14	
Fe_2O_3	0,11	
Cr_2O_3	0,0002	
CaO	0,01	
Na_2O	0,02	
K_2O	0,05	

1 sand S-55. 4.1.78

SiO_2	99,4	%
Al_2O_3	0,15	
Fe_2O_3	0,10	
Cr_2O_3	$<$ 0,0001	
CaO	0,02	
Na_2O	0,01	
K_2O	0,07	

1 sand S-95. 4.1.78

SiO_2	99,5	%
Al_2O_3	0,14	
Fe_2O_3	0,06	
Cr_2O_3	0,0001	
CaO	0,02	
Na_2O	0,02	
K_2O	0,07	

Växjö 1978-02-03
GLASTEKNISK UTVECKLING AB

S.Linzander

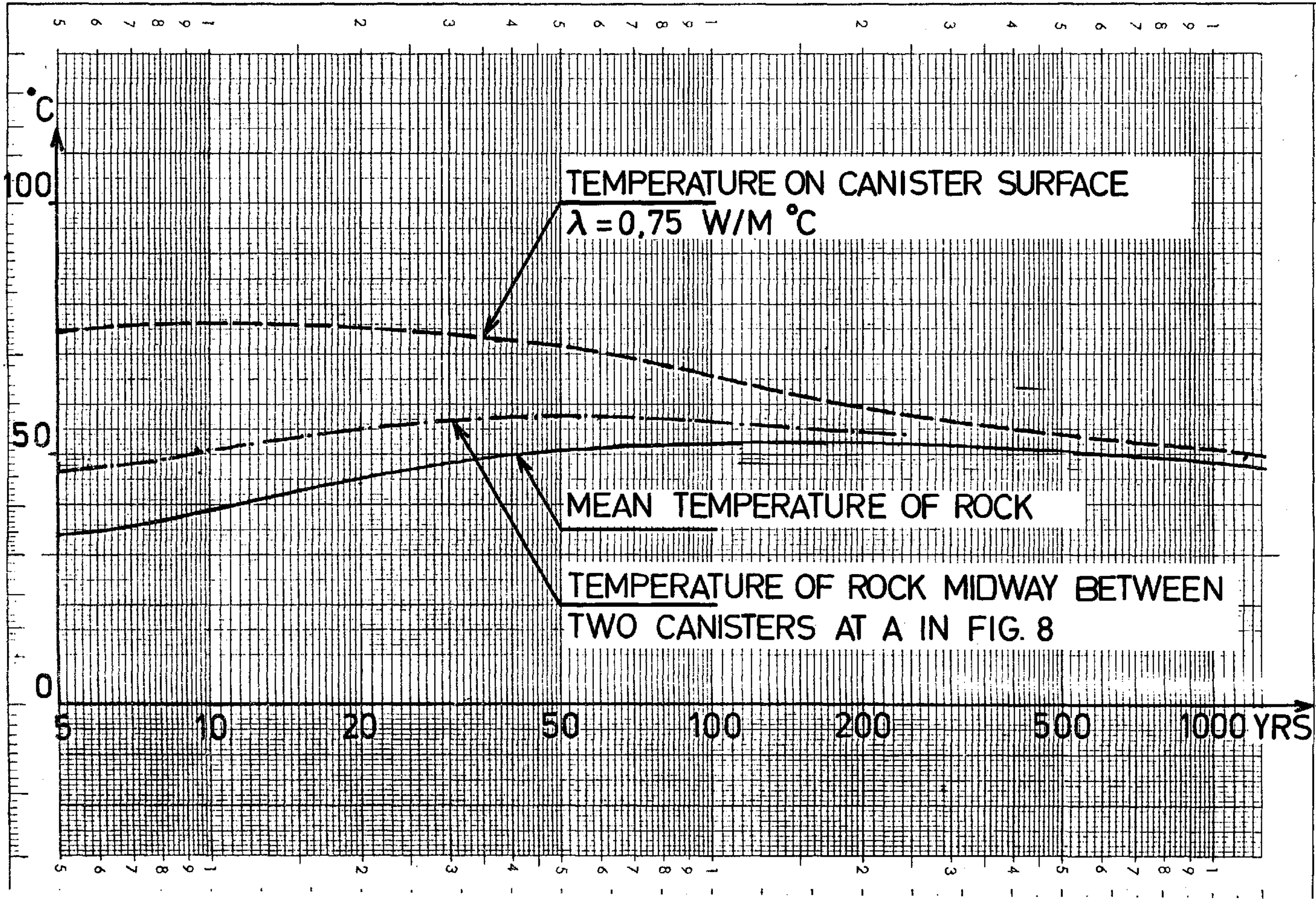

FIG. 7

VARIATION OF TEMPERATURE AT CENTRE OF FINAL REPOSITORY

SUBAPPENDIX

A:4.1

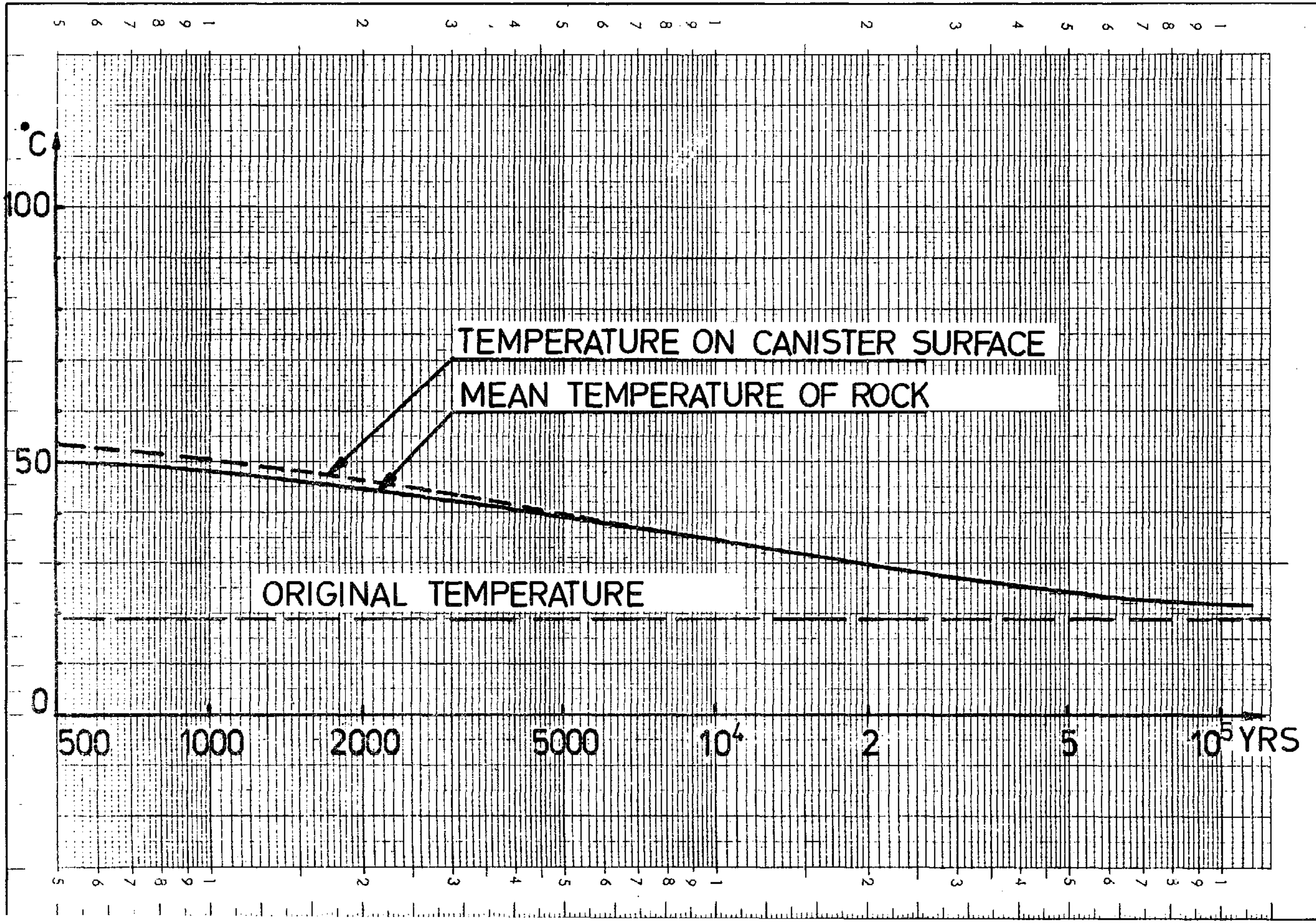

FIG. 7B

VARIATION OF TEMPERATURE AT CENTRE OF FINAL REPOSITORY 500 - 100 000 YEARS

SUBAPPENDIX A:4.2

Summary of some studies concerning iron(II) phosphate.

Margareta Vannerberg and Nils-Gösta Vannerberg

General

Iron(II) phosphate occurs in nature in the form of the mineral vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$. This mineral occurs in reducing sediments and can, alternatively with iron sulphide (mackinawite and pyrite) and carbonates (siderite), comprise a natural redox buffer. This appears to be the case in the healthier northern part of Chesapeake Bay. The water is saturated with respect to iron(II) ion and phosphate ion (the solubility product for vivianite is slightly exceeded). Vivianite occurs in the sediment. In this water, the pH is 7.6 while the redox potential in reference to a standard hydrogen gas electrode is -0.225 (pe = -3.8). Our measurements for a similar solution give -0.15 (pe = -2.5), which shows good agreement in view of the fact that the natural system contains so much else which can affect the potential. Vivianite soaked in clay sediment (kaolinite) reacts rapidly with oxygen gas (2).

A wet sample of vivianite can only be observed for 10 minutes in a diffractometer. But this does not mean that the sample has been completely oxidized, but rather merely that the vivianite crystals have burst apart. Free or complex-bound ferrous ions in solution appear to have a very short life at the pH in question.

The solubility product for vivianite has been determined to be $10^{-36.0}$. The concentrations at pH = 7.6 in the water in question appear to be 10^{-4} for Fe^{2+} and 10^{-9} for PO_4^{3-}. The water in Chesapeake Bay is thus considerably supersaturated (2).

Previous experiments

Previous reports have described how vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ can be prepared and how, when suspended in water, it reacts with oxygen gas. The reaction between oxygen and vivianite in a water slurry proceeds slightly more slowly than the reaction between oxygen gas and moist, solid vivianite (1). This is probably attributable to the low level of gaseous oxygen in the water and lower diffusion rates.

Attempts to get vivianite to react with bentonite in autoclave trials at 200-250°C over a period of 1-2 weeks have been fruitless. This result was expected and was also verified by the fact that vivianite in its natural environment occurs in sediments consisting of kaolinite.

In all previous experiments, vivianite has been prepared and tested without being allowed to come into contact with gaseous oxygen. In an actual engineering application, it is obviously not possible to exclude air during the period in which work is in progress in tunnels and repositories. It is thus important to modify the properties of the iron(II) phosphate so that it reacts at a moderate rate with gaseous oxygen and thereby functions as a redox buffer over a longer period of time.

Working hypothesis

Vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$ shall be liberated from its lattice water so that water-free $Fe_3(PO_4)_2$ is obtained. The latter reacts only sluggishly with gaseous oxygen. In a water suspension, the water-free phosphate is converted to water-soluble complexes and solid vivianite, which reacts rapidly with gaseous oxygen.

Preparation of vivianite

I Preparation from metallic iron

3 g iron powder were dissolved in 100 ml hot 2 M phosphoric acid through which nitrogen gas was bubbled. The phosphoric acid solution was prepared from commercial phosphoric acid purris (75%) and distilled water.

After the iron had dissolved, the vivianite was precipitated with a concentrated solution of disodium hydrogen phosphate to pH = 7. The obtained precipitate was white with a slightly bluish tint. It was filtered off while protected by nitrogen gas, and washed with distilled water and alcohol. It was then placed in a tube furnace in a nitrogen gas atmosphere. The furnace was heated to 300°C and then allowed to cool. The resultant sample was light green in colour. It was ground and subjected to further examination. The sample contained sodium phosphate as an impurity.

II Preparation from iron sulphate

A concentrated solution of sodium dihydrogen phosphate was added in slight excess to a saturated solution of iron sulphate and water (15 g/100 ml) at 70°C. All the solutions were prepared from PA chemicals and distilled water.

The resultant precipitate was white with a slight greenish tint. The precipitate was easy to filter and well-crystallized. The yield was poor due to a low pH. The product reacted with atmospheric oxygen just as rapidly as the product prepared by method I. The sample contained sodium phosphate.

Analysis

The samples were analyzed with respect to iron(III) in the following manner. A suitable sample, as a rule 0.1 g, was weighed in and dissolved in 100 ml sulphuric acid. A sample of 5 ml was taken from this solution and mixed with 5 ml 2 M KSCN solution. Absorbance was measured in a Beckman spectrophotometer at a wavelength of 500 nm. The corresponding molar absorpivity for absorbing iron species were found to be 3430 mole^{-1} cm^{-1}. The total iron content was determined by boiling 50 ml of the sulphuric acid solution with a few ml of 40% H_2O_2 solution until the hydrogen peroxide decomposed. The solution was then diluted to 1000 ml. 5 ml was taken from this solution and mixed with 5 ml 2M KSCN solution, after which absorption was measured.

Reactions with oxygen

a) A fresh sample was found to contain $0.04 \cdot 10^{-3}$ moles of Fe^{3+} and $4.65 \cdot 10^{-3}$ moles of Fe^{2+}. Thus, impurities of iron(III) are less than 1%. This concentration did not change over a period of 1 week of storage in a glass jar.

b) One sample was left to stand for one week on a watch glass, completely uncovered. After the week, the iron(III) content had increased to 1.5% of the total iron content.

c) 0.5 g of a fresh sample containing $0.01 \cdot 10^{-3}$ moles of Fe^{3+} was dissolved in water. The water was aerated for two days. It was then found to contain $1.2 \cdot 10^{-3}$ moles of Fe^{3+}. Approximately 30% of the available Fe^{2+} had been oxidized.

d) Different samples were treated as follows: 15 g bentonite, 15 g water and 85 g sand were mixed with 1 g $Fe_3(PO_4)_2$ and placed in the bottom of a glass beaker. The thickness of the layer was 4.5 cm. Another layer, consisting only of bentonite, water and sand, was laid on top of this layer. After a week, the sample was taken out for analysis. It was found to contain 20-21% ferric ions, in proportion to the total iron content.

e) Reactions with vivianite and bentonite

3 g vivianite were mixed in a nitrogen-filled autoclave with bentonite and water. The mixture was analyzed with the aid of an X-ray diffractometer. The autoclave was heated to 250°C for two weeks. No changes could be observed with the diffractometer. The reducing properties of the mixture were tested by bubbling air through a water slurry of the mixture 1 g of mixture contained $0.01 \cdot 10^{-3}$ moles of ferric ions from the start; after 72 hours of oxidation, it contained $0.12 \cdot 10^{-3}$ moles of ferric ions.

Conclusions

The working hypothesis has been verified in all respects. Vivianite deprived of its lattice water reacts very sluggishly in damp air. If it is moistened or mixed with water to a slurry, it regains its good reducing properties.

Recommendations

Iron(II) phosphate is a compound which occurs in redox buffers in nature. Iron(II)-iron(III) phosphate has a very suitable pe and thus a suitable redox potential. Iron(II) phosphate reacts rapidly with gaseous oxygen in the moist condition, while it is poorly reactive and easy to handle in the dry condition. We therefore recommend that KBS use an iron phosphate buffer as a protection for copper canisters intended for the storage of radioactive material.

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2. Troup Bruce N., J. Hopkins University,
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Distribution KBS (2 ex) Prof Vannerberg, CTH Prof Mattson, Korr.Inst. (9 ex) ASEA/KYDK Elgh	Från/From T	Datum/Date 78-04-05	Reg.	Page Sida 1
	Författare/Author Kåre Hannerz, Lennart Hydén			
	Granskad/Examined		Godkänd/Approved	

Titel/Title

Removal of free oxygen from bentonite-sand mixtures
with the aid of a deoxidizer. Preliminary report.

Sammanfattning/Abstract

1 Background

The experimental study described here was intended to shed further light on certain circumstances of importance for an evaluation of the proposal for a method for the final storage of spent nuclear fuel which the KBS project intends to present in the spring of 1978.

In this proposal, the fuel is encapsulated in a thick-walled copper canister. This canister is placed in a drilled storage hole in the bottom of a horizontal tunnel and surrounded by a buffer material in the holes consisting of compacted bentonite. This material is characterized by low porosity, low diffusivity, extremely low permeability and a high swelling capacity, this last-named property guaranteeing the absence of water-bearing fissures in the buffer material.

Penetration of the copper canister due to corrosion can only occur as a result of an inflow of oxidizing agents from the environment (e.g. free oxygen), while a reaction with the groundwater itself is impossible for thermodynamic reasons. Due to its low diffusivity and freedom from fissures, the buffer material guarantees a low inflow of oxidizing agents. The level of such agents in the circulating groundwater is also very low.

The tunnel which runs above the storage holes, and which has a volume several times greater than the combined volume of the storage holes which it connects, is filled for economic reasons with a mixture of quartz sand and bentonite instead of pure compacted bentonite. Due to its larger volume and higher porosity, this mixture will contain considerably greater quantities of free oxygen after the final repository has been filled than the storage holes. Furthermore, it is possible that this oxygen will preferentially attack the upper end of the copper canister, the end towards the tunnel. The presence of this oxygen could therefore be considered to entail a certain risk of corrosion penetration of the top end of the canister. For this reason, the oxygen in the tunnel fill should be removed chemically after the final repository has been filled by the addition of a deoxidizer.

The properties of the deoxidizer must be such that it does not react with atmospheric oxygen during the period when the sand-bentonite mixture in which it is entrapped is handled openly in air, but can still remove atmospheric oxygen more or less completely over a longer period of time. The speed requirement in this respect is very low; owing to the slow rate of diffusion, many years are available.

When the tunnel is filled, pulverized deoxidizer is mixed in with the dry bentonite powder. This is then mixed with quartz sand, after which the mixture is moistened with water to a water content of 10-15% (whereby it loses its tendency to dust). The mixture is driven out into the tunnel by special vehicles and compacted by rollers in layers. After compacting, the mixture no longer contains any open porosity, and oxygen can only be transported through the material by diffusion.

The time between water admixture and sealing from external oxygen supply through compaction amounts to no more than a week.

The top part of the tunnel is filled by spraying, whereby some open porosity may remain. Any oxygen remaining in this part of the tunnel must, however, diffuse through the lower, compacted layers in order to reach the copper canisters. The oxygen in these layers can be gotten rid of by the addition of a surplus of deoxidizer.

2 Purpose of the study

The Swedish Corrosion Institute has been commissioned to carry out an independent assessment of the corrosion life of the copper canister. For this purpose, the Institute has assembled a reference group of researchers with competence in associated fields. This group has expressed a wish for an experimental demonstration to prove that deoxidants suitable for the purpose are available. The study reported here was conducted for this purpose. The purpose of the study has only been to demonstrate in general terms that effective oxygen reduction really does take place and that it does not take place so rapidly that the deoxidizer is consumed during the period when the bentonite and sand mixture to which it has been added is handled freely in the air. No detailed information on kinetics, reaction mechanism etc. has been sought.

Owing to the fact that only three weeks were available for the experiment, a high-grade elimination of oxygen could not be carried out at room temperature, so the experiments had to be conducted at a slightly higher temperature.

3 Deoxidizers tested

3.1 General

There are a large number of substances which react with oxygen and could therefore be of interest as deoxidizers. In this case, however, the choice was severely restricted by a number of factors. Organic compounds can be excluded owing to the fundamental risk that they could function as a substrate for sulphate-reducing bacteria. Reducing sulphur compunds have been excluded in view of the risk of sulphide formation. In the case in question, the choice was limited to two different compounds containing bivalent iron. For thermodynamic reasons, their presence leads to a very low oxygen pressure, amd their ability to eliminate oxygen from groundwater has also been geochemically verified.

Attention has been concentrated primarily on iron(II) phosphate, which was proposed as a deoxidizer by N.G. Vannerberg (1). Olivine sand, magnetite and fayalite slag have also been tested.

3.2 Iron(II) phosphate

Iron(II) phosphate was prepared by precipitating a solution of ferrous sulphate in water by titration with Na_2HPO_4 to pH 7. The precipitate was allowed to stand at 50^oC for 2 hours, during which time nitrogen gas was bubbled through it in order to improve its filtration properties. It was then vacuum-filtered through a büchner funnel under nitrogen gas and washed with acetone. It was then heated under nitrogen gas to 200^oC. After cooling, the compound exhibited no tendency to oxidize in air.

3.3 Magnetite

A sample of relatively pure magnetite, which has stood in air in coarse-grained form for many years, was ground down to < 400 mesh and used directly in this condition.

3.4 Fayalite slag

Fayalite slag is obtained in connection with certain types of steel production. Its main constituent is iron(II) silicate (fayalite Fe_2SiO_4).

A piece of slag was obtained from the Hofors steelworks and ground down to < 400 mesh and used directly in this condition.

4 Experimental method

The experiments were conducted under completely authentic conditions, except that the temperature was varied.

Weighed quantities of quartz sand (grain size distribution according to specification for tunnel fill), bentonite and deoxidizer were mixed dry, after which 15% by weight water was added. The mixture was homogenized in a mortar, after which it was packed with the aid of a rubber stopper into a glass tube with a ground glass stopper, whose volume and weight had previously been determined. A density of about 1.8 g/cm^3 was obtained using this packing method, which, on the basis of the values used for the theoretical density of the constituents, corresponds to an air-filled pore volume of about 20%.

The test tubes were placed (with grease-sealed stoppers) in thermostat-regulated baths at a number of different temperatures and were taken out after different periods of time, 1-12 days.

The test tubes were then placed in an airtight stainless steel container with a volume of about 500 ml together with some steel balls. The container was evacuated and filled with helium a number of times, after which it was filled with airless, helium-saturated water. Finally, 50 ml of helium gas were added, after which the container was sealed. The glass tube was then crushed by the steel balls, after which the clay-water-helium mixture was brought to equilibrium with respect to its gas content by means of vigorous shaking. The container was then connected to a computer-controlled Hewlett-Packard gas chromatograph, whereby the nitrogen and oxygen contents of the gas were determined.

A number of blanks were used to make sure that no oxygen entered the sample except from the test tubes.

The experimental apparatus is illustrated in fig. 1.

The gas chromatograph was used to determine the amount of nitrogen and oxygen in the helium mixture obtained after the test tube had been crushed. It was assumed that the nitrogen was not consumed in any manner. By determining the ratio between the amounts of oxygen and nitrogen, oxygen consumption can be determined as a percentage without knowing the exact total quantity of oxygen present from the start.

The spread in the values for the remaining quantity of oxygen can be expected to be relatively large, especially when most of the oxygen has been consumed.

It proved to be difficult to avoid a certain unfilled volume just underneath the glass stopper. Consumption of the oxygen present in this gas volume naturally proceeds more slowly, since it must diffuse down a certain distance into the fill. Moreover, the air-fill ratio varied, since the tubes were packed manually by different laboratory technicians. In view of the qualitative character of the study, undue efforts were not made to eliminate these sources of error.

Another possible source of error is air leakage into the tube through the greased standard ground seal. Although the stopper was held down by a spring during the course of the test, accidental leakage in connection with handling upon removal of the sample cannot be excluded.

5 Results

5.1 Experiment with iron(II) phosphate

Oxygen absorption trials were carried out 25°C, 40°C, 55°C and 70°C with the addition of 0.5% iron(II) phosphate dried at 200°C (3 H_2O).

The results are presented in fig. 2.

As can be seen, a high-grade elimination of oxygen is obtained after only 10 days at 70°C. But the results indicate that a certain residual quantity of oxygen tends to remain. The probable explanation is that this oxygen derives from a free volume at the top of the test tube. This is confirmed by the fact that the addition of 3 times the amount of iron phosphate did not appreciably reduce the residual oxygen content. In other words, it cannot be that the deoxidizer has been activated after the reaction of a certain portion.

The initial course of events corresponds roughly to a logarythmically decreasing oxygen content. A comparison between the curves shows that the reaction rate increases by a factor of about 2.5 when the temperature is increased 15°. This indicates that a high-grade oxygen elimination at room temperature would require a period of about 100 d. This period of time is short enough that any copper corrosion occurring during it would be negligible.

The results at 25°C show that consumption of the deoxidizer during the time the mixture is handled openly in air is not a problem.

5.2 Experiments with other deoxidzers

As was mentioned previously, a number of trials were conducted with two inexpensive commercially available materials, namely ground magnetite and ground open-hearth slag.

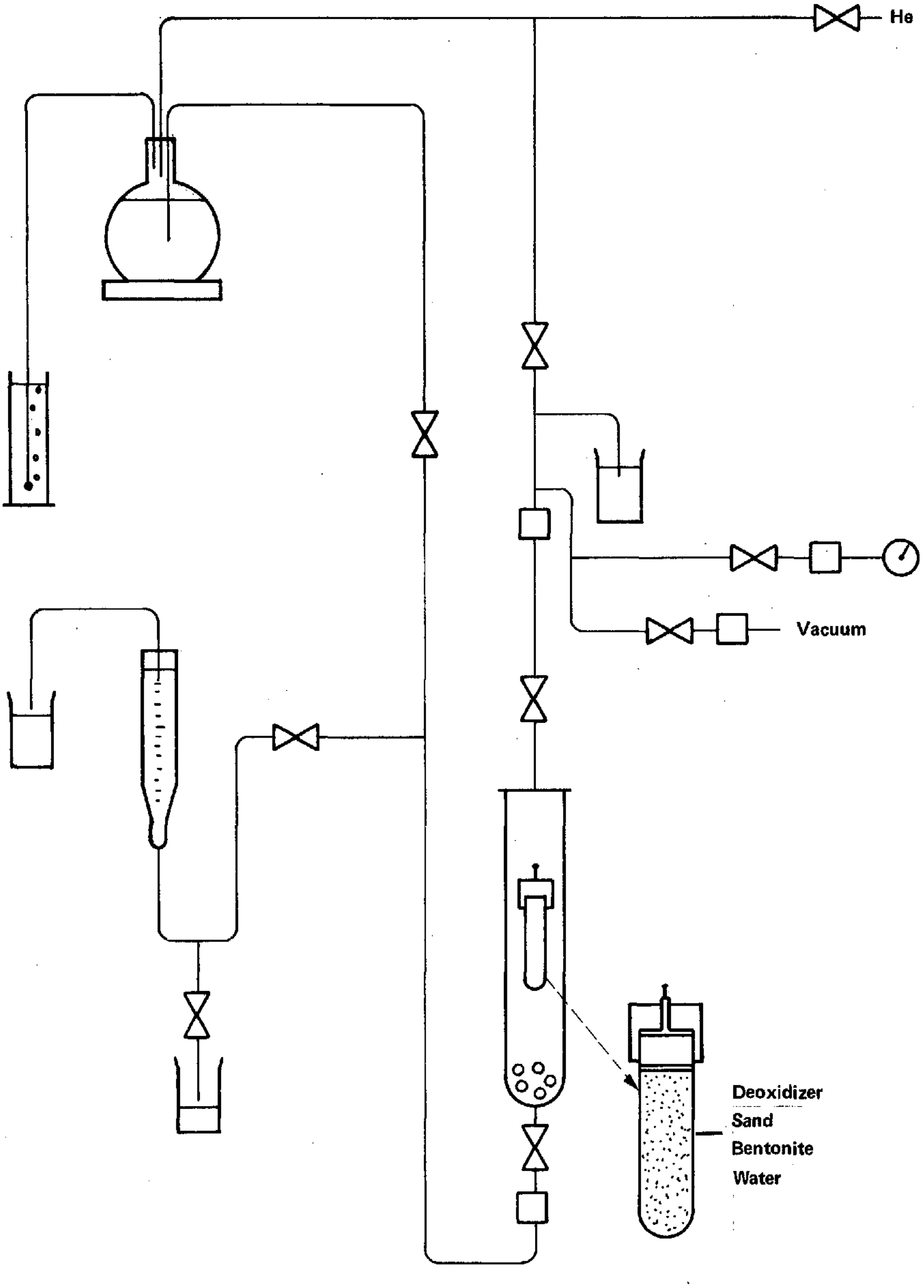
The results are presented in the table below.

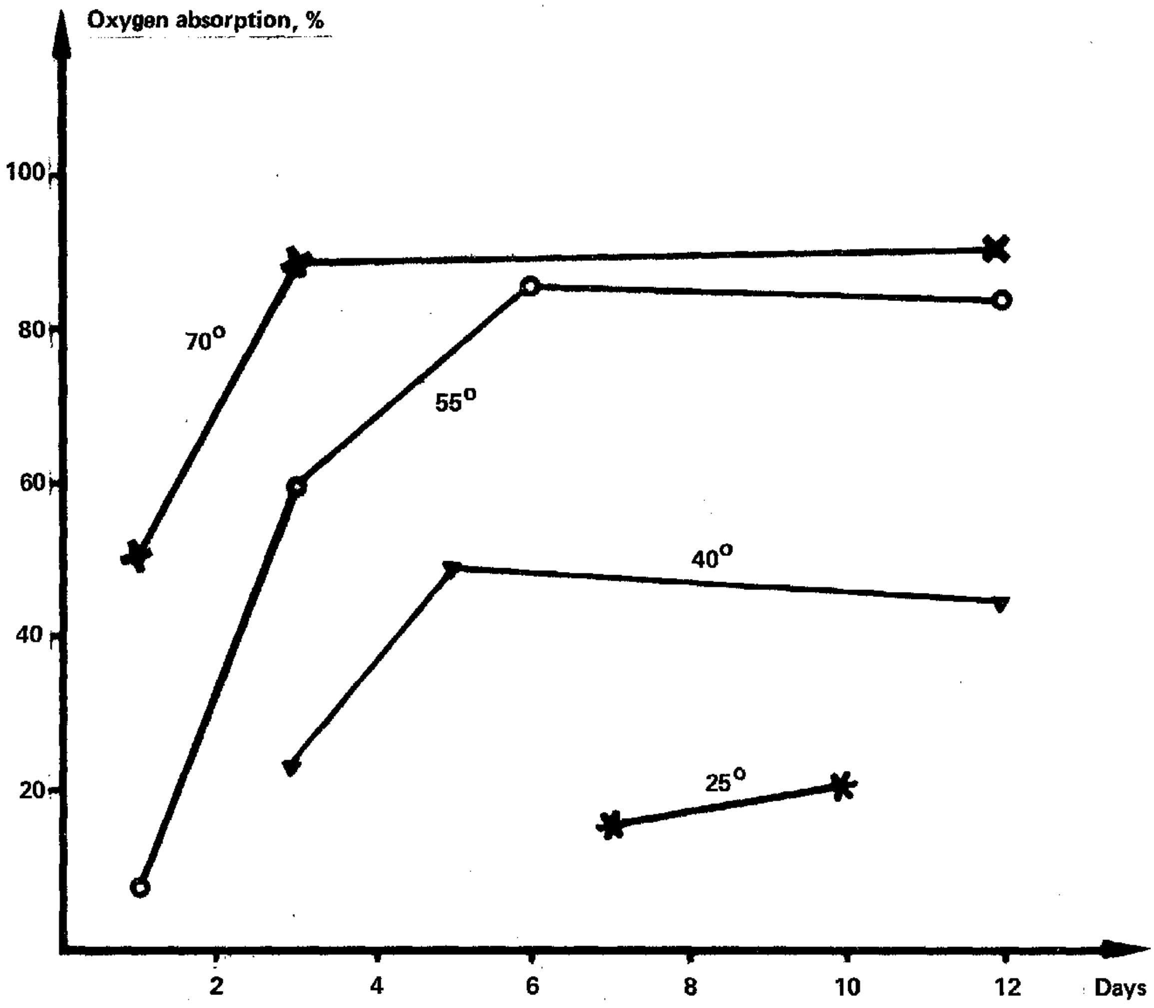
Material	Content	Temp.	Time	Oxygen absorbtion, %
Magnetite	5%	70°C	11 d	85
Open-hearth slag	5%	70°C	11 d	90

The results show that these materials are also probably suitable for use as deoxidizers.

6 Conclusions

The test results which were obtained show, to the extent which this is possible given the limited time available for experimentation, that iron(II) phosphate is suitable for use as a deoxidizer for the high-grade elimination of free oxygen in the bentonite-quartz mixture which is intended to be used as fill in the tunnels above the storage holes.


He
Vacuum
Deoxidizer
Sand
Bentonite
Water



Graph illustrating oxygen absorption as a percentage of the oxygen (atmospheric) present in a mixture of sand (85%) + bentonite (15%) + water (15% of the mixture) + 0.5% vivianite.

THERMODYNAMIC ASPECTS OF COPPER ENCAPSULATION AND THE CORROSION ENVIRONMENT IN A WASTE REPOSITORY

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Department of Inorganic Chemistry,
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A prerequisite for an evaluation of the long-term stability of metallic copper is a thorough knowledge of the chemical processes which can take place in the system composed of the copper canister, the buffer material, the rock and the groundwater. The following thermodynamic study has been conducted in order to gather the data necessary for an evaluation of the corrosion environment in the waste repository and to determine which chemical reactions are possible in the system.

The thermodynamic system is complex and consists of rock of a given mineralogical composition, a system of tunnels filled with waste canisters and buffer mass and, finally, groundwater. The rock-groundwater system is initially in equilibrium; but this equilibrium is disturbed by the input of oxidants when the repository is built. The tunnel system with its buffer mass has a mineral composition which is different from that of the rock and is therefore not initially in equilibrium with inflowing groundwater. The composition of the system, i.e. the corrosion environment, can thus change with time. The flow rate in the system is low, which should mean that changes in the system take place relatively slowly and that the system is, for the most part, in local equilibrium. This is discussed further on pages 5-8.

The chemical composition of the rock, the buffer mass and the groundwater for several different possible waste repositories has been specified in the specifications supplied by KBS (Appendix A).

(1978-03-30)

Copper is the most noble of the common constructional metals. The stability range of copper can most easily be represented with the aid of various types of redox diagrams, for example Pourbaix diagrams (page 10) or so-called "relative diagrams" (Appendix B3, page 12). Equilibrium concentrations for various copper species, under the conditions which can prevail in the waste repository at equilibrium between metallic copper and groundwater of a given composition, are reported in the following chapter.

I. Thermodynamic calculations of the equilibrium concentrations in the system $Cu-H_2O-Cl^{-}-CO_3^{2-}-SO_4^{2-}-F^{-}$ at different redox potentials and temperatures

The equilibrium calculations have been carried out for a system containing so-called "normal water", i.e. a groundwater of the same composition as that which normally occurs at great depths. The concentration of the sulphide-bearing species has been assumed to be zero,a condition which is not always met in natural groundwater. The detailed thermodynamic calculations are presented in Appendices B1 and B2.

The calculations show that metallic copper is stable in "normal water" of specified composition, provided that the level of free oxygen is low. Analyses of actual groundwaters from potential sites for a waste repository have shown that this condition can be fulfilled. In other words, the formation of oxidized copper phases can be prevented. Deep-lying groundwater often contains sulphides in varying quantities. Copper oxidation with the formation of Cu_2S is therefore a possibility which must be taken into consideration. This problem is discussed in the following section.

II. Thermodynamic conditions for the oxidation of copper with the formation of sulphidic phases

In order for an oxidation of metallic copper to be possible, an electron acceptor (an oxidant) must be present, normally oxygen dissolved in water. Other oxidants are also possible, e.g. sulphur(VI) in sulphate, hydrogen(I) in water, sulphur(-I) in pyrite or iron(III) in various types of minerals. The two first-named oxidants are particularly important, since their concentrations are relatively high.

The oxidation of copper with the formation of sulphidic phases is examined in Appendix B3. The study shows that the oxidation of copper by sulphate with the formation of sulphide is thermodynamically possible under the conditions which are expected to prevail in the waste repository. Geological and other chemical evidence shows, however, that the oxidation is negligibly slow, even over very long periods of time (Appendix C).

The thermodynamic calculations also show that copper can be oxidized by water and hydrogen sulphide with the formation of $Cu_2S(s)$. The oxidation rate is determined by the rate at which hydrogen sulphide is transported to the copper canister.

The stability conditions for copper do not change appreciably at higher temperatures. The calculations show that a high temperature is more likely to have a favourable effect on the thermodynamic stability of the copper canister.

III. Thermodynamic conditions for the oxidation of copper by nitrate

Nitrate occurs in varying quantities in groundwater and is also a potential oxidant for metallic copper. Appendix B4 reports the thermodynamic conditions necessary for the oxidation of copper by nitrate. The study shows that the oxidation is thermodynamically possible. The reaction rate, however, is as in the case of sulphate, extremely slow, so it should be possible to disregard nitrate/nitrite as possible oxidants for copper. But if one nevertheless wishes to consider the possibility of an oxidation, the quantity of oxidized copper will be determined by the total concentration of nitrate/nitrite and the rate with which these species are transported to the copper surface.

IV. Organic material in the groundwater and buffer and its effect on copper corrosion

Organic material in the groundwater and buffer material can act as a complexing agent for copper(I) and copper(II) species and can thereby affect the equilibrium concentrations of these ions and molecules. The organic material can also act as a substrate for sulphate-reducing bacteria which convert sulphate to sulphide. Hydrogen sulphide can then participate in the oxidation of copper with the formation of Cu_2S (see Appendix B3, page 5). A summary of the factors which influence the bacterial sulphate reduction is provided by Hallberg (Appendix C).

Groundwater from Forsmark and Finnsjö contains approximately 13 mg organic material per litre (Appendix A), mainly in the form of fulvic acids and humus substances. These are not uniform substances, but rather a group of substances with molecular weights of between $7 \cdot 10^2$ and $50 \cdot 10^3$, containing carboxylate and phenol groups. They can form chelate complexes with most metal ions; there is reason to presume that a large portion of the dissolved iron is complex-bound to these substances.

Buffle, Greter and Haerdy (1) have made an experimental study of copper(II) complex formation with humus and fulvic acids. Copper(II) will be complex-bound relatively strongly. Complex-formers of this type should produce weaker complexes with copper(I) than with copper(II) since the ligands contain typically "hard" donor atoms. Thus, complex formation with humus and fulvic acids does not lead to any substantial change in the redox properties of the copper system. This means that the previously reported conclusions concerning the stability of copper should still be correct.

If the soluble organic substances contain sulphur, e.g. in the form of either sulphur or -SH groups, the situation will be a different one. Sulphur is a typical "soft" donor atom which stabilizes copper(I) very strongly relative to copper(II), a situation which leads to substantial changes in the redox properties of the copper system. We therefore assume that the waste repository will be located at a site where the level of sulphur-containing organic material in the groundwater is negligible.

V. The redox potential in the rock-groundwater system and in the buffer-groundwater system

The redox potential in the rock-groundwater system is determined primarily by the mineralogical composition of the rock, more specifically by iron(II) and iron(III) minerals present in the rock. A geochemical study has been conducted by Brotzen (2), who states:

$$E_h = (0.26 - 0.06\ \mathrm{pH}) \pm 0.10$$

i.e., the redox potential at pH = 8.5 is -0.25 ± 0.1 V and pe is -4.2 ± 1.7.

These values agree well with direct experimental determinations of the redox potential in groundwater from Finnsjö and Stripa. The results (Appendix B5) show a redox potential of -0.17 ± 0.04 V. Brotzen's model gives -0.25 ± 0.10 V. The relatively good agreement between model and experiment shows that the thermodynamic data provide a sufficiently good basis for an estimation of the redox potential in the system and thereby also the thermodynamic stability of the copper canister.

The buffer material contains relatively large quantities of iron (∿ 2.7% by weight Fe_2O_3 and 0.12% by weight iron(II) - Appendix A). The buffer system has such a large mass that its redox buffer properties at the specified water composition and flow should not change appreciably over a period of 100 000 years. The redox potential at the copper canister will therefore be determined by the equilibrium between the buffer mineral and the groundwater within the foreseeable future.

After an oxidation treatment, the buffer material will contain very small quantities of sulphides, mainly in the form of pyrite (Appendix A); it will also contain small amounts of magnetite, goethite and hematite, and possibly iron(II) and iron(III) silicates.

If the buffer mass initially contains oxygen, all iron(II), manganese(II) and all hydrogen sulphide present in the groundwater will be oxidized. When the oxygen has been consumed by groundwater leaking into the repository or by the addition of an oxygen-consuming redox buffer, the redox potential will be determined by the redox pair $Fe_2O_3(s)$ - $Fe_3O_4(s)$, or possibly $Fe_2O_3(s)$ - $Fe(OH)_2(s)$. The following Pourbaix diagrams show that the redox potential is roughly the same as in the rock-groundwater system. But conditions are different at elevated temperature (Appendix B3, page 15, fig. 5).

Any iron(II) sulphide which remains after the thermal treatment of the bentonite is not thermodynamically stable and is converted to pyrite. This phase is stable and is not oxidized by iron(III).

$$4Fe_2O_3(s) + 2FeS(s) \rightarrow 3Fe_3O_4(s) + FeS_2(s)$$
$$\Delta G^o = -10.4 \text{ kcal}$$

$$3Fe_2O_3(s) + FeS_2(s) + H_2O \rightarrow 2Fe_3O_4(s) + Fe(OH)_2(s) + 2S(s)$$
$$\Delta G^o = 28.2 \text{ kcal}$$

An idea of which sulphur-containing ions and solid phases may be present in the buffer material can be obtained by means of the standard free energies of formation for the various species present in the system.

The equilibrium concentration of hydrogen sulphide can be calculated from either of the following expressions:

$12Fe_2O_3(s) + HS^-(aq) + OH^-(aq) \rightarrow 8Fe_3O_4(s) + SO_4{}^{2-}(aq) + H_2O(l)$
$\Delta G^o = -12.75$ kcal

$2Fe_2O_3(s) + 2HS^-(aq) + 2H^+(aq) \rightarrow Fe_3O_4(s) + FeS_2(s) + 2H_2O(l)$
$\Delta G^o = -46.9$ kcal

The uncertainty in the ΔG^o -value for the first reaction is relatively great due to the large stoichiometric coefficients. With 0.1 kcal uncertainty in ΔG^o for the formation of Fe_2O_3 and Fe_3O_4, the maximum error is ±2 kcal, i.e. the level of hydrogen sulphide will be $10^{-6.8(\pm 1.4)}$ and $10^{-8.7}$M, respectively.

The equilibrium concentration of hydrogen sulphide at pH = 8.5 for the two reactions is: $10^{-6.8}$M (0.005 mg/l) and $10^{-8.7}$M, respectively.

The groundwater which flows into the system contains iron(II) and sulphide at levels of less than 5 mg/l (Appendix A).

Judging from equilibrium data, hydrogen sulphide should be oxidized to pyrite even at levels of hydrogen sulphide in the inflowing groundwater which are considerably lower than these values. Published analysis data from Forsmark 1 and Finnsjö 2 show hydrogen sulphide levels of $1.5 \cdot 10^{-4}$ M and $<3.10^{-6}$ M, respectively. The latter value is of the same order of magnitude as the expected equilibrium value (see above). Additional analyses should, however, be carried out in order to confirm this result.

When initial oxygen in the buffer material is consumed, the redox potential will be roughly the same as in the rock-groundwater system. The concentration of hydrogen sulphide is fixed as long as solid phases of Fe_2O_3, Fe_3O_4 and FeS_2 are present in the system. The maximum equilibrium concentration is about $10^{-(6.8 \pm 1.4)}$ M. Pyrite FeS_2 is the only thermodynamically stable iron sulphide in the system, if we consider only the buffer-rock-groundwater equilibria.

CONCLUSIONS

Copper is a relatively noble metal and possesses good stability in oxygen- and sulphide-free water. Under the conditions prevailng in the waste repository, the following chemical processes which lead to the corrosion of copper can occur:

a. Oxidation of copper by oxygen initially present in the buffer material. The rate of the process is determined by the speed with which oxygen diffuses to the copper canister. The total quantity of copper which is oxidized is determined by the initial quantity of oxygen. Some of this oxygen may, however, be reduced by reactions with sulphide, iron(II) or manganese(II) which are transported into the buffer material.

b. Oxidation of copper with the formation of Cu_2S and H_2. This process is controlled by the total concentration of dissolved sulphide species and the rate at which they are transported to the copper surface.

c. Due to the extremely low reaction rate, it should be possible to disregard the oxidation of copper by sulphate and/or nitrate.

d. Degradable organic material can reduce sulphate to sulphide as a result of biological activity. According to b. above, hydrogen sulphide gives rise to Cu_2S.

The scale of the process is determined by the quantity of degradable organic material and, as in b., by the rate at which sulphide is transported to the copper surface.

e. Solid redox pairs containing Fe(II) and Fe(III) fix the redox potential in the buffer system at a value which is lower than the pe value for the formation of Cu_2O. The redox potential should be close to that which prevails in the rock-groundwater system.

f. The high initial temperature at the waste canister will increase the thermodynamic stability of metallic copper.

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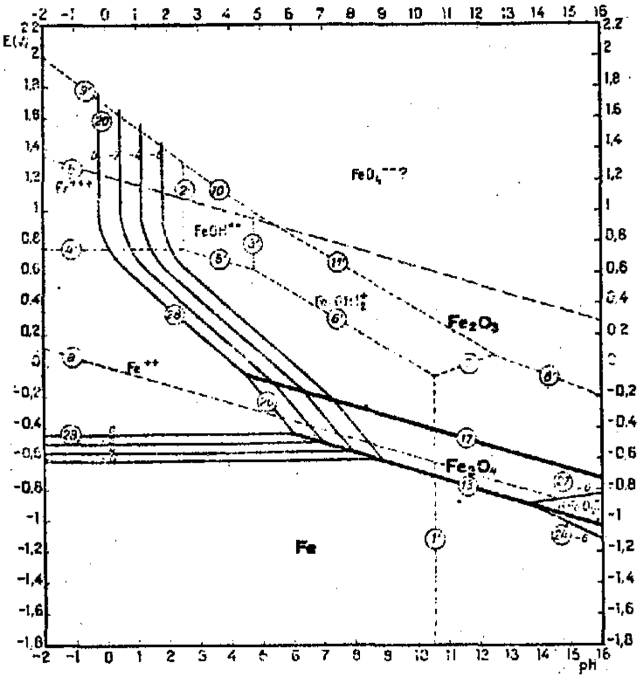

Fig. 4. Potential pH equilibrium diagram for the system iron-water at 25°C (considering as solid substances only Fe, Fe_3O_4 and Fe_2O_3)

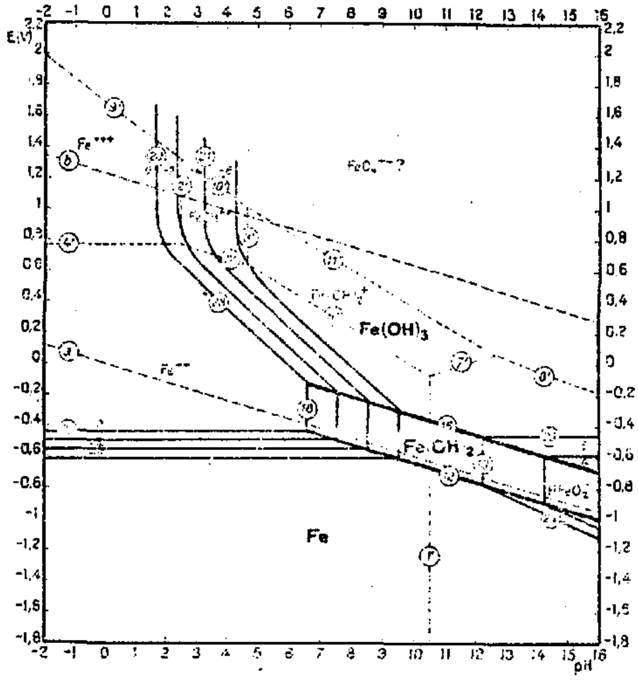

Fig. [illegible] Potential pH equilibrium diagram for the system iron-water, at 25°C (considering as solid substances only Fe, $Fe(OH)_2$ and $Fe(OH)_3$)

Fig. 1 Pourbaix diagrams for the iron-water system at 25°C (3)

Thermodynamic calculations of equilibrium concentrations for the system $Cu-H_2O-Cl^--CO_3^{2-}-SO_4^{2-}-F^-$ at various redox potentials and temperatures.

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INTRODUCTION

In connection with an investigation of the suitability of various metals for the encapsulation of radioactive waste for "final storage", KBS (1) has asked for estimates of the equilibrium concentrations of copper species in a specified groundwater, known as "normal water", which is in thermodynamic equilibrium with pure metallic copper.

The present report summarizes the results of a study of the considerable amount of thermodynamic data which is required for an estimate of the total copper concentration at equilibrium in the system $Cu-H_2O-Cl^--CO_3^{2-}-SO_4^{2-}-F^-$ at various temperatures.

The study has been conducted in the following stages:

1. Review of the literature for a definition of known copper species in the solid phase and in solution under the given conditions.

2. Collection and evaluation of published thermodynamic data for all relevant equilibria.

3. Calculations to estimate equilibrium constants for the predominant species at temperatures up to 125°C.

4. Calculation of relative activity ratios of the individual species within the system at 25°C and at various redox potentials (relative diagrams - redox diagrams).

5. Estimation of the total copper concentration which is attained when pure metallic copper at 25°C and 100°C is in thermodynamic equilibrium with "normal water", or in the event of some reasonable deviations from "normal water" with respect to pH and $[Cl^-]$. Equilibrium concentrations are expressed as a function of the system's redox potential.

6. Discussion of some factors which can affect corrosion processes in the real system.

BASIC ASSUMPTIONS FOR THE THERMODYNAMIC CALCULATIONS - DEFINITION OF SYSTEM

Thermodynamic calculations for pure (unalloyed) metallic copper in equilibrium with so-called "normal water" are sought for the temperature range 20-130°C. The following composition has been specified for "normal water" (1):

Table 1 Data for "normal water"

pH	8.5	
$[Cl^-]_{tot}$	500 mg/l	14.1 mM
$[H_2CO_3]_{tot}$	120 "	2.7 "
$[SO_4^{2-}]_{tot}$	100 "	1.0 "
$[F^-]_{tot}$	1.5 "	0.08 "
$[PO_4^{3-}]_{tot}$	0.04 "	0.4 μM
$[O_2]$	0	

There is also great interest as to how the copper concentration would be affected by deviations from "normal" towards Baltic seawater, whereby the pH drops to 7.8, $[Cl^-]$ increases to approx. 115 mM, the carbonate concentration drops to 1.6 mM and the sulphate concentration increases to 5.7 mM. The oxygen content of Baltic seawater is 8-14 mg/l.

The presence of a natural and suitable redox buffer with appreciable buffering capacity cannot be assumed. The calculations have therefore been carried out so that a suitable redox potential can be selected in the event of the addition of a redox buffer system. It has been assumed that the above concentrations apply at both 25°C and 100°C and that the pressure has been close to 1 atm.

COPPER-BEARING SPECIES AND THERMODYNAMIC DATA

A review of the literature, primarily via Stability Constants (2.), has been undertaken in order to establish known copper species in the system and relevant equilibrium data. In assessing equilibrium constants, comparisons with assessments in other tabular collections of thermodynamic data (3 - 6) have also been made. Some recently published studies (7 - 9) have dealt with smaller parts of the system in question.

Very few equilibrium data have been determined experimentally at temperatures higher than 25°C. A special study has been conducted to estimate the temperature-dependence of the equilibrium constants (Appendix B2).

Table 2 lists relevant copper species and equilibrium constants at 25°C and 100°C in the system $Cu\text{-}H_2O\text{-}Cl^-\text{-}CO_3{}^{2-}\text{-}SO_4{}^{2-}\text{-}F^-$

The equilibrium constants, $\log_T K_r$, in Table 2 have been defined as reduction constants for the formation of one mole of Cu(s) with, in relevant cases, the consumption of H^+ and the formation of Cl^-, HCO_3^-, SO_4^{2-} and F^- according to the equation.

$$1/x\ A + yH^+ + ze^- \rightleftarrows Cu(s) + pCl^- + qHCO_3^- + rSO_4^{2-} + sF^- + tH_2O$$

$$\log_T K_r = zpe + \log \frac{[Cl^-]^p [HCO_3^-]^q [SO_4^{2-}]^r [F^-]^s}{[H^+]^y} - \log \frac{a_A^{1/x}}{a_{Cu(s)}}$$

where x is the number of copper atoms in the Cu-bearing species A with activity a_A. The activity of copper with oxidation number zero, $a_{Cu(s)}$, has been taken to be equal to one for pure metallic copper. pe $\equiv \frac{F}{RT\ln 10} \cdot E_{SHE}$ where E_{SHE} = the redox potential relative to a standard hydrogen electrode (at 25°C, pe $\simeq \frac{E_{SHE}}{60}$ (mV); at 100°C, pe $\simeq \frac{E_{SHE}}{74}$).

Extrapolation to the higher temperature has not been carried out for certain species which, after examination of the data at 25°C, have been judged to make only a negligible contribution to the total copper concentration.

The following protolysis constants have been used:

	$\log_T K$ 25°C	$\log_T K$ 100°C
$H^+ + OH^- \rightleftarrows H_2O$	14.00	12.3
$H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$	10.329	10.26
$H^+ + HCO_3^- \rightleftarrows H_2CO_3$	6.352	5.97

Table 2. Species and reduction constants (see text) considered here for the system $Cu\text{-}H_2O\text{-}Cl^-\text{-}CO_3^{2-}\text{-}SO_4^{2-}\text{-}F^-$ at 25°C and 100°C

	Species	$\log_T K_r$	
		25°C	100°C
Dissolved	Cu^+	8.76	7.66
	Cu^{2+}	11.44	10.72
	$Cu(OH)^+$	19.44	15.90
	$Cu(OH)_2$	26.5	21.42
	$Cu(OH)_3^-$	39.2	32.3
	$Cu(OH)_4^{2-}$	51.05	-
	$1/2Cu_2(OH)_2^{4+}$	16.62	14.82
	$CuCl$	6.06	4.93
	$CuCl_2^-$	3.26	1.98
	$CuCl_3^{2-}$	3.06	3.42
	$1/2Cu_2Cl_4^{2-}$	2.21	3.57
	$CuCl^+$	11.04	-
	$CuCO_3$	15.04	11.58
	$Cu(CO_3)_2^{2-}$	22.27	16.44
	$CuSO_4$	9.08	-
	CuF^+	10.14	-
Solid	$1/2Cu_2O(s)$	7.96	7.65
	$CuO(s)$	19.06	16.00
	$CuO(H_2O)(s)$	20.08	17.80
	$CuO(H_2O)_2(s)$	20.74	-
	$CuCl(s)$	2.03	1.49
	$Cu(OH)_{1.5}Cl_{0.5}(s)$	15.14	13.06
	$CuCO_3(s)$	12.14	16.38
	$1/3Cu_3(OH)_2(CO_3)_2(s)$	12.34	10.56
	$Cu(OH)_{1.5}(SO_4)_{0.25}(s)$	15.69	-
	$1/3Cu_3(OH)_4SO_4(s)$	14.37	-
	$1/2Cu_2(OH)_2CO_3(s)$	14.02	12.00

CONCENTRATION CONDITIONS

Figure 1 presents the relative activity of different Cu-bearing species as a function of the redox potential, pe. The logarithmic diagram has been plotted with the concentrations which were given for "normal water". The activity of copper, $a_{Cu(s)}$, has been used as a reference for the activity ratio.

Figure 2 shows the corresponding diagram for the equilibria at 100°C. Some minor species have not been included.

In the part of the diagrams where pure copper is stable ($a_{Cu(s)} = 1$), the concentration ($\log[CuY_z]$) for all mononuclear species can be read directly at different redox potentials. In the case of polynuclear complexes, Cu_xY_z, $\log[Cu_xY_z]^{1/x}$ is read instead. The positions of some solid phases which are not stable at equilibrium for the concentration present in "normal water" have also been marked.

The diagram is intended to be used quantitatively only in the region where Cu(s) is stable, but it can also give an indication of what might occur if the redox potential were displaced out of this region or if the composition of the water is altered slightly.

As is evident from the diagrams, no copper species occur with a concentration greater than 10^{-6}M ($\sim$ 0.05 mg Cu/l) at redox potentials lower than -100 mV. The copper(I) chloride complexes dominate the entire region below -100 mV at 25°C, while the hydrolysis and carbonate complexes become more significant above -150 mV at 100°C and at the pH level of the "normal water".

In figure 3, the total concentration of dissolved copper species has been plotted as a function of the redox potential at 25°C and 100°C. The values which would be obtained if the chloride concentration were increased by a power of 10 (to

141 mM = 5000 mg/l) and if the pH were increased by one unit to 9.5 have also been plotted. At pH = 9.5, Cu(s) is not stable above approx. -100 mV. A pH reduction would only lead to a reduction of the total copper concentration at 100°C and E values above -150 mV. (The effects of redox buffer systems are not dealt with here.)

DISCUSSION

This report is concerned with the thermodynamic stability of copper and it is appropriate to list briefly some of the factors to be considered if it is used in the assessment of the corrosion of copper

1. There is some uncertainty in the present results, which arises mainly for the following reasons:

   a) The assumption that quantitative data have been published for all relevant Cu species. However, copper equilibria have indeed been comparatively thoroughly studied.

   b) Practically all experimental determinations of equilibrium constants for Cu-species have been carried out at considerably higher Cu concentrations, which has necessitated long extrapolations.

   c) Extrapolation to temperatures higher than 25°C introduces an uncertainty which is estimated to be usually less than ±0.5 log units (see Appendix B2). Experimental results for higher temperatures, however, are almost entirely lacking.
   In cases where constants for higher temperatures have been particularly uncertain (e.g. $Cu(CO_3)_2^{2-}$ and $CuCO_3$), the least favourable value from the viewpoint of corrosion has been used.

d) The uncertainty in the total concentration of copper is probably considerably less than ±0.5 log units at 25°C and approx. ±1 log unit at 100°C.

2. The thermodynamic calculations are based entirely on the given system specification. Thus, it is assumed that:

   a) No other molecular species which can form complexes with copper, e.g. biological degradation products, are present.

   b) No nitrogen compounds (e.g. NO_3^-, organic complexing agents) which could form NH_3 are present.

   c) No biochemical processes (bacterial).

   d) The data apply to very pure Cu(s).

In assessing the <u>corrosion</u> of copper on the basis of the thermodynamic data presented here, it is also essential to take into account kinetic factors and specific medium effects, as well as considerations such as:

a) The risk of corrosion currents due to temperature gradients in the system.

b) The risk of the formation of local cells, if the copper is impure or if it is in contact with other metals or alloys.

c) The risk that the equilibrium constants which apply in aqueous solutions may not be valid for the medium in question (gel?).

d) Irradiation effects (e.g. H_2O_2 formation).

Addition of redox buffer necessitates thermodynamic analysis of the new system which can be expected to arise.

Experimental data should be obtained for any system intended for practical use. The thermodynamic calculations provide an effective basis for planning such an experimental programme.

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Figure 1

Redox diagram for the system
$Cu-H_2O-Cl^- -CO_3^{2-} -SO_4^{2-} -F^-$
"Normal water" at 25°C

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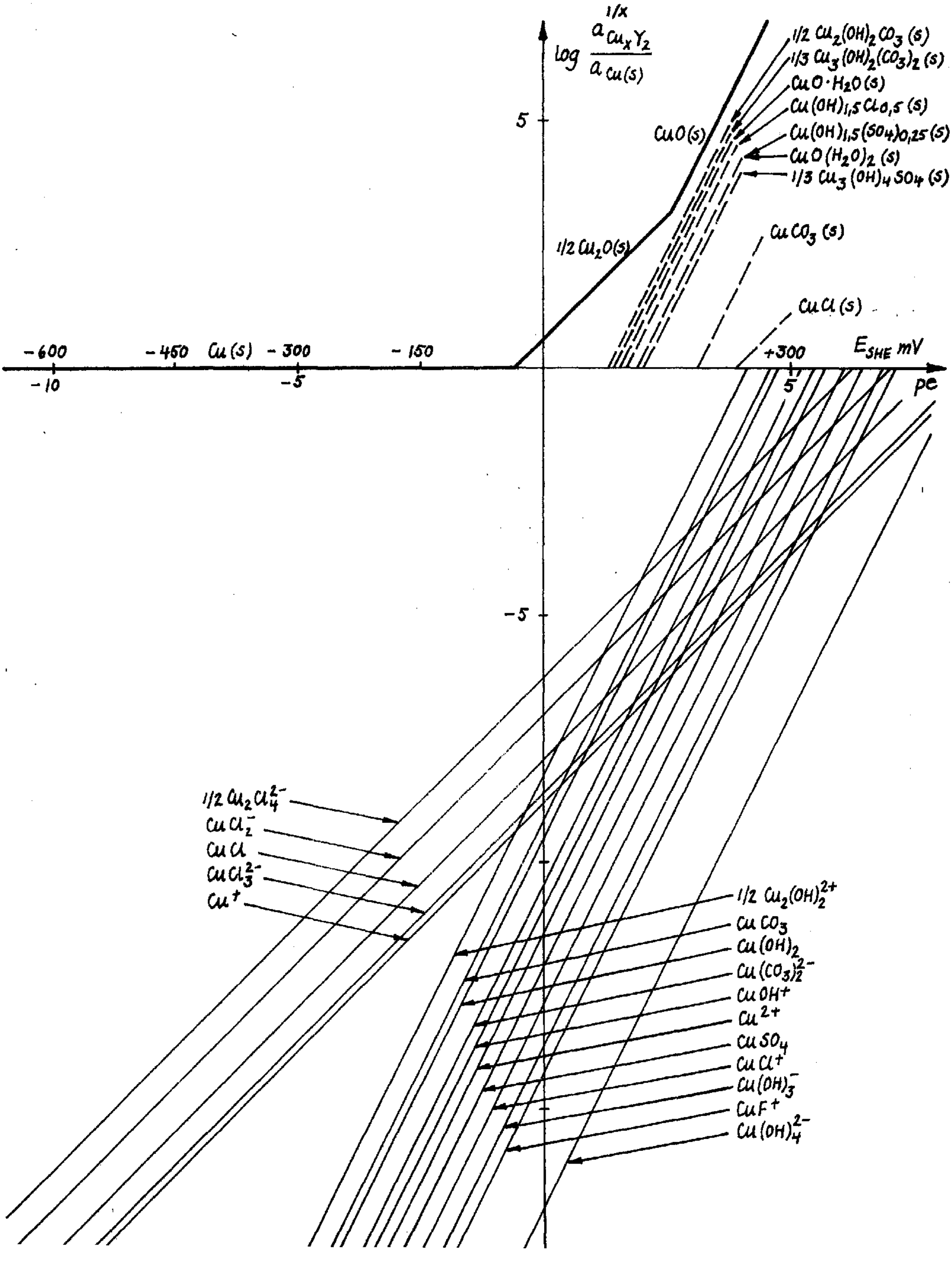


Figure 2

Redox diagram for the system
$Cu-H_2O-Cl^--CO_3^{2-}$
"Normal water" at 100°C

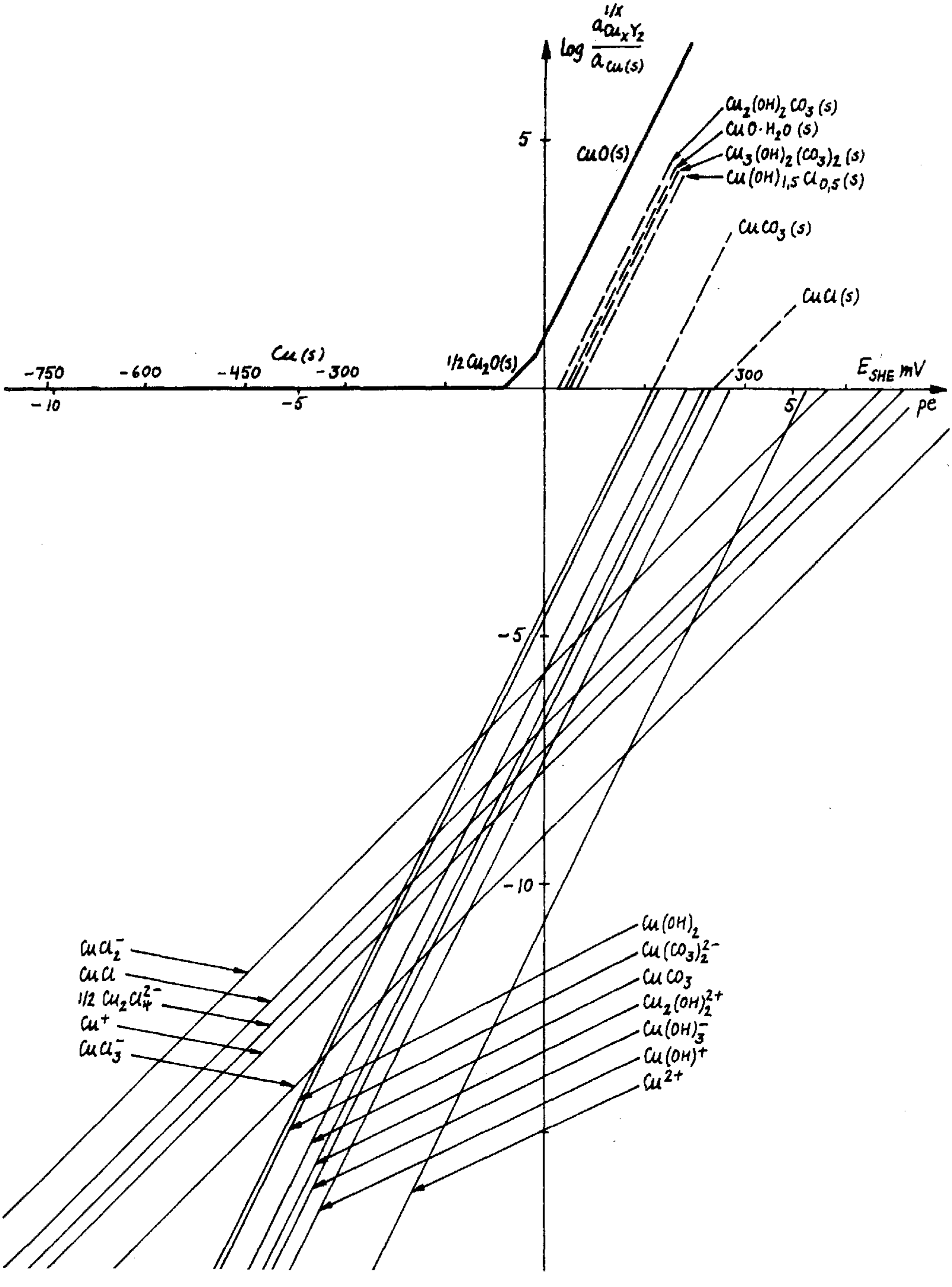
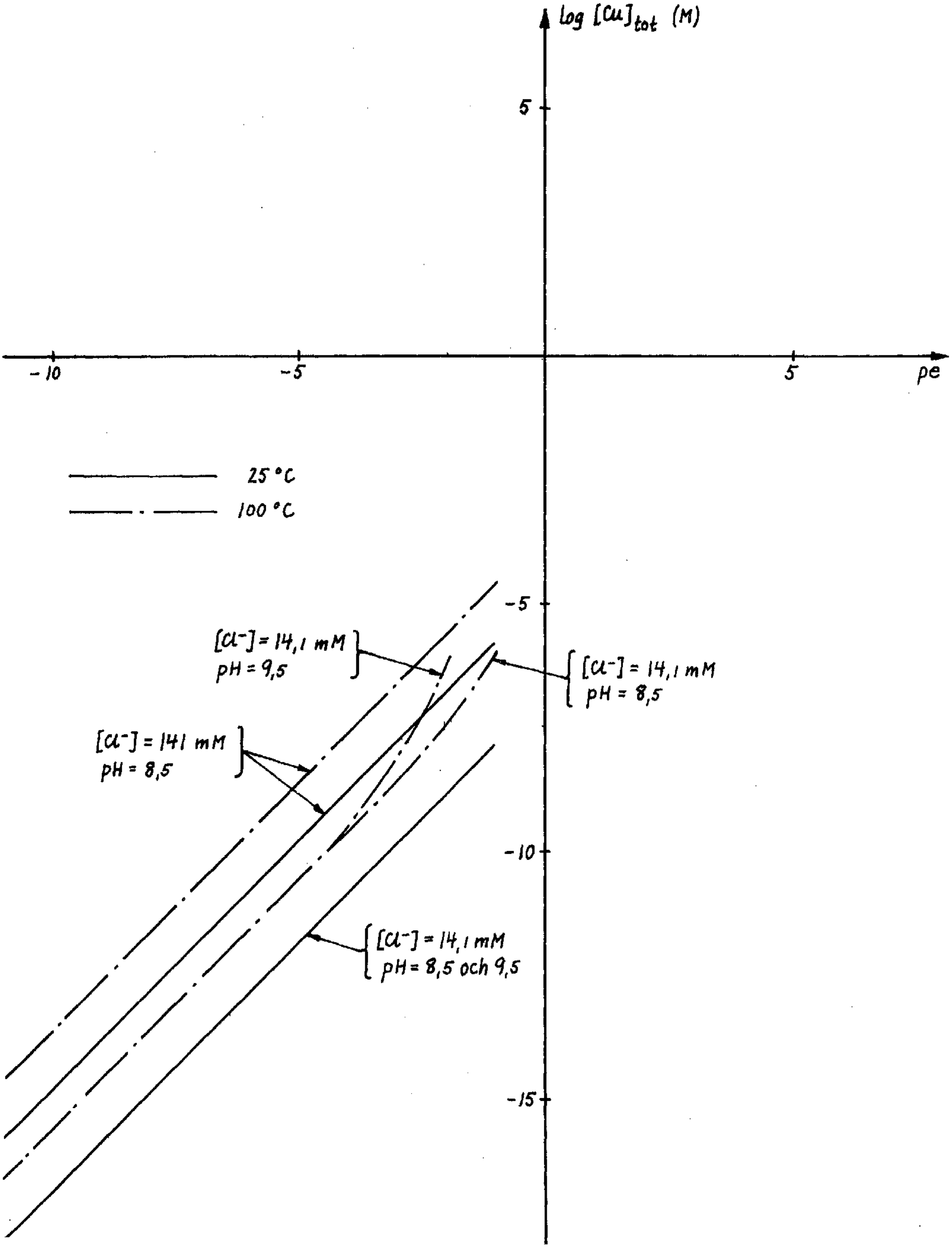


Figure 3 Total copper concentration for "normal water" in thermodynamic equilibrium with metallic copper at various T, pH and $[Cl^-]$.



AKTIEBOLAGET ATOMENERGI AE-MS-142
1977-05-11

The thermodynamics of the system Cu - H_2O - Cl^- - CO_3^{2-} at elevated temperatures - A preliminary investigation

Derek Lewis

SUMMARY

An estimate of the values of the equilibrium constants for some processes in the system Cu - H_2O - Cl^- - CO_3^{2-} at temperatures up to 125°C has been asked for in connection with a KBS investigation. The present report summarizes the results of the most significant of these processes as obtained by means of the method described in a previous report concerning the thermodynamics of redox processes in water at elevated temperatures.

AKTIEBOLAGET ATOMENERGI AE-MS-142
1977-05-11

1 INTRODUCTION

A report on a preliminary study of the system Cu - H_2O at elevated temperatures has been submitted in connection with a study of the thermodynamics of the so-called "neutral" mode of operation in steam power plants (1). In connection with the question of the thermodynamic stability of copper in contact with natural water, this study has now been extended to reactions with chloride and carbonate ions.

2 BASIC THERMODYNAMIC DATA

Very few equilibrium data for copper ions and copper compounds in water above 25°C are available. In particular, very little is known about the entropy of copper ions, even at 25°C. This means that experimental values for the property which is decisive in determining the change of the equilibrium constant with temperature are lacking.

In this study, the missing data have been estimated through the use of empirical formulae, for example the equations for the entropy of single ions established by Latimer and his co-workers (2). In most cases, these formulae are based on numerous reliable experimental measurements. The estimated values which are presented here for the entropy of copper compounds must, however, be regarded as highly uncertain as long as none of them has been experimentally verified.

Table 1 summarizes the data which are used here.

3 RESULTS

Values for the equilibrium constants calculated by means of the TEMCON program (3) for selected reactions in the copper system at 50, 75, 100 and 125°C are presented in table 2. Values for corresponding processes at 25°C taken from a standard reference work (4) have been used.

Pourbaix diagram, pe(pH)$_T$, illustrating the stability of the various copper species in equilibrium with pure water at 50°C and 150°C are presented in figures 1 and 2.

The limits of error are estimated to be ± 0.5 log units, unless otherwise specified.

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Table 1. Basic thermodynamic data for the system $Cu - H_2O - Cl^- - CO_3^{2-}$

Species	$-\Delta_{298} G^o{}_f$	$-\Delta_{298} H^o{}_f$	$_{298}S^o$	a	$bx10^3$	$cx10^{-4}$
	cal/mol x 10^{-3}			cal/mol deg.		
H_2O (1)	56,7	68,3	16,7	18,03	0	0
H^+	-	0	- 5,0	0	92,25	0
Cu (s)	0	0	7,96	5,4	1,5	0
$Cu(OH)_2$ (s)	85,3	106,1	19,0	(9,3)	(4,8)	0
Cu_2O (s)	33,3	39,8	24,1	14,9	5,7	0
CuO (s)	30,4	37,1	10,4	9,3	4,8	0
CuCl (s)	28,4	32,2	21,9	15,4	12,0	0
$Cu_2(OH)_3Cl$ (s)	-	-	(43)	(30)	(40)	0
$CuCO_3$ (s)	123,8	142,2	21	(10)	(30)	0
$Cu(OH)_2CO_3$ (s)	-	-	(42)	(25)	(60)	0
$Cu_3(OH)_2(CO_3)_2$ (s)	-	-	(64)	(35)	(90)	0
Cu^+	12,0	-12,4	-11,3	0	152	0
Cu^{2+}	15,5	-15,4	-33,6	0	188	0
$Cu(OH)^+$	23,3	-25,7	8,1	0	119	0
$Cu(OH)_2$	-	-	(42)	(9)	(5)	0
$Cu_2(OH)_2^{2+}$	(78)	-72,6	-17,8	0	162	0
$HCuO_2^-$	(50)	-55,9	19,7	0	-177	0
CuCl	-	-	(18)	(6)	(19)	0
$CuCl_2^-$	-	-	(53)	0	(-175)	0
$CuCl_3^{2-}$	-	-	(41)	0	(-175)	0
$Cu_2Cl_4^{2-}$	-	-	(-10)	0	(-172)	0
$Cu(CO_3)_2^{2-}$	250,5	-	(57)	0	(851)	0
$CuCO_3$	119,9	-	(45)	(10)	(30)	0
H_2CO_3	-	-	(40)	(28)	(2)	0
HCO_3^-	140,3	165,2	27,7	0	-87,4	0
CO_3^{2-}	126,2	161,6	- 2,7	0	-456	0

Table 2. Estimated values of equilibrium constants for reactions in the system $Cu - H_2O - Cl^- - CO_3^{2-}$ at temperatures above 25°C

t^oC		50	75	100	125
			$\log_T k$		
(Cu1)	$Cu^+ + e^- = Cu(s)$	8,4	8,0	7,7	7,3
(Cu2)	$\frac{1}{2}Cu_2O(s) + H^+ = Cu^+ + \frac{1}{2}H_2O$	0,1	0,0	0,0	-0,1
(Cu3)	$Cu^{2+} + e^- = Cu^+$	2,8	3,0	3,1	3,1
(Cu4)	$Cu(OH)^+ + H^+ = Cu^{2+} + H_2O$	6,6	5,8	5,2	4,6
(Cu5)	$Cu(OH)_2^0 + 2H^+ = Cu^{2+} + 2\,H_2O$	13,3	11,9	10,7	9,7
(Cu6A)	$Cu(OH)_2(s) + 2\,H^+ = Cu^{2+} + 2\,H_2O$	8,4	7,7	7,1	6,6
(Cu6B)	$CuO(s) + 2\,H^+ = Cu^{2+} + H_2O$	6,6	5,9	5,3	4,8
(Cu7A)	$Cu(OH)_2(s) + H^+ = Cu(OH)^+ + H_2O$	1,8	1,8	1,9	2,0
(Cu7B)	$CuO(s) + H^+ = Cu(OH)^+$	$0{,}0_5$	$0{,}0_9$	0,1	0,1
(Cu8A)	$Cu(OH)_2(s) + H^+ + e^- = \frac{1}{2}Cu_2O(s) + \frac{3}{2}H_2O$	11,1	10,7	10,3	9,9
(Cu8B)	$CuO(s) + H^+ + e^- = \frac{1}{2}Cu_2O(s) + \frac{1}{2}H_2O$	9,8	9,2	8,8	8,4

Table 2 (cont.)

t^oC		50	75	100	125
			$\log_T k$		
(Cu9A)	$HCuO_2^- + H^+ = Cu(OH)_2\ (s)$	16,3	15,3	14,5	13,7
(Cu9B)	$HCuO_2^- + H^+ = CuO(s) + H_2O$	18,1	17,1	16,2	15,6
(Cu10)	$\frac{1}{2}\ HCuO_2^- + \frac{3}{2}\ H^+ + e^- = \frac{1}{2}\ Cu(s) + H_2O$	17,9	17,0	16,1	15,4
(Cu11)	$Cu_2(OH)_2^{2+} + 2\ H^+ = 2\ Cu^{2+} + 2\ H_2O$	9,4	8,8	8,2	7,8
(CuCl1)	$Cu^+ + Cl^- = CuCl^0$	$2,6_9$	$2,7_0$	$2,7_3$	$2,7_6$
(CuCl2)	$Cu^+ + 2\ Cl^- = CuCl_2^-$	$5,6_0$	$5,6_3$	$5,6_8$	$5,7_3$
(CuCl3)	$Cu^+ + 3\ Cl^- = CuCl_3^{2-}$	4,6	4,4	4,2	$4,1_7$
(CuCl4)	$Cu^+ + Cl^- = CuCl(s)$	6,5	6,3	6,2	6,1
(CuCl5)	$CuCl(s) + Cl^- = CuCl_2^-$	-0,9	-0,7	-0,5	-0,4
(CuCl6)	$CuCl(s) + 2\ Cl^- = CuCl_3^{2-}$	-1,8	-1,9	-1,9	-1,9
(CuCl7)	$2\ Cu^{2+} + Cl^- + 3\ H_2O = Cu_2(OH)_3Cl(s) + 3\ H^+$	-6,4	-5,5	-4,7	-4,0
(CuCl8)	$2\ Cu^+ + 4\ Cl^- = Cu_2Cl_4^{2-}$	11,1	9,5	8,2	7,1

Table 2 (cont.)

t^{o}C		50	75	100	125
			$\log_T$ k		
(C4)	$HCO_3^- + H^+ = H_2CO_3$	6,2	$6{,}0_5$	6,0	5,9
(C5)	$CO_3^{2-} + H^+ = HCO_3^-$	$10{,}1_9$	$10{,}1_7$	$10{,}2_6$	$10{,}4_4$
(CuL1)	$Cu^{2+} + CO_3^{2-} = CuCO_3^0$	7,5	8,5	9,4-8,8	10,3-9,4
(CuL2)	$Cu^{2+} + 2\ CO_3^{2-} = Cu(CO_3)_2^{2-}$	11,2	12,8-11,6	14,8-12,2	17,1-12,8
(CuL3)	$Cu^{2+} + CO_3^{2-} = CuCO_3(s)$	9,9	10,3	10,7	11,2-10,3
(CuL4)	$2\ Cu^{2+} + CO_3^{2-} + 2\ H_2O = Cu_2(OH)_2CO_3(s) + 2\ H^+$	6,1	6,9	7,7	8,5-7,8
(CuL5)	$3\ Cu^{2+} + 2\ CO_3^{2-} + 2\ H_2O = Cu_3(OH)_2(CO_3)_2(s) + 2\ H^+$	18,9	19,9	21,0-20,0	22,2-20,5

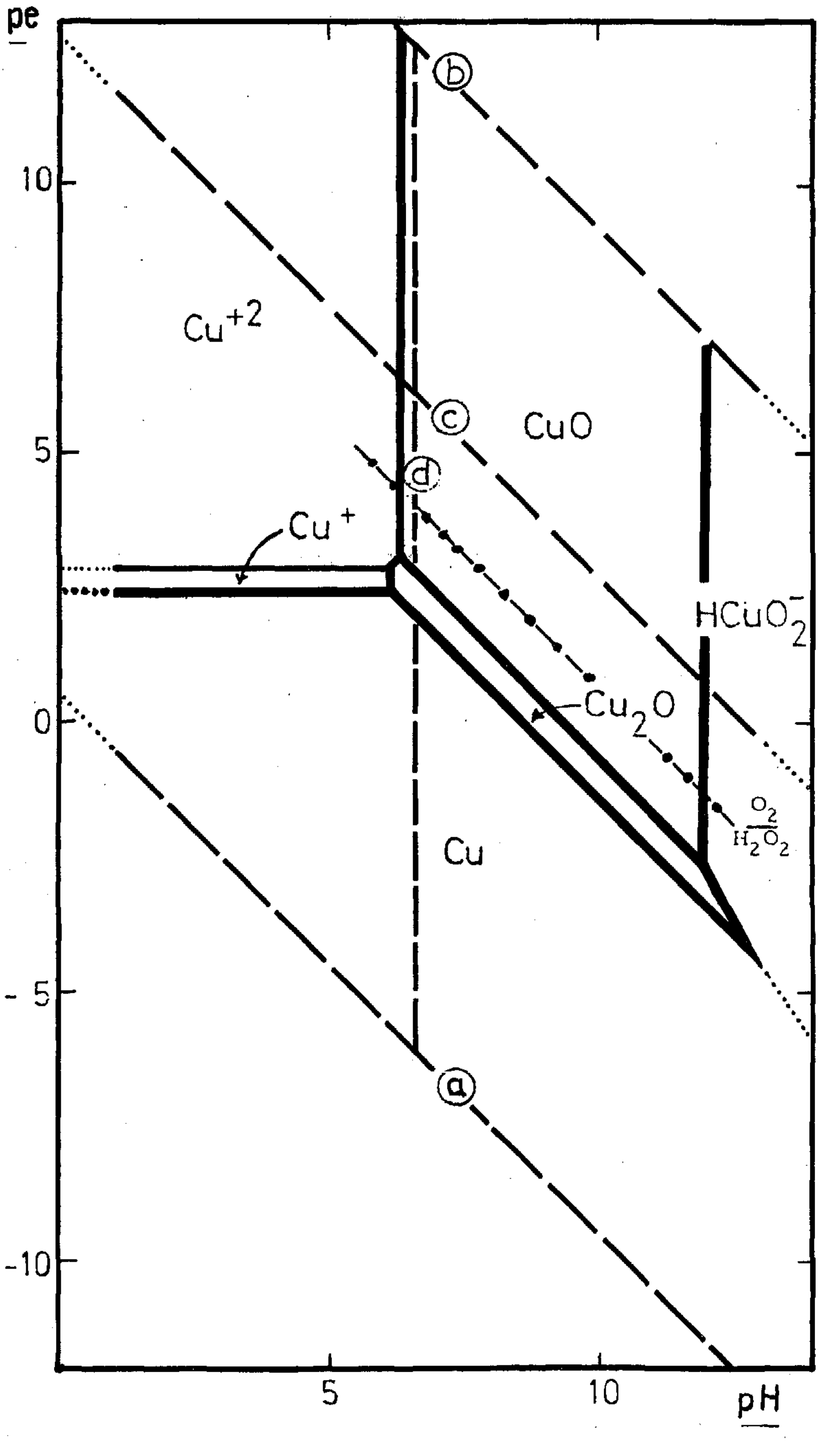

Fig. 1. pe(pH)$_T$ diagram for the copper-water system at 50°C, 1 atg.

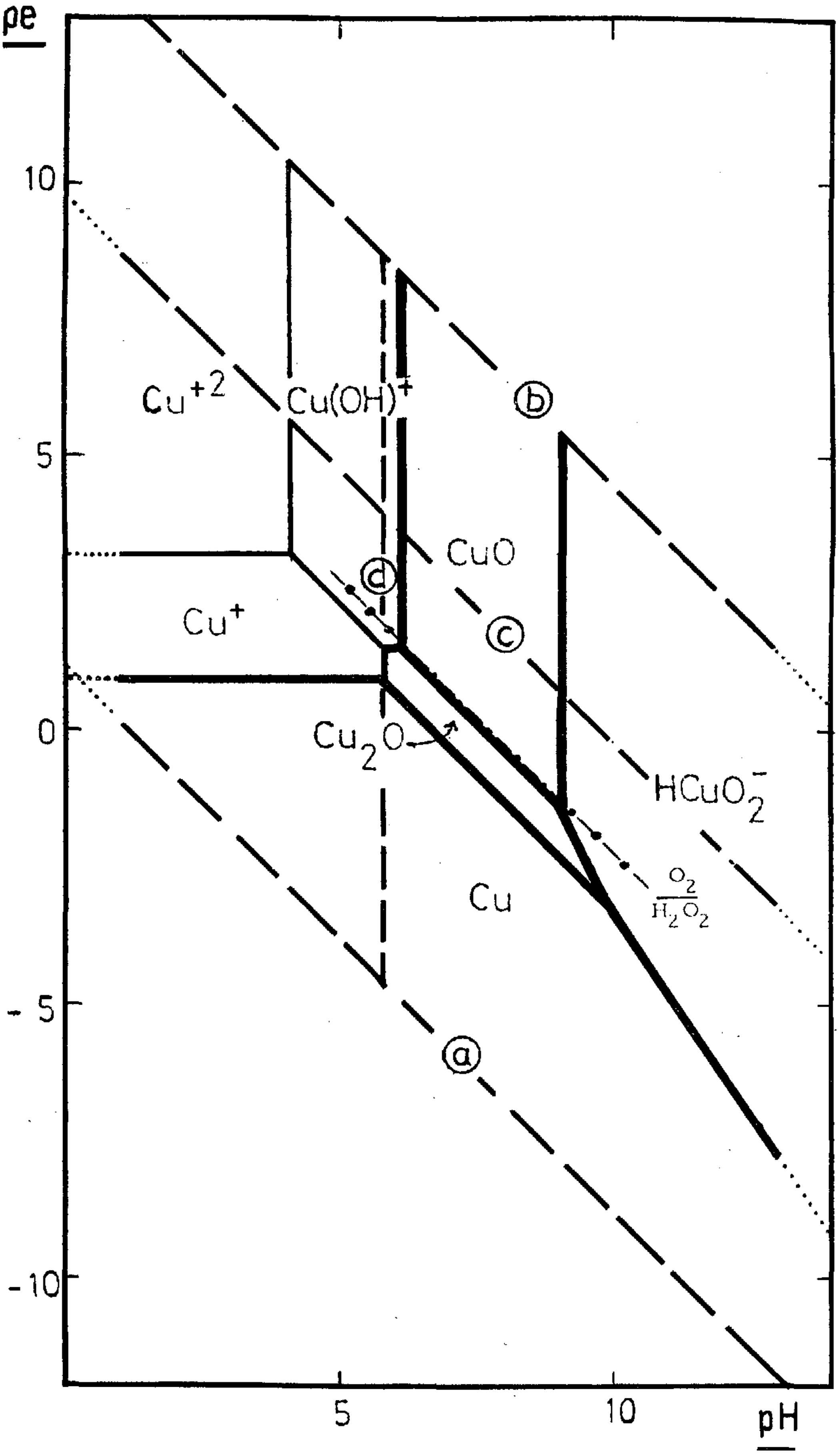

Fig. 2. pe(pH)$_T$ diagram for the copper-water system at 150°C, 5 atg.

THERMODYNAMIC CALCULATIONS OF EQUILIBRIUM CONCENTRATIONS FOR THE SYSTEM $Cu-H_2O-Cl^--CO_3^{2-}-SO_4^{2-}-HS^--F^-$ AT VARIOUS REDOX POTENTIALS AND TEMPERATURES

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Sulphur-bearing species and thermodynamic data

Sulphur(VI) can be reduced to several different lower oxidation states. The redox equilibria are highly pH-dependent. These factors complicate a thermodynamic study of the system. In order to visualize the main reaction(s), redox diagrams have been constructed. These diagrams apply at pH = 8.5 (figure 1a), pH = 7.5 (figure 1b) and pH = 9.5 (figure 1c). The reduction constants given in Table 1 (1-4) were used.

Table 1. Relevant species and reduction constants in the sulphur system at 25°C.

Reaction	$\log_T K_r$
$SO_4^{2-} + H_2O + 2e^- \rightleftarrows SO_3^{2-} + 2OH^-$	- 31.3
$SO_4^{2-} + 4H_2O + 6e^- \rightleftarrows S(s) + 8OH^-$	- 75.7
$2SO_4^{2-} + 4H_2O + 6e^- \rightleftarrows S_2O_4^{2-} + 8OH^-$	-100.6
$2SO_4^{2-} + 5H_2O + 8e^- \rightleftarrows S_2O_3^{2-} + 10OH^-$	-101.2
$SO_4^{2-} + 5H_2O + 8e^- \rightleftarrows HS^- + 9OH^-$	- 92.9
$\frac{1}{2}Cu_2S(s) + \frac{1}{2}H^+ + e^- \rightleftarrows Cu(s) + \frac{1}{2}HS^-$	- 8.56
$CuCl_2^- + e^- \rightleftarrows Cu(s) + 2Cl^-$	3.26
$CuS(s) + H^+ + 2e^- \rightleftarrows Cu(s) + HS^-$	- 33.4

In constructing the redox diagram for the sulphur system, $[SO_4^{2-}]$ has been used as a reference. The equations for the straight lines at pH = 8.5 are:

$$\log \frac{[SO_3^{2-}]}{[SO_4^{2-}]} = -31.3 - 2pe - 2\ pH + 2pK_W = -20.3 - 2pe$$

$$\log \frac{a_{S(s)}}{[SO_4^{2-}]} = -31.7 - 6pe \quad ; \quad \log \frac{[S_2O_4^{2-}]^{\frac{1}{2}}}{[SO_4^{2-}]} = -28.3 - 3pe$$

$$\log \frac{[S_2O_3^{2-}]^{\frac{1}{2}}}{[SO_4^{2-}]} = -23.1 - 4pe \; ; \; \log \frac{[HS^-]}{[SO_4^{2-}]} = -43.4 - 8pe$$

The copper-sulphur system, definition of the system, thermodynamic data

The same premises as in Appendix B1 have been applied to the calculations. Figure 2 shows the redox diagram for copper in "normal water" at pH = 8.5, pCl = 1.85, $pSO_4^{2-} = 3$, T = 25°C. To the left of the line for 1/2 $Cu_2S(s)$, copper(I) sulphide is thermodynamically stable, while metallic copper is stable to the right of the line.

The equilibrium constant for the reaction:

$2Cu(s) + SO_4^{2-} + 8H^+ + 6e^- \rightleftarrows Cu_2S(s) + 4H_2O$ at 25° is $\log K_r = 50$. At 100°C, according to Vannerberg (5), the constant has the value $\log K_r = 28$, i.e. the existence region for metallic copper will be extended towards lower pe values at increasing temperature (figure 2b).

The oxidation of copper can also take place through the following reactions:

$$2Cu(s) + SO_4^{2-} + 4Cl^- + 2H^+ \rightleftarrows 2CuCl_2^- + SO_3^{2-} + H_2O \quad (1)$$

$$6Cu(s) + SO_4^{2-} + 12Cl^- + 8H^+ \rightleftarrows 6CuCl_2^- + S(s) + 4H_2O \quad (2)$$

$$8Cu(s) + SO_4^{2-} + 12Cl^- + 8H^+ \rightleftarrows Cu_2S(s) + 6CuCl_2^- + 4H_2O \quad (3)$$

In all redox processes, even those where solid sulphidic copper phases are formed, $CuCl_2^-$ is obtained in solution, since this species is, according to figure 2, dominant under the conditions which prevail in "normal water".

It is evident from figure 1a that the reduction of SO_4^{2-} to SO_3^{2-} dominates at pe > -3, the ratio $[SO_3^{2-}]/[SO_4^{2-}]^4$ is $< 10^{-14.5}$, i.e. the amount of copper which is oxidized by SO_4^{2-} is negligible. At pe < -3, SO_4^{2-} is reduced to free sulphur or hydrogen sulphide. Reduction to thiosulphate does not dominate in the pe range in question.

The equilibrium concentration of $CuCl_2^-$ can be calculated for the above three main reactions. The results can only be used in the concentration and pe ranges where the respective reaction dominates.

For (1):

$$\frac{[SO_3^{2-}]\,[CuCl_2^-]^2}{[SO_4^{2-}]\,[Cl^-]^4[H^+]^2} = 10^{-9.8}$$

According to the redox diagram, the reduction of SO_4^{2-} will be insignificant, so

$[SO_4^{2-}] = 10^{-3}$, pH = 8.5, pCl = 1.85

$[CuCl_2^-] = 2\,[SO_3^{2-}] = x$

i.e. $1/2x^3 = 10^{-9.8} \cdot 10^{-3} \cdot 10^{-4 \cdot 1.85} \cdot 10^{-2 \cdot 8.5} = 10^{-37.20}$

$x = 10^{-36.9/3} = 10^{-12.3}$.

The oxidation of copper will be negligible.

For (2):

$$\frac{[CuCl_2^-]^6}{[SO_4^{-2}]\,[Cl^-]^{12}\,[H^+]^8} = 10^{16.7}$$

$[CuCl_2^-] = x$

$x^6 = 10^{16.7} \cdot 10^{-3} \cdot 10^{-12 \cdot 1.85} \cdot 10^{-8 \cdot 8.5} = 10^{-76.5}$

$x = 10^{-12.75}$

In this case as well, the oxidation of copper by sulphate will be negligible.

$$\frac{[CuCl_2^-]^6}{[SO_4^{2-}][Cl^-]^{12}[H^+]^8} = 10^{30.66} \; ; \; x^6 = 10^{-62.5} \; ; \; x = 10^{-10.4}.$$

Thus oxidation is negligible.

The most favourable case for an oxidation of copper by sulphate occurs at a combination of high chloride concentration and low pH.

For a solution with pCl = 0.85 and pH = 7.5, the concentration of $CuCl_2^-$ calculated in accordance with (3) will be:

$$x^6 = 10^{30.7} \cdot 10^{-3} \cdot 10^{-12 \cdot 0.85} \cdot 10^{-8 \cdot 6.5} = 10^{-42.5}$$
$$x = 10^{-7.1}$$

pCl = 8.5 corresponds to the chloride concentration of Baltic seawater, and it is unlikely that this level will be exceeded if the waste repository is located on the Swedish east coast. The pH of the groundwater should not be allowed to drop below 7. Considering the composition of the groundwater and the buffer material in the tunnel system in the waste repository, the buffer capacity of the system is expected to be sufficient to prevent a pH drop.

The possibility of a pH drop due to pyrite oxidation need not be taken into consideration; in the first place, the amount of oxygen will be very small and in the second place the buffer capacity of the system is high.

The amount of solid copper which is removed by oxidation by sulphate ion can be calculated in the same manner as oxidation by oxygen.

At pCl = 0.85 and pH = 7.5, the equilibrium concentration of $CuCl_2^-$ is $10^{-7.1}$M. The original sulphate concentration has been reduced by $(10^{-7.1})/6$ M, i.e. each m^3 of water can oxidize a maximum of about 6.4 mg of copper. As a comparison, it can be mentioned that each m^3 of water with an oxygen content of 10 ppm can oxidize a maximum of <u>80 g</u> of copper.

Thus, reactions (1) - (3) do not lead to any substantial oxidation of metallic copper under the conditions which can be expected to prevail in "normal water". But some oxidation can be expected, which will probably lead to a surface coating of sulphidic copper phases.

The oxidation of metallic copper by sulphate is negligible if it does not lead to the formation of Cu_2S (see page 3). This process is thermodynamically possible only at low values ($pe < -3.5$ at 25°C).

Copper could also be oxidized by water and hydrogen sulphide with the formation of Cu_2S and hydrogen gas.

$$2\ Cu(s) + HS^-(aq) + H_2O(l) \rightarrow Cu_2S(s) + H_2(g) + OH^-(aq)$$

$$\Delta G^o = -4.38 \text{ kcal} \qquad T = 25^oC$$

At pH = 8.5 and equilibrium, the ratio is $P_{H_2} / [HS^-] = 10^{8.7}$

i.e., hydrogen sulphide in the groundwater produces roughly an equivalent amount of copper(I) sulphide. The amount of Cu_2S which is formed is determined by the flow rate in the system, by the concentration of hydrogen sulphide in the aqueous phase and by the rate of diffusion of HS^-.

The copper-iron system; possible reactions with the buffer material

A number of different reactions between copper on the one hand and iron and sulphide-bearing species on the other hand are possible.

The redox potential in the system should be so low that no oxidic copper phases are formed. This is evident from figures 2a and 2b and from ΔG^o for the following process:

$$2Cu(s) + 3Fe_2O_3(s) \rightarrow Cu_2O(s) + 2Fe_3O_4(s), \Delta G^o = 11.9 \text{ kcal}, T = 25^oC \ (6$$

Cu_2S can also be formed by, for example, the following reaction:

$4Cu(s) + 4Fe_2O_3(s) + FeS_2(s) \rightarrow 2Cu_2S(s) + 3Fe_3O_4(s), \Delta G^o = -19.8$ kcal (6)

All iron-bearing phases are present in the buffer material or are formed due to the presence of groundwater.

The redox potential in the buffer material may be so low that the oxidation of copper by sulphate is thermodynamically possible e.g. as follows:

$2Cu(s) + SO_4^{2-}(aq) + 6Fe_3O_4(s) + 2H^+(aq) \rightarrow Cu_2S(s) + 9Fe_2O_3(s) + H_2O$

$\Delta G^o = -40.8$ kcal (6)

Iron(II) can occur as a silicate and the following reactions are also thermodynamically possible.

$2Cu(s) + SO_4^{2-}(aq) + 3Fe_2SiO_4(2) + 2H^+(aq) \rightarrow Cu_2S(s) + 3Fe_2O_3(s) + 3SiO_2(s) +$
$+ H_2O(l)$
$\Delta G^o = -55.0$ kcal (6)
$4Cu(s) + 2SO_4^{2-}(aq) + 9Fe_2SiO_4(s) + 4H^+(aq) \rightarrow 2Cu_2S(s) + 6Fe_3O_4(s) +$
$+ 9SiO_2(s) + 2H_2O(l)$
$\Delta G^o = -127.0$ kcal (6)

The last reaction may be the principal one. Under the conditions which prevail in the buffer, i.e. pH = 8.5, pHS = 6.8 ± 1.4 and $pSO_4 = 3$, $\Delta G = -75$ kcal, the reaction is spontaneous to the right i.e. SO_4^{2-} oxidizes copper with the formation of Cu_2S. The ΔG^o values all apply at a temperature of 25°C. (6).

There is much geological evidence to support the postulate that sulphate ion is stable in a strongly reducing environment, e.g. gypsum deposits at great depths. The reason for this is the presence of a very strong kinetic inhibition of the oxidation process. As a result, the rate at which sulphate ion oxidizes copper is very low. The amount of copper which is oxidized by sulphate will therefore probably be negligible, even over periods of hundreds of thousands of years.

A survey of the dominant species in the systems copper-sulphur-water and copper-iron-sulphur-water is presented in the following Pourbaix diagrams (figs. 3, 4) taken from P. Duby (7). These data apply at a temperature of 25°C and an activity of 1 (one) for all participating species. The conditions in the buffer material are such that the formation of Cu_5FeS_4 is unlikely.

Ferreira (8) has assembled the redox data for the system Fe-S-H_2O and Cu-S-H_2O at temperatures of 25°C, 100°C and 150°C (figs. 5, 6).

Figure 5 shows $E_h = f(pH)$ in the Fe-S-H_2O system at 100°C. At pH = 8.5, the redox potential should be determined by the solid phases Fe_2O_3 - Fe_3O_4 - FeS_2, i.e. $E_h \simeq -0.4$ V. Figure 6 shows that the system is within the stability range for Cu_2S at this temperature. The concentration of sulphur-containing ions is 0.1 M, i.e. much higher than in the groundwater in the waste repository. According to the relative diagram, figure 2b, we are within the stability range for metallic copper - when the sulphide concentration is 100 mg/l, 10^{-3} M.

Therefore the initially high temperature in the repository ought to increase the stability of the copper canister.

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Figure 1a REDOX DIAGRAM FOR THE SULPHUR SYSTEM at pH = 8.5, T = 25°C

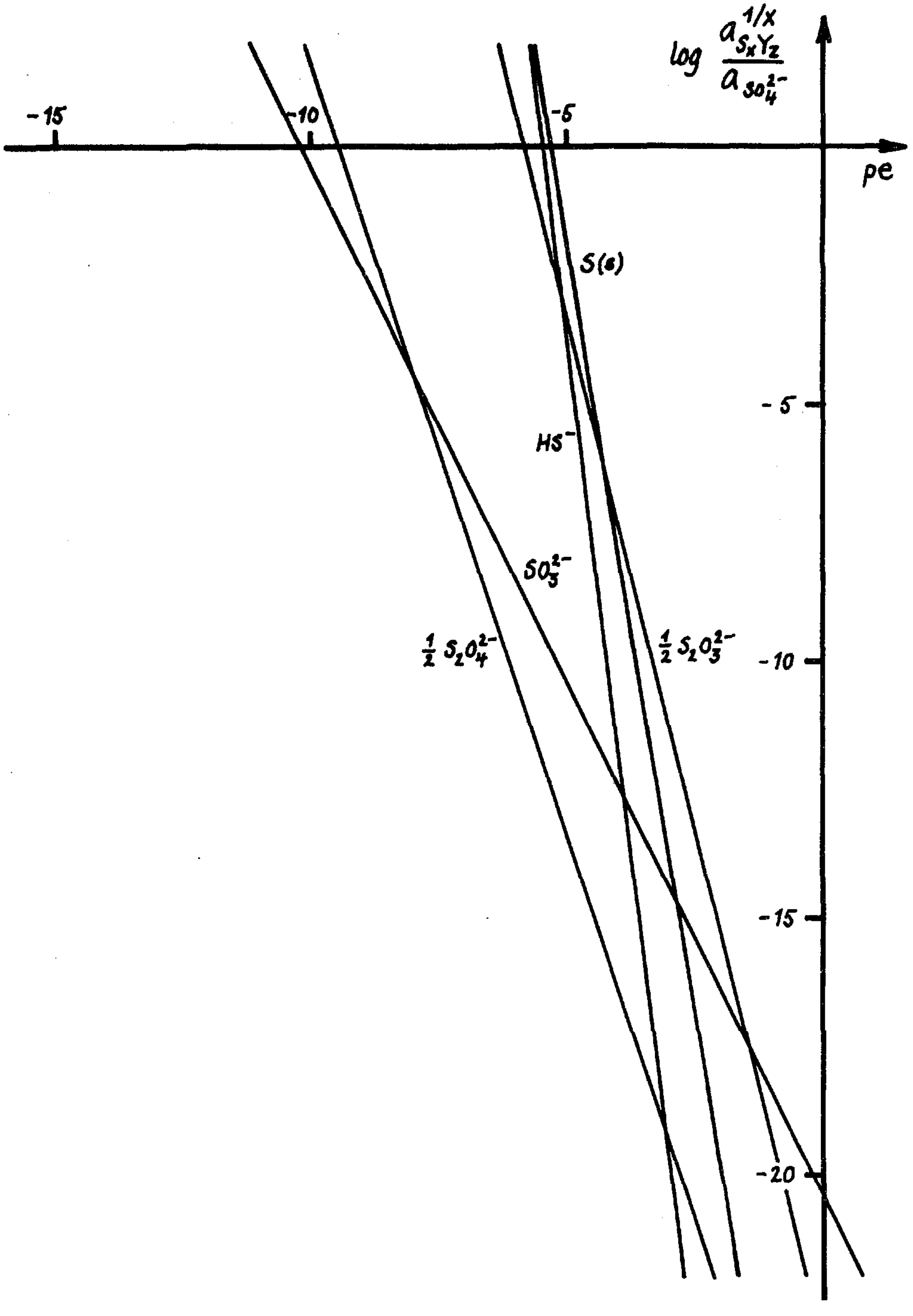


Figure 1b

REDOX DIAGRAM FOR THE SULPHUR SYSTEM
at pH = 7.5, T = 25°C

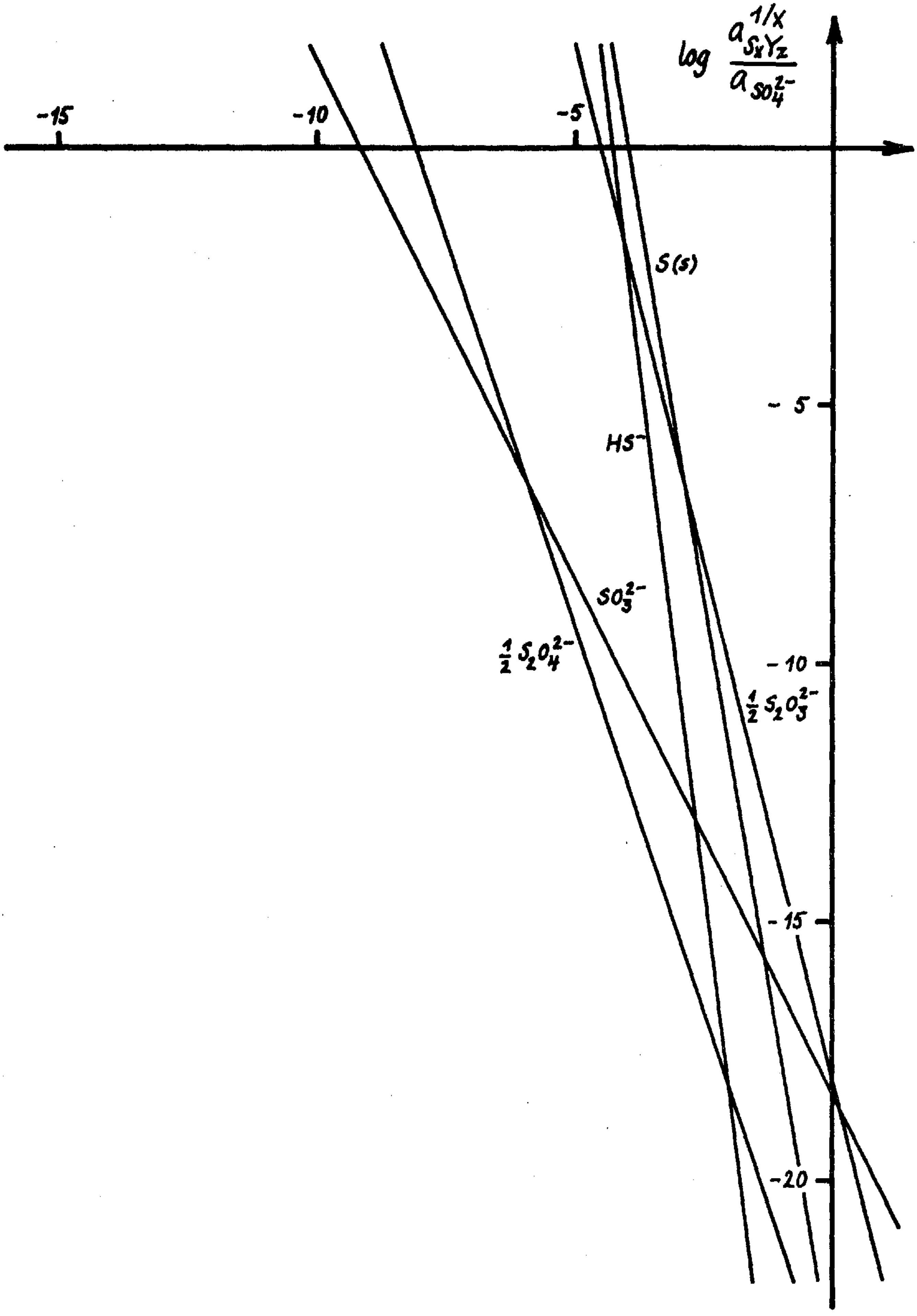


Figure 1c REDOX DIAGRAM FOR THE SULPHUR SYSTEM at pH = 9.5, T = 25°C

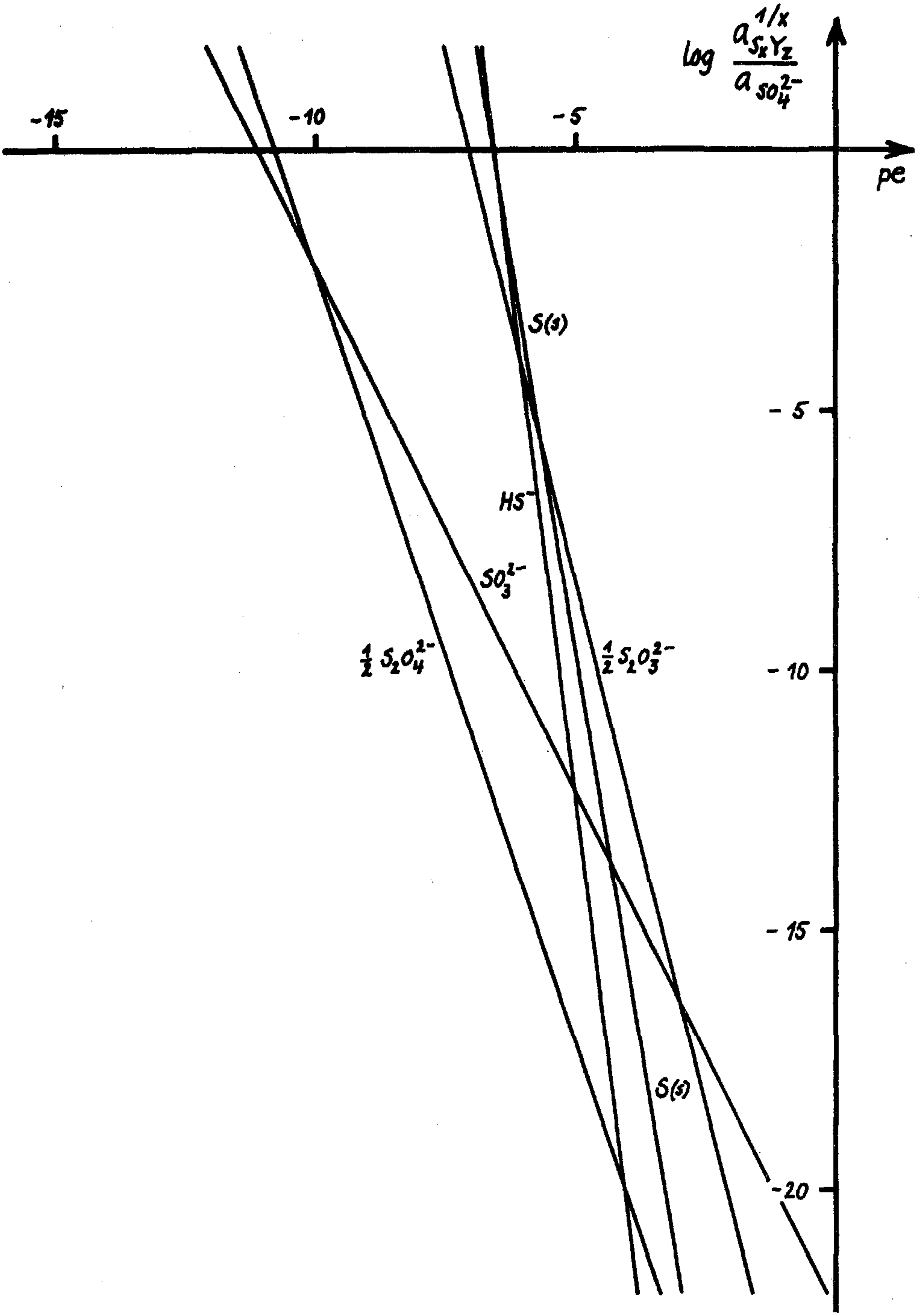
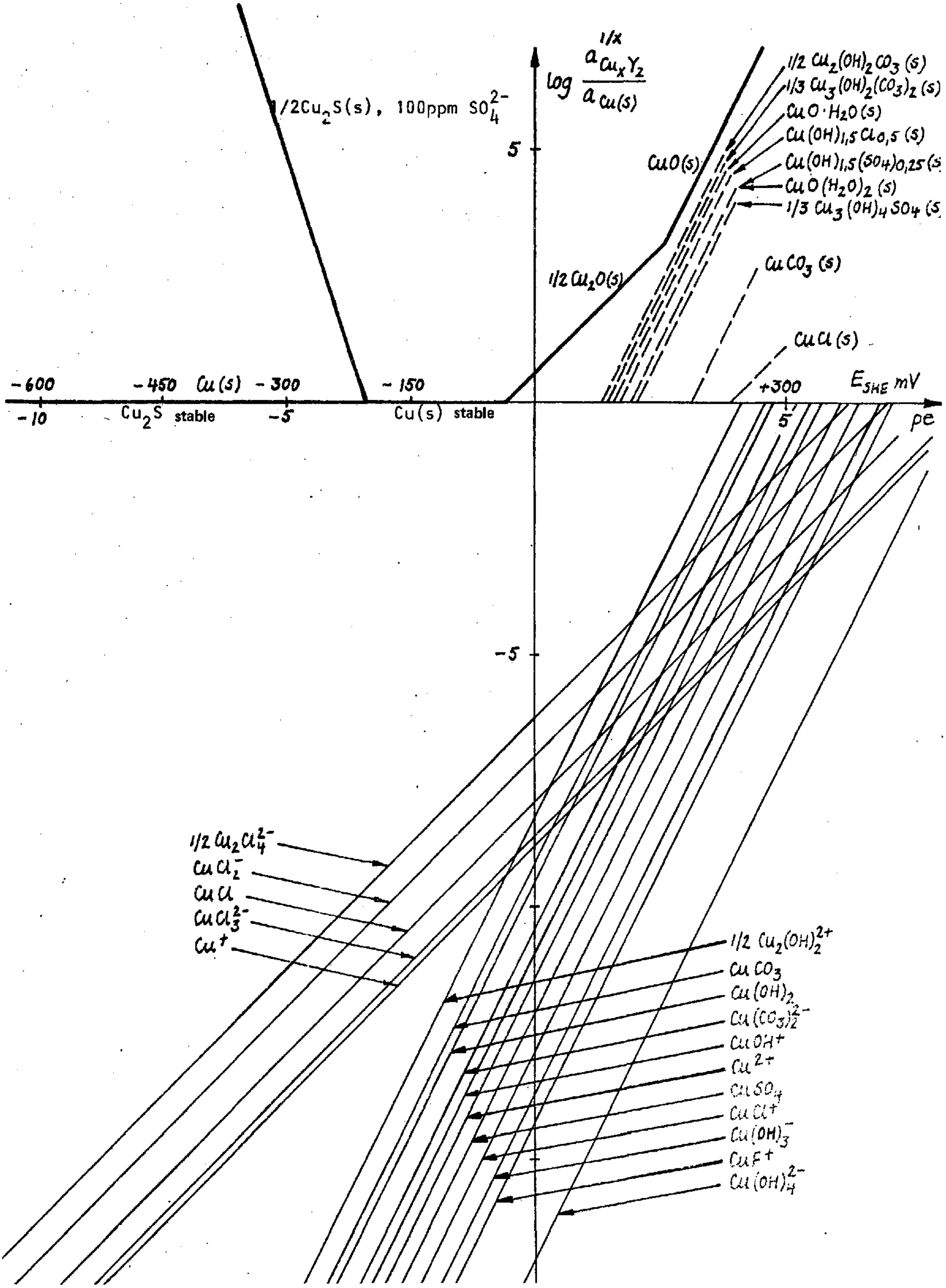


Figure 2a

Redox diagram for the system
$Cu-H_2O-Cl^--CO_3^{2-}-SO_4^{2-}-F^-$
"Normal water" at 25°C, pH=8.5



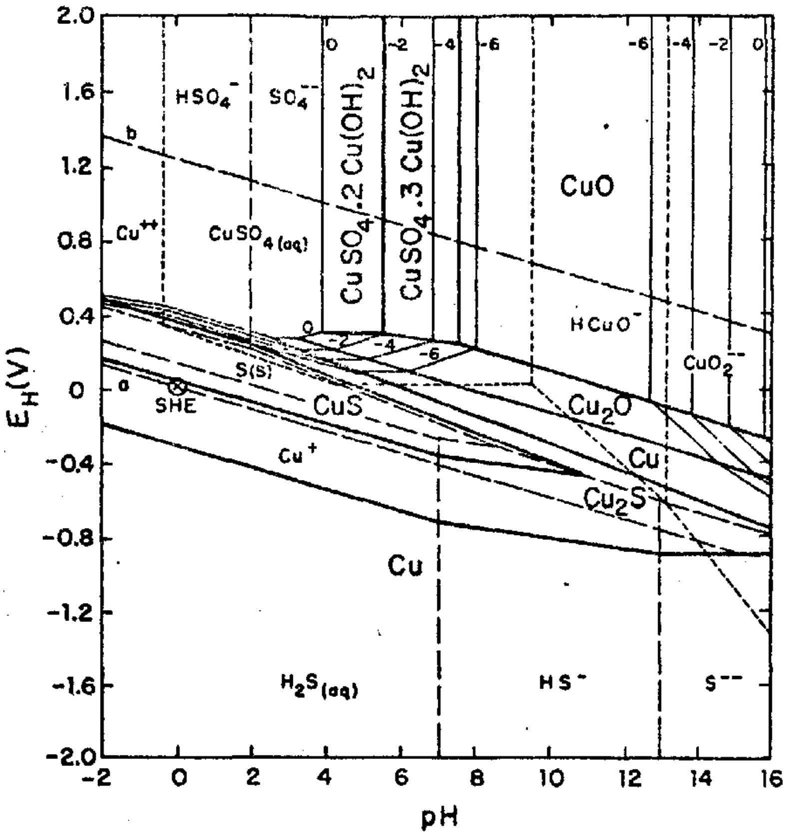


Fig. 3 Potential-pH equilibrium diagram for the copper-sulfur-water system at 25°C, for unit activities of the sulfur ligands. [7]

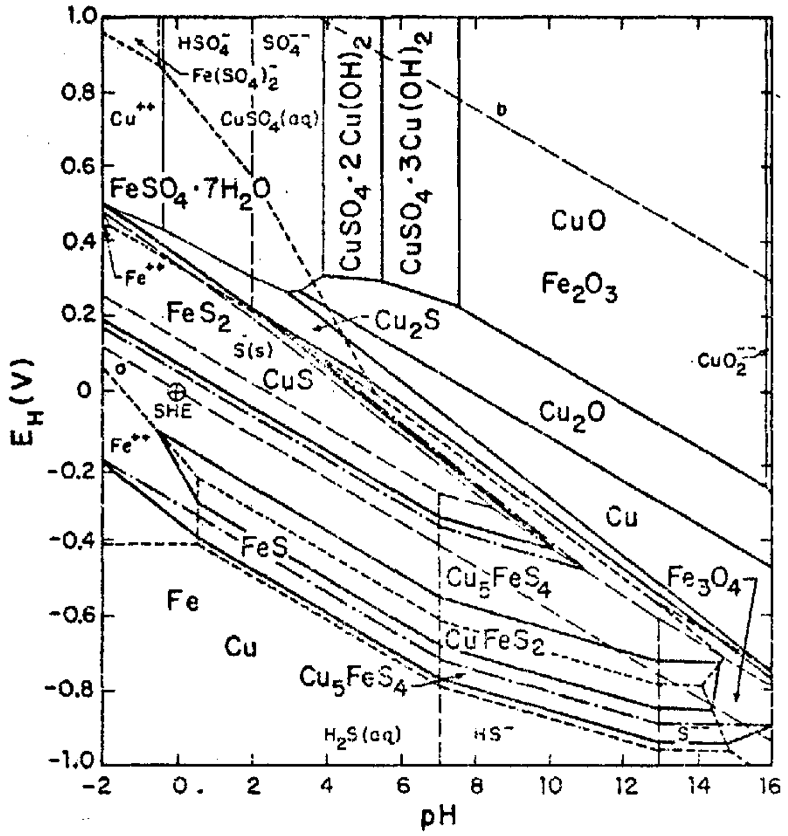
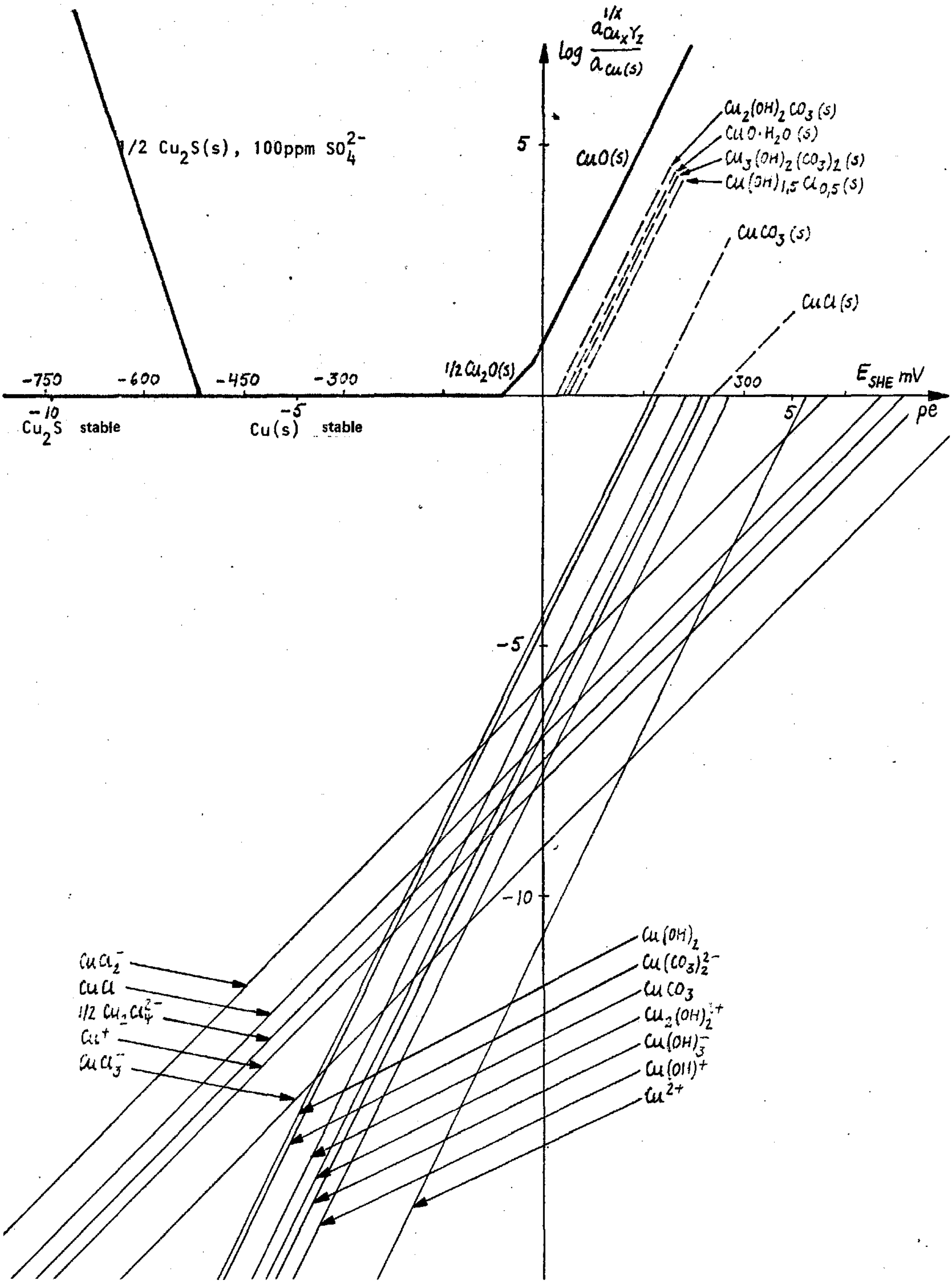


Fig. 4 Potential-pH equilibrium diagram for the copper-iron-sulfur-water system at 25°C, for unit activities of all dissolved species. [7]

Figure 2b

Redox diagram for the system
Cu-H_2O-Cl^--CO_3^{2-}
"Normal water" at 100°C, pH=8.5



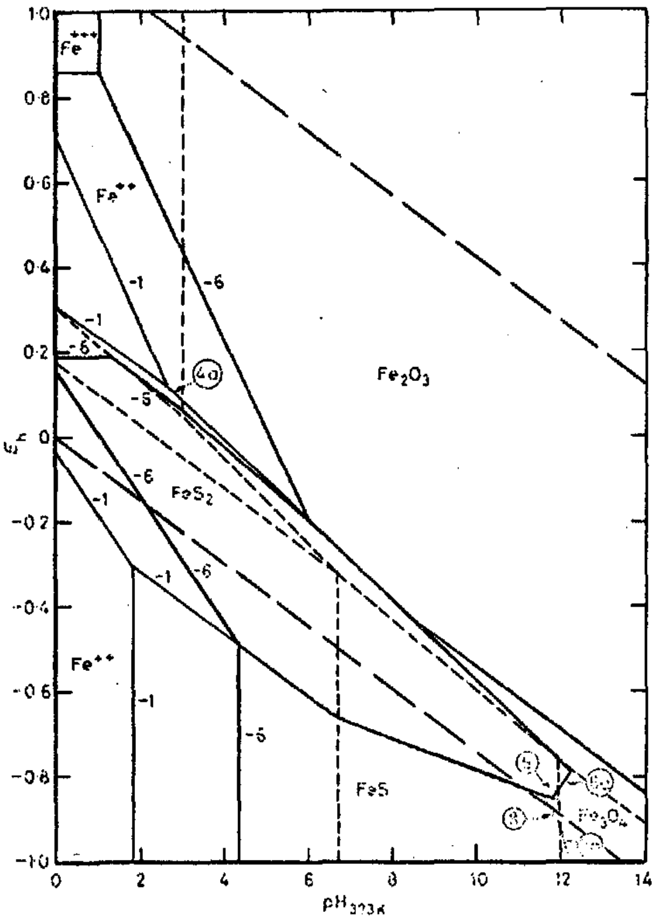


Fig. 5 Equilibrium diagram for iron oxides and sulphides in water at 373K and 1 atm pressure. Activities of iron ions, 10^{-1} and 10^{-6} M; sulphur-containing ions, 10^{-1} M

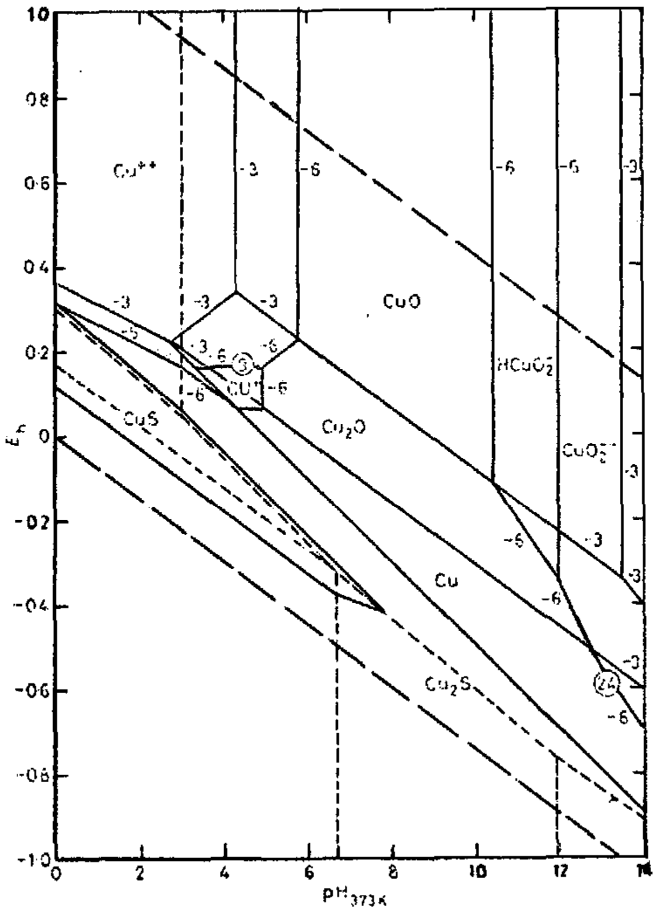


Fig. 6 Equilibrium diagram for copper oxides and sulphides in water at 373K and 1 atm pressure. Activities of copper-containing ions, 10^{-3} and 10^{-6} M; sulphur-containing ions, 10^{-1} M

THERMODYNAMICS OF OXIDATION OF COPPER BY NITRATE

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Premises

- System - Pure Cu(s) + NO_3^- + catalyst (possibly bacteria); no redox buffer; normal water, pH = 7.5 - 9.5; t = 25°C.

- Thermodynamics - No reaction inhibitions, which are normally of decisive importance for most redox processes in the N system.

- Radiolysis - No radiolysis considered; in some cases, however, radiolysis could conceivably facilitate the attainment of equilibrium.

- Reservation - Due to difficulties in achieving equilibrium in actual systems, nitrogen equilibria in aqueous solutions are among the less certain of these which have been studied (despite their great technical importance); a high level of uncertainty therefore characterizes the equilibrium constants.

- Units - For dissolved species: moles/litre (M)
  For gaseous species: atm.

Nitrogen-containing species and thermodynamic data (Figure 1)

The nitrogen in NO_3^- has an oxidation number of V and could be reduced to one or more of its oxidation states down to -III (NH_4^+). The redox diagram includes mainly the dominant species, and for the protolysis equilibria only the species which dominate at pH = 8.5 have been plotted.

(1978-03-29)

Table 1. Species and equilibrium constants for the formation of $\frac{1}{2}$ N_2 (g) (1,2,3)

	$\log_{298}K$
NO_3^-	105.2
NO_2^-	76.9
NO(g)	56.7
$\frac{1}{2}$ N_2O(g)	26.7
$\frac{1}{2}$ N_2H_4	11.7
NH_4^+	-13.9

The following important protolysis products have not been plotted:

HNO_2, $N_2H_5^+$ and NH_3.

The following less dominant species have been accorded little importance in this context and have therefore not been plotted:

NO_2(g), $H_2N_2O_2$. $HN_2O_2^-$, $N_2O_2^{2-}$, NO_2NH^-, NO_2NH_2, HN_3, N_3^-
NH_3OH^+, NH_2OH, NO^+.

The solubility equilibria for NO, N_2O and N_2 have not been marked, but this does not alter the following conclusions.

Possible effects of NO_3^-

Study of the redox diagrams for copper and nitrogen reveals that, provided that thermodynamic equilibrium can be achieved, three different possibilities can be distinguished at pH = 8.5:

1. There is so little NO_3^- that NH_4^+ dominates

   Main reaction:

   $$NO_3^- + 8Cu(s) + 10H^+ + 16Cl^- \rightarrow 8CuCl_2^- + NH_4^+ + 3H_2O$$

   In this pe range (pe < -7), the equilibrium concentration of $CuCl_2^- < 10^{-13.5}$. Thus, copper oxidation is negligible.

2. Nitrogen gas is the main product, but there is not enough NO_3^- present for $Cu_2O(s)$ to form

   Main reaction:

   $$NO_3^- + 5Cu(s) + 6H^+ + 10Cl^- \longrightarrow 5CuCl_2^- + \frac{1}{2}N_2(g)$$

   $-7 < pe < -1$. $\left[CuCl_2^-\right] < 10^{-8}$

   Thus, insignificant oxidation of Cu(s).

3. Nitrogen gas is the main product and there is enough NO_3^- for $Cu_2O(s)$ to form

   $$NO_3^- + 5Cu(s) + H^+ \longrightarrow 2\frac{1}{2}Cu_2O(s) + \frac{1}{2}H_2O$$

   pe = -o.94. $\left[CuCl_2^-\right] \simeq 10^{-8}$, sufficient $\left[NO_3^-\right] > 10^{-8}/5$

   All $\left[NO_3^-\right] > 10^{-8}/5 = 2 \cdot 10^{-9}$ causes formation of $Cu_2O(s)$ and therefore consumption of a quantity of Cu corresponding to 5 x $\left[NO_3^-\right]$.

Copper(I) oxide is formed even at very low concentrations (nitrate + nitrite). The concentrations in "normal water" should be very low - according to the analysis data (Appendix A), less than 2.4 mg/l. Total concentration and waterflow rate determine how much copper will be oxidized.

The calculation shows that the oxidation of copper by nitrate is thermodynamically possible. The reaction rate is, as in the case of sulphate, extremely low. Nitrate/nitrite can therefore be disregarded as possible oxidants of copper.

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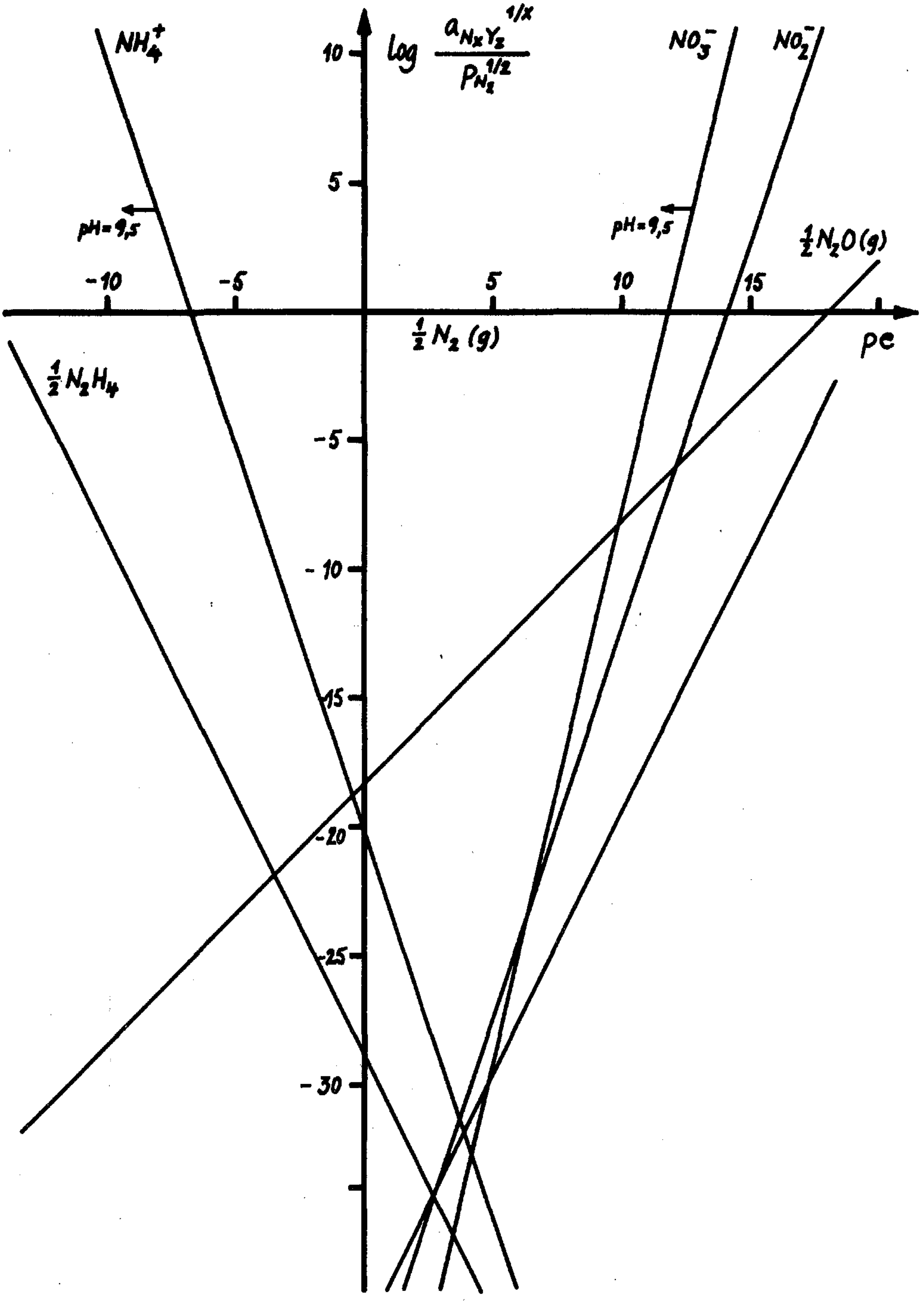
(1978-03-29)

Figure 1.

REDOX DIAGRAM FOR NITROGEN
(dominant species)
T=25°C, pH=8.5 (9.5) "Normal water"



Appendix B5

DETERMINATION OF REDOX POTENTIAL IN GROUNDWATER FROM STRIPA AND FINNSJÖ

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Introduction. It is often possible to determine whether general corrosion of metallic material is possible or not from the redox potential of the system. This is illustrated by a relative diagram for copper in an aquatic system of roughly the same composition as the groundwater studied here. Appendix B1, page 9. As is evident from the diagram, metallic copper is not stable at redox potentials greater than approximately -45 mV.

The redox potential in most groundwaters is determined by various mineral equilibria, e.g. oxidic phases and silicates of iron(II) and iron(III). Redox potentials in systems such as we are dealing with here (2,3) are normally calculated on the basis of the standard free formation energy ΔG_j^{o}. It is obviously of great value if the result can be verified by direct experiment, but measurements of this type are often complicated by the relatively low redox buffer capacity of the system; furthermore, in some cases soluble sulphides are present, which can "poison" the redox electrodes.

The results of redox potential measurements in water from Stripa and Finnsjö are reported in this report. The samples were taken from a depth of approximately 400 m and kept in rubber-stoppered flasks in order to prevent contact with oxygen. The sampling technique and the test flasks were developed by Orrje & Co.

Measurement method. The redox potential is calculated on the basis of the voltage measured in a galvanic cell, where one half-cell consists of the sampling flask with electrode and the other of an external reference electrode. The two half-cells are connected by a salt bridge. The galvanic cell is illustrated in Figure 1.

A silver electrode in 10 mM $AgClO_4$ solution is used as a reference electrode. Two different types of redox electrodes were tested - a platinum electrode, which was present in the sampling flask at the time of sampling, and a gold electrode. The gold electrode was a needle-shaped solid gold rod which was pushed through the rubber stopper after sampling. The part of the salt bridge which was connected to the water sample consisted of a needle-shaped capillary tube, which could also be pushed through the rubber stopper.

Results.

Measurements with the platinum electrode in the groundwater from the Stripa area gave a half-cell potential of 225 mV in reference to a standard hydrogen gas electrode. This corresponds to a pe value of 3.8, i.e. within the corrosion range for copper. Analyses (Appendix A) of the same water indicate the presence of Fe(II) and Mn(II) as well as dissolved (?) sulphides. At the pH in question, Fe(II) and Mn(II) cannot occur at the measured redox potential. Thus, there is reason to believe that the measured potential does not represent the redox potential of the system. A possible explanation may be that sulphides present in the system "poison" the platinum electrode.

According to Rennerfeldt from Orrje, gold electrodes work much better than platinum electrodes in sulphide-containing solutions. In a new series of experiments, the platinum electrode was therefore replaced by a gold electrode. The measured emf values and the calculated half-cell potentials are presented in Table 1.

Table 1. Emf values and half-cell potential in reference to standard hydrogen gas electrode for groundwater from Stripa and Finnsjö.

Sample No.	Place	Measured emf/mV	Half-cell potential/mV
7	Stripa	-834	-152
8	Stripa	-713	-31
18	Stripa	-855	-173
19	Finnsjön	-873	-191
21	Stripa	-892	-210
14	Stripa	-707	-26
20	Finnsjön	-839	-157
24	Stripa	-821	-140

A stable potential of ±2 mV was obtained after approximately 30 minutes. Its stability was checked over a 12-hour period.

Two of the measured results deviate significantly from the others. Before the results are discussed, it is necessary to verify that the measured potential is influenced by the oxygen content of the system. This was done by injecting 5 ml air through a syringe into the left-hand half-cell. If all of the oxygen dissolves, the injected quantity corresponds to approximately 3.5 ppm oxygen. The measured results are presented in Table 2.

Table 2. Measured emf and half-cell potentials in groundwater from Stripa, solution 24, which was oxygenated by the injection of air.

ml air	Measured emf/mV	Half-cell potential/mW
0	-821	-140
5	-670	+12
15	-498	+184

The experiment shows that the addition of an oxidant increases the measured emf. This indicates that the potential of the gold electrode which was used is a measure of the system's redox potential.

It is possible that the deviant redox potentials for samples 8 and 14 stem from the fact that oxygen entered the system in connection with sampling. These solutions have much lower iron(II) and manganese(II) contents than the Finnsjö water. The redox buffer capacity is thus low and the water is more sensitive to contamination with oxygen than the water from Finnsjö.

If we disregard these two samples, the average redox potential in deep groundwater from both Stripa and Finnsjö is -0.17 ±0.04 V, i.e. the results lie within the interval -0.25 ± 0.10 V obtained by Brotzen from a thermodynamic model calculation. Approximately the same results are obtained from the Pourbaix diagram in Appendix B, page 8.

Conclusion

The results of the measurements show that meaningful redox potentials can be determined experimentally in groundwater and that thermodynamic model calculations provide a sufficiently good description of actual systems to serve as a basis for a determination of the properties of the systems.

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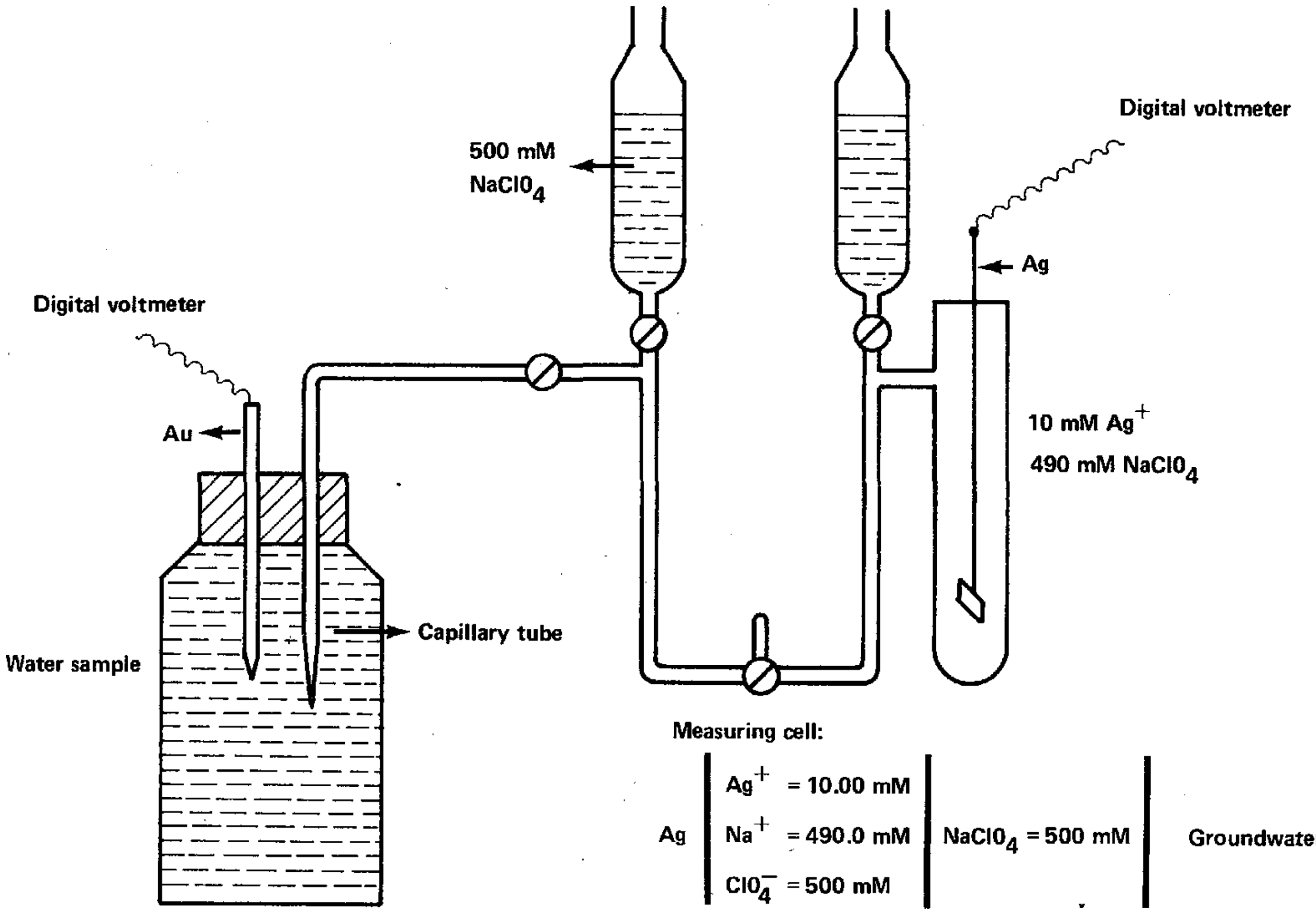
FIGURE 2.



Measuring cell:

Ag | Ag^+ = 10.00 mM, Na^+ = 490.0 mM, ClO_4^- = 500 mM | $NaClO_4$ = 500 mM | Groundwater | Au(s)

KNOWN GEOLOGICAL PROCESSES FOR THE REDUCTION OF SULPHATE TO SULPHIDE

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I Bacterial sulphate reduction

Microbiological activities are the most important components of the sulphur cycle. Without the aid of these organisms, most sulphur would occur as sulphate, which is the most stable form of sulphur in relation to purely chemical processes.

Sulphur compounds in nature exhibit oxidation numbers for sulphur of between -2 and +6 . Many bacterial processes participate in the reduction and oxidation of these compounds. The oxidizing processes are performed by autotrophic bacteria, i.e. bacteria which only require carbon dioxide as a source of carbon in order to build up their cells. The reducing processes are performed by heterotrophic bacteria, i.e. bacteria which must make use of organic compounds in order to build up their own cell mass.

The sulphate in seawater is the largest, most easily accessible sulphur source, and it is on the bottom of the ocean that a large part of the sulphur cycle takes place.

The most important sulphur-reducing bacteria belong to the genera *Desulfovibrio* and *Desulfotomaculum*. They reduce sulphate to hydrogen sulphide when they break down (oxidize) organic materials. These bacteria require oxygen-free conditions (they are anaerobic). They are found in nearly all oxygen-free environments but mainly marine sediments. They are heterotrophic, i.e. dependent upon organic substances which they decompose and use as carbon sources in order to build up their own cellular material.

The bacterial reduction of sulphate takes place in the presence of, for example, lactic acid in accordance with the following formula:

$$2CH_3 \cdot CHOH \cdot COOH + HSO_4^- \rightarrow 2CH_3 \cdot COOH + HS^- + 2CO_2$$
$$+ 2H_2O \quad (1)$$

This formula was proposed by Baars (1930) and has since been verified experimentally by Ghose (1965). Two moles of lactic acid are required for the formation of one mole of sulphide.

The kinetics of the reaction in the natural environment have been studied by Bågander (1977). The kinetics of the reactions can be considered to be of the 0th order down to a sulphate concentration of about 2 mM. At this concentration, the reaction proceeds according to the 1st order with $k_1 = 0.89 \times 10^{-2}$/day with respect to sulphate. The main factor which limits the activity of the bacteria in groundwater in rock is the availability of degradable organic material. The bacteria prefer organic molecules with 3 to 4 carbon atoms. But these bacteria are also found in connection with oil deposits, which would indicate that they can probably break down organic material with a much broader carbon atom spectrum.

Optimal pH value for the process is ~7. The bacteria tolerate pH values between 3 and 10.

The salt content tolerances are from fresh water to saturated solution. The activity of the bacteria generally declines drastically at temperatures above 60°C, but ZoBell (1963) has reported several strains which survive at up to 104°C.

The result of the process is a formation of sulphide ions. In the natural environment, these ions are bound mainly to the most commonly occurring heavy metal ion, which is iron. The iron sulphide which is formed is a precursor to the stable phase, pyrite (FeS_2). The first iron sulphide has a solubility product which is $10^{-17.1}$ at 25°C (Lindström and Bågander, MS), which is considerably higher than the value for the stable phase.

II Non-biological sulphate reduction with organic material

It is thermodynamically possible to reduce sulphate with the aid of organic material without bacteria to catalyze the process (Boström, 1967, Thorstenson, 1970). In order for this reaction to occur, however, temperatures of more than 80°C are required (Orr, 1974). According to Goldhaber and Kaplan (1974): "this reaction is known not to take place at earth surface temperatures and pressures, except when biologically mediated". Orr has studied the process in connection with oil deposits where large quantities of H_2S have been found which have the same ratios between S^{34} and S^{32} as sulphate solution which is present. This indicates that a biological reduction of sulphate to sulphide has not taken place. Moreover, the H_2S quantities which are formed are so high that they would be toxic to sulphate-reducing bacteria. The mechanism of the process would be as follows: an initial reaction between H_2S and SO_4^{2-} at higher temperatures (at least 80°C), producing elementary sulphur and/or polysulphide.

$$SO_4^{2-} + 3H_2S \rightleftharpoons 4S^o + 2H_2O + 2OH^- \qquad (2)$$

The elementary sulphur will then rapidly oxidize and dehydrogenate organic material, forming H_2S.

$$4S^o + 1.33(CH_2) + 2.66H_2O \rightleftharpoons 4H_2S + 1.33CO_2 \qquad (3)$$

H_2S is produced in the reaction at the same time as it mediates as a catalyst.

The process can therefore be regarded as being autocatalytic.

Toland (1960) has shown that sulphate is reduced by a number of organic substances, including saturated hydrocarbons. The reaction is very rapid if H_2S is present and the temperature is 300-350°C. For example, m-xylene was converted completely to isophthalic acid at 325°C in 60 minutes.

$$2C_5H_4(CH_3)_2 + 3SO_4^{2-} + 6H^+ \rightleftharpoons 2C_6H_4(CO_2H)_2 + 4H_2O + 3H_2S \qquad (4)$$

The reaction rate is considerably accelerated by high H_2S pressures.

The lower temperature limit for the reaction is based on assumed temperatures at the oil deposits where this type of H_2S is found. Orr has not been able to demonstrate the reaction in laboratory trials at temperatures of between 80° and 120°C. It is therefore probable that the lower temperature limit for the reaction is higher than 80°C.

III Inorganic sulphate reduction

A completely inorganic reaction which leads to a reduction of sulphate in the presence of sulphide is also thermodynamically possible (see Appendix B).

$$8Cu + 3HS^- + SO_4^{2-} + 5H^+ \rightleftharpoons 4Cu_2S + 4H_2O \qquad (5)$$

This reaction has not been demonstrated in nature. A possible source of sulphate could be the gypsum which is present in the buffer material (bentonite). In actuality, however, it has been found that gypsum is formed in connection with the cultivation of sulphate-reducing bacteria in the presence of high quantities of sulphide with $CaCO_3$ as a pH buffer. The sulphate which was thereby converted to solid phase in the form of gypsum $CaSO_4 . 2H_2O$ did not subsequently go into solution (Hallberg, 1967). The only inorganic source of sulphide known to geologists is volcanic gases.

IV Maximum quantity of sulphide formed through bacterial sulphate reduction

According to what has been said above, the limiting factor for sulphate-reducing bacteria is the availability of degradable organic material. To begin with, we can disregard which types of organic material these bacteria can use in their metabolism and instead assume that they can degrade the total quantity of organic material at the repository site. In this manner, we obtain a maximum value for this type of corrosion and can then make a reservation on the basis of the composition of the organic material, which will not permit total utilization.

Three types of organic material will be present at the repository site:

A. organic material deposited with the buffer material
B. organic material which is supplied via the groundwater
C. organic material which is formed due to other microbiological processes.

Types A and B can be decomposed by other bacteria than sulphate-reducing bacteria. This requires the presence of O_2 or NO_3.

$$OM + O_2 \rightleftharpoons (CH_2O) + CO_2 \qquad (6)$$
$$OM + NO_3^- \rightleftharpoons (CH_2O) + N_2 + CO_2 \qquad (7)$$

OM = organic material
CH_2O = newly-formed biomass

The formulae are not stoichiometrically accurate, but illustrate the principle.

These processes consume some of the organic material, which is converted to CO_2. But if we are to maximize the potential for sulphate reduction, we must disregard reactions 6 and 7.

The amount of newly-formed organic material, type C, is limited by the available quantity of O_2. O_2 will be consumed in reaction 6, but if we once again are to strive for maximum possible sulphate reduction, we must assume that all oxygen is available for reactions of the following types:

$$8Fe^{2+} + 13H_2O + O_2 + CO_2 \rightleftharpoons (CH_2O) + 8FeOOH + 16H^+ \qquad (8)$$
$$4S + 7H_2O + 3O_2 + 3CO_2 \rightleftharpoons 3(CH_2O) + 4H_2SO_4 \qquad (9)$$

Reaction 8 is buffered in nature at about pH = 6, while reaction 9 gives rise to very low pH values, about 1-2. Elementary sulphur is not present, but the reaction proceeds just as well with sulphide in ionic or mineral form. According to analyses from Forsmark, the groundwater contains 5 ppm sulphur in the form of sulphide. The limiting factor for reactions 8 and 9 is thus not the amount of Fe^{2+} or S^{2-}, but rather the amount of O_2. This O_2 can, however, corrode Cu directly without bacterial mediation. The values for this process have been calculated (see Appendix D). Since these reactions give rise to a greater corrosion attack on the copper than those which involve the formation of new organic material, the latter have not been included in the calculations of sulphide corrosion.

The bacterial reduction of sulphate can take place with, for example, lactic acid according to formula (1). Two moles of lactic acid are required for the formation of one mole of sulphide. Following heat treatment of the bentonite, all degradable organic material can be regarded as having been oxidized away. This means that organic material of type A is eliminated. Similarly, type C is eliminated, since higher values are obtained for direct corrosion with O_2. Type B, oxygen which is supplied via the groundwater, remains. A conservative calculation should thus be based on the maximum COD value, which corresponds to 13 mg/l of organic material (OM). The following equivalences are obtained:

13 mg OM $\leftrightarrow$ 0.144 mmole lactic acid $\leftrightarrow$ 0.072 mmole sulphide $\leftrightarrow$
$\leftrightarrow$ 2.4 mg HS^- $\leftrightarrow$ 9 mg Cu

<u>Summary</u>

Geological evidence exists for sulphate reduction to sulphide <u>only</u> in the presence of organic material. This reaction is catalyzed by bacteria, but can be assumed to occur without bacterial mediation if the temperature is above 80°C and H_2S is available for autocatalysis of the reaction.

In order to obtain minimum corrosion, it is therefore necessary to limit and control the amounts of organic material and oxygen.

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Appendix D

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1978-03-31

CALCULATION OF THE AMOUNT OF OXIDANTS PRESENT IN A WASTE REPOSITORY WITH COPPER CANISTERS

1. PREMISES

The repository is designed according to KBS's specifications, as shown in fig. 1. Copper canisters have been placed in vertical holes and surrounded by compacted bentonite. The tunnels contain a sand-bentonite mixture.

The compacted bentonite which surrounds the canister exhibits the following data:

Dry bulk density	approx. 1.8 t/m^3 (in situ)
Porosity	33%
Moisture ratio	10%
Permeability	$< 10^{-12}$ m/s
Diffusion constant (at 50°C, half at 25°C):	
for metal ions	approx. $4 \cdot 10^{-11}$ m^2/s
for oxygen and anions, e.g. S^{2-}, SO_4^{2-}	$8 \cdot 10^{-11}$ m^2/s.

The quartz sand (85%) - bentonite (15%) mixture which fills the tunnels exhibits the following data:

Dry bulk density	approx. 1.6 t/m^3
Porosity	42%
Moisture ratio	approx. 15%
Permeability	approx. 10^{-10} m/s
Diffusion constant (at 50°C, half at 25°C):	
for metal ions	$2 \cdot 10^{-10}$ m^2/s
for oxygen and anions, e.g. S^{2-}, SO_4^{2-}	$4 \cdot 10^{-10}$ m^2/s.

The content of substances in the bentonite which are interesting from the viewpoint of corrosion is stated to be as follows, after heat treatment at 425-500°C:

Fe^{2+}	~0.1%
Fe^{3+}	2.7%
S	< 200 mg/kg (as pyrite, FeS_2)
SO_4^{2-}	0.3 - 0.7%
OM (organic material)	< 200 mg/kg.

The following composition has been given for the groundwater:

	Probable interval		Max. value[x)]	
Fe^{2+}	0.5 - 15	mg/l	30	mg/l
SO_4^{2-}	1 - 15	"	50	"
HS^-	< 0.1 - 1	"	5	"
O_2	< 0.01- 0.07	"	0.1	"
OM	5 - 10	"	13	"

[x)] Max value at 95% confidence level.

The groundwater flow in the rock surrounding the repository is assumed to be 0.2 l/m² and year. In calculating the transport of oxidants via the groundwater into tunnels and deposition holes, a model with rock of higher-than-normal fissure content has been assumed. According to Neretnieks (1), it has been assumed that the rock contains fissures spaced at a distance of 1 m with a width of 0.1 mm.

The volume of the bentonite which surrounds the canister in the vertical hole is 10 m³, and its mass is 18 tons. The volume of the portion of the tunnel located immediately above each deposition hole is 80 m³, corresponding to 128 tonnes of sand-bentonite mixture, fig. 2.

2. CHEMICAL REACTIONS

A review of possible reactions between various components of the groundwater and buffer mass on the one hand and the copper canister on the other hand is provided in a study by Grenthe (Appendix B). The effect of bacterial activity on possible reactions with the copper in the canister has been described by Hallberg (C). The following types of reactions have been taken into consideration in calculating the supply of oxidants:

Reaction of copper with oxygen:

$$4\ Cu\ (s) + O_2 \rightarrow 2\ Cu_2O.$$

Formation of sulphide from organic material with the mediation of bacteria:

$$2\ CH_3 \cdot CHOH \cdot COOH + HSO_4^- \rightarrow 2\ CH_3 \cdot COOH + HS^- + 2\ CO_2 + H_2O$$

Reaction of copper with sulphide in the presence of oxidants:

$$2\ Cu + HS^- + H_2O \rightarrow Cu_2S + OH^- + H_2.$$

Although a number of other possible reactions can occur, the above reactions produce maximum attack on the copper and therefore represent a conservative evaluation.

In order to calculate the maximum attack on the copper canister as a function of time, it is therefore necessary to carry out a calculation of the amount of oxygen and sulphide which is supplied to the canister. The amount of sulphide also includes that which is formed by bacterial action in the presence of organic material.

3. DIFFUSION CALCULATIONS

3.1 General

The maximum amount of copper which can be oxidized can be determined by calculating the quantity of oxidants which is transported up to the canister, whereby transport via the groundwater is also taken into consideration.

The permeability of compacted bentonite is so low (10^{-12} m/s) that the transport of oxidants through the bentonite is dominated by diffusion. The sand-bentonite mixture possesses higher permeability (10^{-10} m/s). Diffusion also takes place at a higher rate (5 times) here than in the bentonite. In the mass transport calculations which have been carried out, it has been conservatively assumed that all transport of substances in the buffer mass in the tunnel takes place so rapidly that the different substances are homogeneously distributed in the buffer. The transport is therefore limited only by diffusion from the tunnel down to the canister, fig. 2.

The diffusion calculations reported here are approximative, since simplified models have generally been used. But the models have been chosen so that the supply of oxidants has not been underestimated.

3.2 Diffusion in the storage hole

The transport of oxidants which are present in the bentonite in the storage hole is illustrated in fig. 3. The concentration (C) of oxidants will decline with time ($t_1 \rightarrow t_4$) due to reaction with the canister surface, where the concentration of oxidants is assumed to be 0. On the basis of Fick's second law, the following equation can be postulated for the initial phase of the diffusion in a case with plane geometry (2):

$$C(x, t) = C_o \operatorname{erf}\left(\frac{x}{2\sqrt{D \cdot t}}\right)$$

where erf is the so-called "error function", which is evaluated in tabular form. If the distance x is set equal to the distance from the canister surface, i.e. $x = 0.35$ m at the rock wall, and the diffusion constant $D = 8 \cdot 10^{-11}$ m^2/s, the concentration at an arbitrary point can be evaluated as a function of time. Since the concentration $C = 0.5\ C_0$ or 50% of the original concentration for a point halfway between the rock wall and the canister (t_3 in fig. 3), approximately half of the quantity of oxidants in the storage hole have been consumed. The expression within parentheses according to the table is then 0.48 or

$$\frac{x}{2\sqrt{DT}} = 0.48$$

$$\frac{0.175}{2\sqrt{8 \cdot 10^{-11} \cdot t}} = 0.48$$

$t = 3.8 \cdot 10^8$ s, which is equal to 12 years.

Approximatively then, the quantity of oxidants in the buffer around the canister will have been reduced to half after 12 years (cf. curve t_3, fig. 3).

The remaining concentration of oxidants decreases exponentially in accordance with the expression:

$$C = C_0 \exp \left[-\frac{t}{\tau} \right]$$

where τ can be set equal to the half-life ($\tau \approx 12$ years). With such an approximation, the time required to reduce the concentration at the rock wall to 1% of the original concentration ($x = 0.35$ m) is calculated to be 60 years.

3.3 Diffusion from fissures in the rock through the buffer mass

A calculation of diffusion from fissures in the rock through the buffer to the canister has been carried out by Neretnieks (1). These calculations have been used in evaluating the supply of oxidants to the canister, whereby it has been assumed that the fissures are not filled with bentonite.

Neretnieks uses a model which is illustrated in fig. 4. Fissures spaced at an interval S are present in the rock around the repository. The canister with radius r_1 is in the storage hole with radius r_2, which is filled with bentonite. The fissures in the rock have been filled with bentonite out to the radius r_3.

According to Neretnieks, three diffusion barriers exist around the repository, represented by the concentration differences ΔC_1 over the buffer mass $(r_2 - r_1)$, ΔC_2 over bentonite-filled fissures $(r_3 - r_2)$ and ΔC_3 over the "film" of groundwater which surrounds the repository.

Diffusion through these three barriers is represented by three equations:

$$J = \frac{2\,\delta}{S}\, 2\,\pi\, L \frac{\overline{r}_1}{\Delta r_1}\, D_1 \quad \Delta\, C_1$$

$$J = \frac{2\,b}{S}\, 2\,\pi\, L \; \frac{\overline{r}_2}{\Delta r_2}\, D_2 \quad \Delta\, C_2$$

$$J = \frac{2\,b}{S}\, 2\,\pi\, L \quad r_3 \quad k_v \quad \Delta\, C_3.$$

$2\,\delta$ is the equivalent mean width of a fictitious diffusion zone in the buffer mass from the fissure to the canister (cf. fig. 4).
$2\,b$ is the width of the fissures (0.1 mm)
L is the length of the canister
$\overline{r}$ is the logarithmic mean of the radius
k_v is the film transfer coefficient, whose value can be determined in accordance with Bird et al (4). Neretnieks finds $k_v = 1.0 \cdot 10^{-8}$ m/s.

Neretnieks finds that the greatest barrier is the bentonite-filled fissures. This barrier has not been taken into consideration in the calculation performed here. The "water film" around the storage hole comprises a barrier which is 10 times as impenetrable as the buffer mass. Neretnieks finds oxygen transport to be $22 \cdot 10^{-6}$ g/year and metre at an oxygen concentration of 0.1 mg/l in the groundwater.

3.4 Diffusion from the tunnel down into the storage hole

In calculating the diffusion of oxidants from the tunnel down into the storage hole, it can be assumed that the concentration of oxidants in the tunnel is constant and that the concentration at the top of the canister is 0. A constant concentration gradient thereby exists and diffusion follows Fick's first law:

$$J = - A D \frac{\Delta C}{\Delta x}$$

where the area A is the cross-sectional area of the storage hole and the diffusion distance Δx is 2.5 m (fig. 2). When the applicable values are inserted, we get:

$$J = 0.71 \cdot D \Delta C.$$

According to the premises, the storage hole can be covered with a copper lid. The passage of oxygen from the tunnel can be calculated approximatively in the following manner. Upon passing down into the storage hole, the oxidants pass through the gap between the rock and the copper lid. Most will probably react with the copper lid. But it is assumed conservatively here that this does not occur, and that the oxidants can diffuse past the lid and on down to the canister, fig. 5.

There are thus three stages in the mass transport, which can be described in the following manner.

Diffusion in the gap between the lid and the rock:

$$J_1 = - AD \frac{\Delta C_1}{\Delta x} = - \frac{1.5 \pi \; 0.01}{0.1} \cdot D \Delta C_1 = - 0.47 D \Delta C_1.$$

After passage through the gap, the oxidants disperse radially in a 90° quadrant in the plane through the centreline of the storage hole.

$$J_2 = \frac{\pi}{2} L D \frac{\Delta C_2}{\ln \frac{r_2}{r_1}} = -\frac{1.5\pi^2}{2 \ln \frac{0.7}{0.005}} D \Delta C_2 = -1.50 D \Delta C_2$$

where

L = the length of the gap between the rock and the lid
$2 r_1$ = the width of the gap between the rock and the lid
r_2 = the largest radius of the radial diffusion zone, i.e. the radius of the lid (cf. fig. 5).

Finally, there is a uniform diffusion down towards the canister:

$$J_3 = - AD \frac{\Delta C_3}{\Delta x} = - \frac{0.75^2 \cdot \pi}{2.0} \cdot D \Delta C_3 = - 0.88 \cdot D \Delta C_3.$$

For the diffusion in its entirety:

$$J = J_1 = J_2 = J_3$$

and

$$\Delta C = \Delta C_1 + \Delta C_2 + \Delta C_3.$$

This gives:

$$\Delta C = 1.80 \cdot \Delta C_1$$

and

$$J = - \frac{0.47}{1.80} D \Delta C = - 0.26 \cdot D \cdot \Delta C.$$

With a lid, diffusion is thus 2.7 times lower than if there were no lid.

4 SUPPLY OF OXYGEN TO THE CANISTER

4.1 Oxygen in the groundwater

The level of oxygen in the groundwater has been specified in the premises to be 0.1 mg/l. A calculation of the amount of oxygen transported in from the groundwater must include the oxygen which enters via fissures around the storage hole and the oxygen which diffuses down from the tunnel to the copper canister.

The oxygen which diffuses in through the fissures (see 3.3) will be, according to Neretnieks calculation and without bentonite in the fissures, $2.2 \cdot 10^{-5}$ g O_2/year and metre of canister. For the entire canister, we get $11 \cdot 10^{-5}$ g O_2/year, and metre of canister. For the entire canister, we get $11 \cdot 10^{-5}$ g O_2/year, equivalent to $8.8 \cdot 10^{-4}$ g Cu/year.

The oxygen which diffuses in via the tunnel (see 3.4) will be, according to the specified calculation methods, $7.1 \cdot 10^{-5}$ g O_2/year and canister, equivalent to $5.7 \cdot 10^{-5}$ g Cu/year and canister.

4.2 Radiolysis oxygen

The total amount of oxidants formed by radiolysis ("radiolysis oxygen") has been calculated by K Lundgren (4) to correspond theoretically to a maximum of:

20 g Cu after 10^4 years
60 g Cu after 10^5 years
400 g Cu after 10^6 years

4.3 Initial oxygen after deposition

During deposition, the repository is exposed to atmospheric oxygen. After sealing, oxygen remains in the buffer mass in the pores between the bentonite grains.

After sealing, the groundwater will slowly (over the course of 1000 years) fill up the pores in the bentonite. After the pores have been filled with water, it is assumed that the oxygen will be dissolved in the water. This oxygen can be consumed by the oxidation of substances which are present from the start or which diffuse into the bentonite, such as sulphide, iron(II), manganese(II) and organic material. But it can be conservatively assumed that all oxygen goes into oxidation of the copper canisters.

The air content of the bentonite has been stated to approximately one m^3 (1 atm, 0^oC) per storage hole. The total quantity of oxygen dissolved in pore water will be 300 g per storage hole, which corresponds to an oxidation of 2.4 kg copper. As was shown by the diffusion calculations, most of the oxygen has been consumed after 60 years, assuming a reaction with the canister. This means that most of the oxygen is consumed while the repository fills with water.

If the tunnel is filled with a sand-bentonite mixture which is said to contain 25 m^3 (1 atm, 0^oC) air per storage hole, the quantity of oxygen there corresponds to the oxidation of 60 kg copper. However, since deoxidant (iron(II) phosphate) has been mixed in with the buffer mass in the tunnel, this oxygen will be consumed by the deoxidant.

It can be of interest to study what would happen if the oxygen in the tunnel should, against all probability, not be reduced. It is assumed that the oxygen diffuses down to the canister and oxidizes it. If there is no copper lid in the storage hole, half of the oxygen will have reached the top end of the copper canister within 32 000 years and will thereby have oxidized no more than 30 kg Cu. After a period of 75 000 years, 90% of the oxygen will have reached the top end of the copper canister and oxidized no more than 54 kg copper.

If the storage hole is provided with a copper lid, these times will be extended to 85 000 years and 200 000 years, respectively.

The quantity of oxygen which reaches the copper canister will, however, be reduced by the flow of the groundwater through the tunnel's buffer mass. With a flow of 0.1 l/m^2 and year and a homogeneous flow through the tunnel, the water would be replaced every 14 000 years. Even if it must be assumed that the flow is low and inhomogeneous, there is a reduction of the total quantity of oxygen, especially if the storage hole is covered with a lid.

A further reduction of this initial oxygen takes place when the oxygen meets sulphide in the storage hole, which has diffused in with the groundwater through rock fissures.

5 SUPPLY OF SULPHIDE TO THE CANISTER

5.1 General

According to Grenthe (1), the sulphide concentration in the groundwater is regulated by the reaction

$$12\ Fe_2O_3(s) + HS^-(aq) + OH^-(aq) \rightarrow 8\ Fe_3O_4(s) + SO_4^{2-}(aq) + H_2O(l)$$

At pH 8.5, $[HS^-] = 10^{-6.8}$ M, which is equivalent to 0.005 mg S/l in the groundwater. The higher levels (5 mg S/l) given in Appendix A and set as the upper limit for the sulphide concentration in the groundwater therefore probably derive from colloidal or molecular sulphide. The additional quantity of sulphide which it is assumed could be formed through the reduction of sulphate mediated by bacteria must, in order to contribute to the reaction also be present in colloidal or molecular form. 13 mg/l of organic material can, according to Hallberg (Appendix C), produce a sulphide content of no more than 2 mg S/l. The maximum sulphide content of the groundwater can therefore be set at 7 mg S/l.

The diffusion of sulphide in colloidal form through the bentonite will naturally be much slower than the diffusion of sulphide ions, by at least two powers of 10. But it will be conservatively assumed here that sulphide has the same diffusion coefficient as HS^-.

5.2 Sulphide in the groundwater

The supply of sulphide via groundwater through rock fissures around the storage hole has been calculated using the model worked out by Neretnieks (cf. 3.3). It has thereby been assumed that the fissures around the repository are not filled with bentonite. With the above-reported assumptions of a groundwater sulphide content of 7 mg S/l and the same diffusion coefficient as for sulphide ions, a total inflow of sulphide of $1.5 \cdot 10^{-3}$ g S/year and metre of canister or $7.7 \cdot 10^{-3}$ g S/year and canister is obtained, which corresponds to reaction with max. 31 mg Cu/year.

The sulphide which diffuses in this manner to the canister will, however, meet a copper surface which has previously been oxidized by oxygen. It will therefore meet a groundwater next to the canister which is in equilibrium with the copper oxide. At the prevailing redox potential, the sulphide will be oxidized to sulphate before the copper is attacked. However, this delay of the attack has not been taken into consideration in this calculation.

Sulphide in the tunnel can diffuse down towards the canister. It is assumed that the level of sulphide in the tunnel's groundwater stabilizes after a period of time at a maximum of 7 mg S/l. The maximum quantity of sulphide which can reach the canister is calculated as shown in section 3.4 to be $4.9 \cdot 10^{-3}$ g S/year, whereby the diffusion of colloidal or molecular sulphide is conservatively assumed to take place at a diffusion rate of $8 \cdot 10^{-11}$ m^2/s. This corresponds to a reaction with a maximum of 19 mg copper per year, whereby the attack is assumed to be concentrated to the top end of the canister. With a lid in the deposition hole, the attack is reduced to no more than 7 mg copper per year.

5.3 Sulphide in the buffer

Sulphide is present in the bentonite after heat treatment in the form of pyrite, FeS_2, at a concentration corresponding to 200 mg S/kg. The solubility of pyrite in groundwater is very low. The solubility product should be $< 10^{-16}$ M^2 (Appendix B). Since it has been assumed that the groundwater is saturated with sulphide ions, pyrite cannot go into solution and contribute to the attack on the copper canister. On the contrary, iron sulphide is precipitated in the buffer, although this has not been taken into consideration in this calculation.

The maximum quantity of pyrite which is present in the bentonite in the storage hole is 3.6 kg S, which corresponds to reaction with no more than 14.4 kg copper.

The quantity of pyrite in the buffer mass in the tunnel is roughly the same as in the storage hole. But this pyrite cannot contribute towards corrosion of the copper canister either.

The amount of organic material present in the bentonite after heat treatment has been said to be < 200 mg/kg. This organic material is probably difficult to break down, but it can be conservatively assumed that it can contribute via bacteria to the breakdown of sulphate, whereby a maximum of 36 mg S/kg of bentonite can be formed. The bentonite present in a storage hole (18 tons) therefore contains organic material corresponding to the formation of max 640 g S. This sulphur can react with max 2.6 kg Cu.

The quantity of organic material in the bentonite in the adjacent portion of the tunnel is a maximum of 25.6 kg. Organic material can, via bacterial sulphide formation, lead to reaction with max. 2.8 kg Cu. Sulphide which can be formed bacterially is transported to the canister in the same manner as has been assumed for sulphide from the groundwater.

6 THERMAL DIFFUSION OF COPPER IONS

Due to the generation of heat in the waste, a temperature gradient will arise in the buffer surrounding the canister which is relatively great in the beginning, approx. 50°C between the canister and the rock wall, but which will have decreased after a thousand years to a few degrees. This temperature gradient could conceivably give rise to a diffusion of copper from the canister out towards the rock wall, since the solubility of the copper-I ions is temperature-dependent. If simple stationary diffusion is assumed from an imaginary flat canister wall (12 m^2) to the rock wall ($\Delta x = 0.35$ m) Ficks first law can be used:

$$J = -AD \frac{\Delta c}{\Delta x}$$

where, at 50°C, $\Delta c = 10^{-7}$ mole/l $H_2O = 10^{-4}$ mole/m^3 H_2O = $10^{-5} \cdot$ mole/m^3 bentonite

$$J = -12 \cdot 4 \cdot 10^{-11} \cdot \frac{10^{-5}}{0.35} \text{ mole/s}$$

$J = 1.5 \cdot 10^{-14}$ mole/s corresponding to 0.03 mg Cu/year.

This diffusion of copper ions can only occur under the special provision that an electron-conducting contact is maintained between the canister and the copper precipitated at the rock wall. If such a contact does not exist, the diffusion will be limited by the very low solubility of the copper-II ions (10^{-16} M) and will be completely negligible.

7 SUMMARY

The largest quantity of reactants which can be transported into and react with the canister is reported in table 1. The calculations are carried out conservatively. An attack on the canister will probably be limited to a light oxidation by initial oxygen. The reaction with sulphide will probably be insignificant, for a number of reasons.

The level of sulphide in the groundwater will probably be much lower than has been assumed. If there is a higher level in colloidal form, it will be transported at a slower rate. It will probably react with various ions in the buffer and will not reach the canister.

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   ("Deposited radiant energy outside of a copper canister containing spent fuel rods")
   ASEA-ATOM Report RF 77-404 (1977-09-26).

(1978-03-31)

Table 1. The largest quantity of copper per canister which can react with oxygen and sulphide. Quantity in kg as a function of time

Rate-determining reactant		Maximum quantity of copper which can react with supplied reactant, kg			
		10^3 years	10^4 years	10^5 years	10^6 years
<u>Oxygen</u>:					
Initial	in storage hole	2.4	2.4	2.4	2.4
	from tunnel	0	0	0	0
Groundwater	via fissures	0	0	0.09	0.9
	via tunnel	0	0	0.06	0.6
Radiolysis		0	0	0.1	0.4
Total, oxygen reaction		2.4	2.4	2.7	4.3
<u>Sulphide</u>:					
Initial	in storage hole	0	2.6	2.6	2.6
	from tunnel	0	0.3	2.8	2.8
Groundwater	via fissures	0	0.3	3.1	31
	via tunnel	0	0.2	1.9	19
Total, sulphide reaction		0	3.4	10.4	55.4

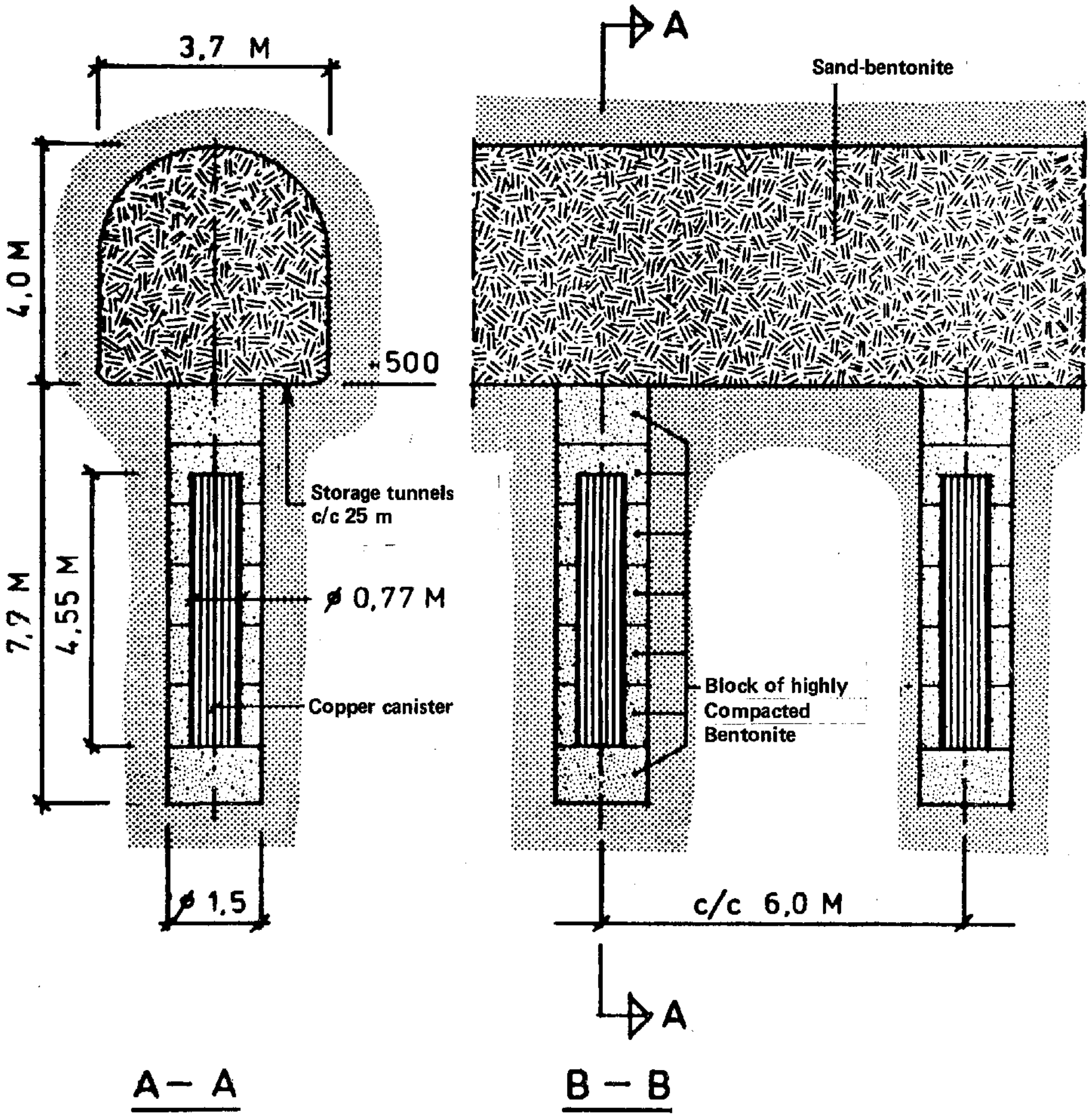

Fig. 1 FINAL REPOSITORY FOR SPENT FUEL

BUFFER MATERIAL OF HIGHLY COMPACTED BENTONITE IN STORAGE HOLES AND OF SAND (85%) AND BENTONITE (15%) IN TUNNELS

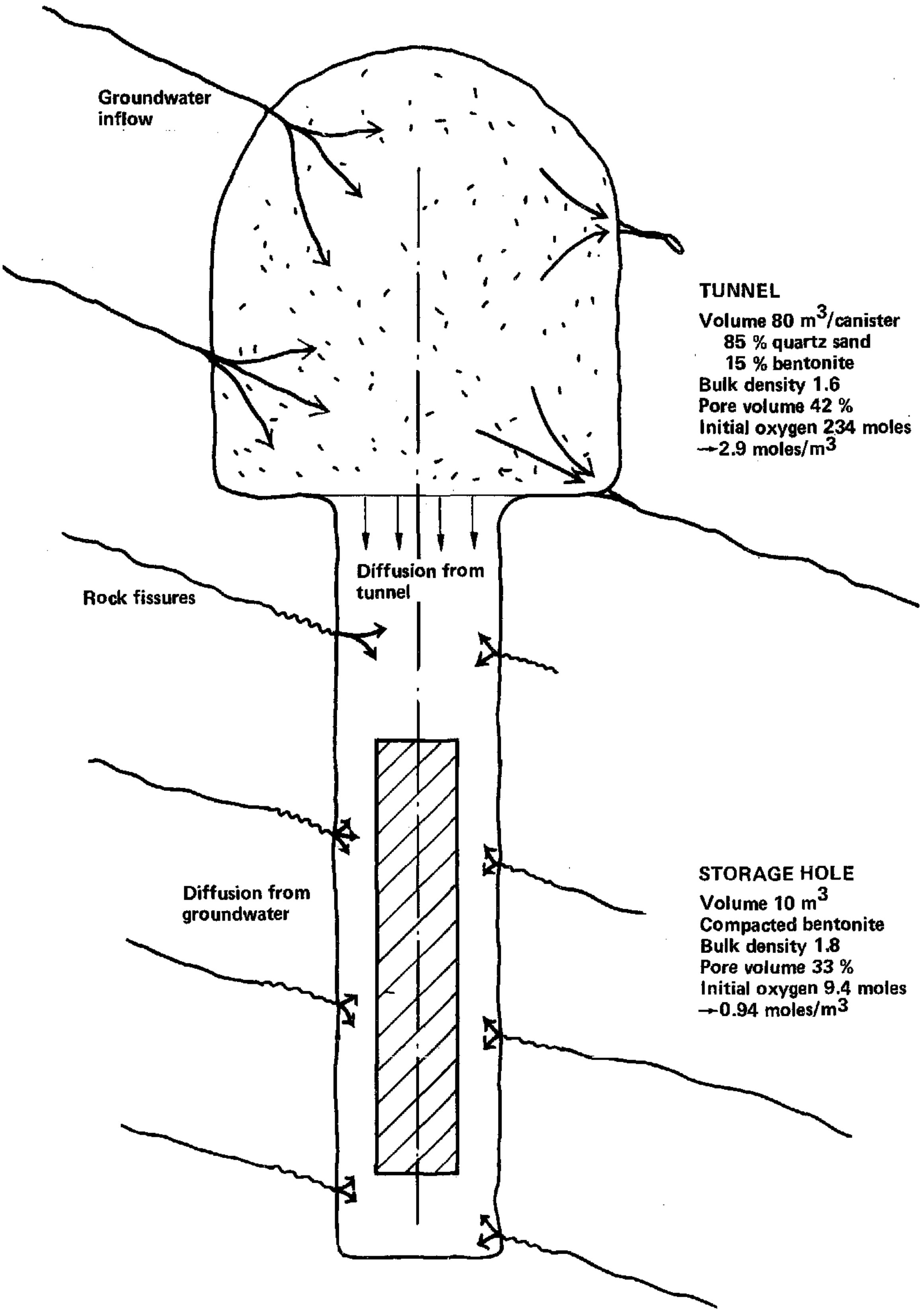

Fig. 2 Premises concerning repository used in calculation of supply of oxidants

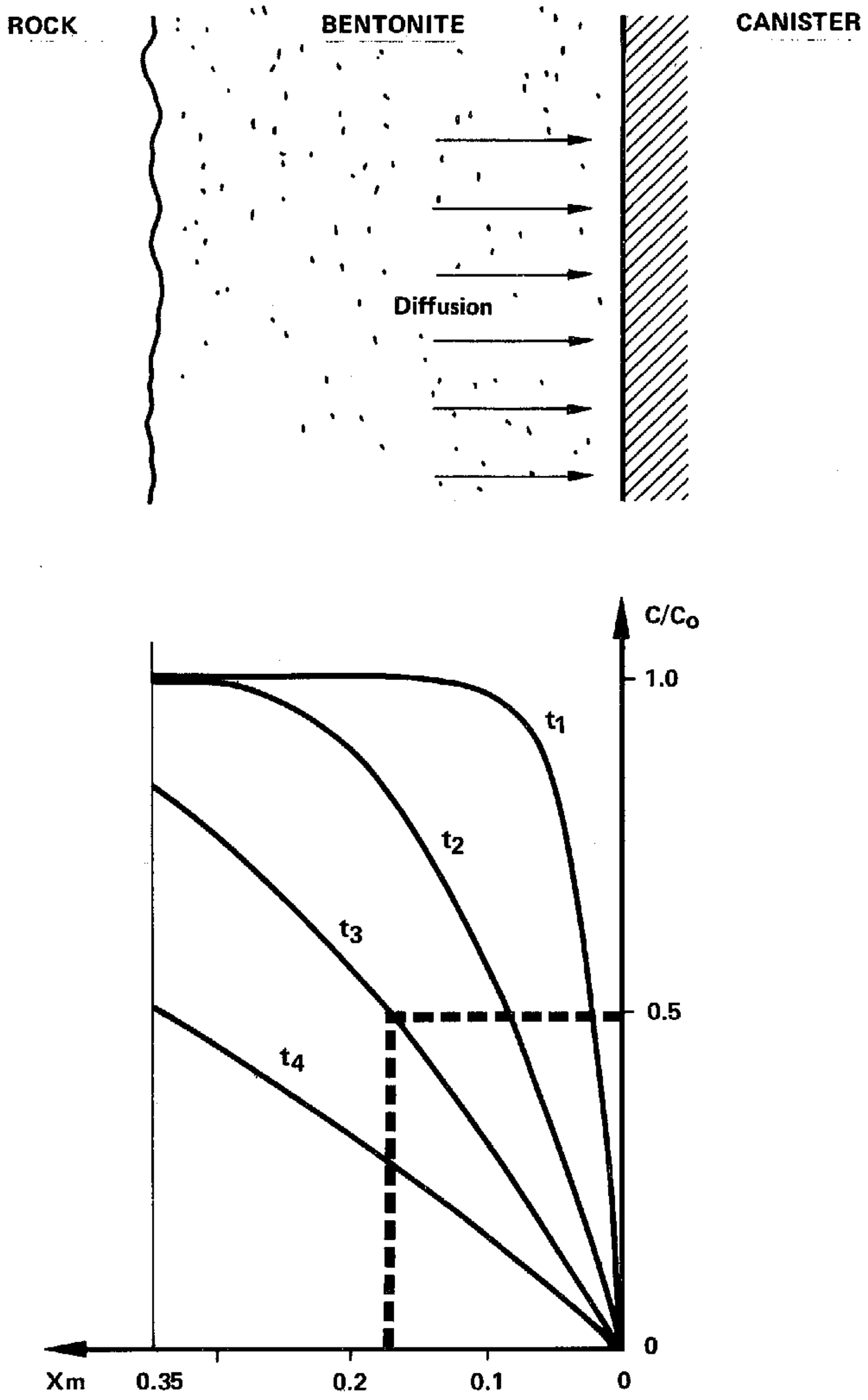

Fig. 3 Diffusion of initial oxidant to canister. Change of relative concentration with time (t_1-t_4).

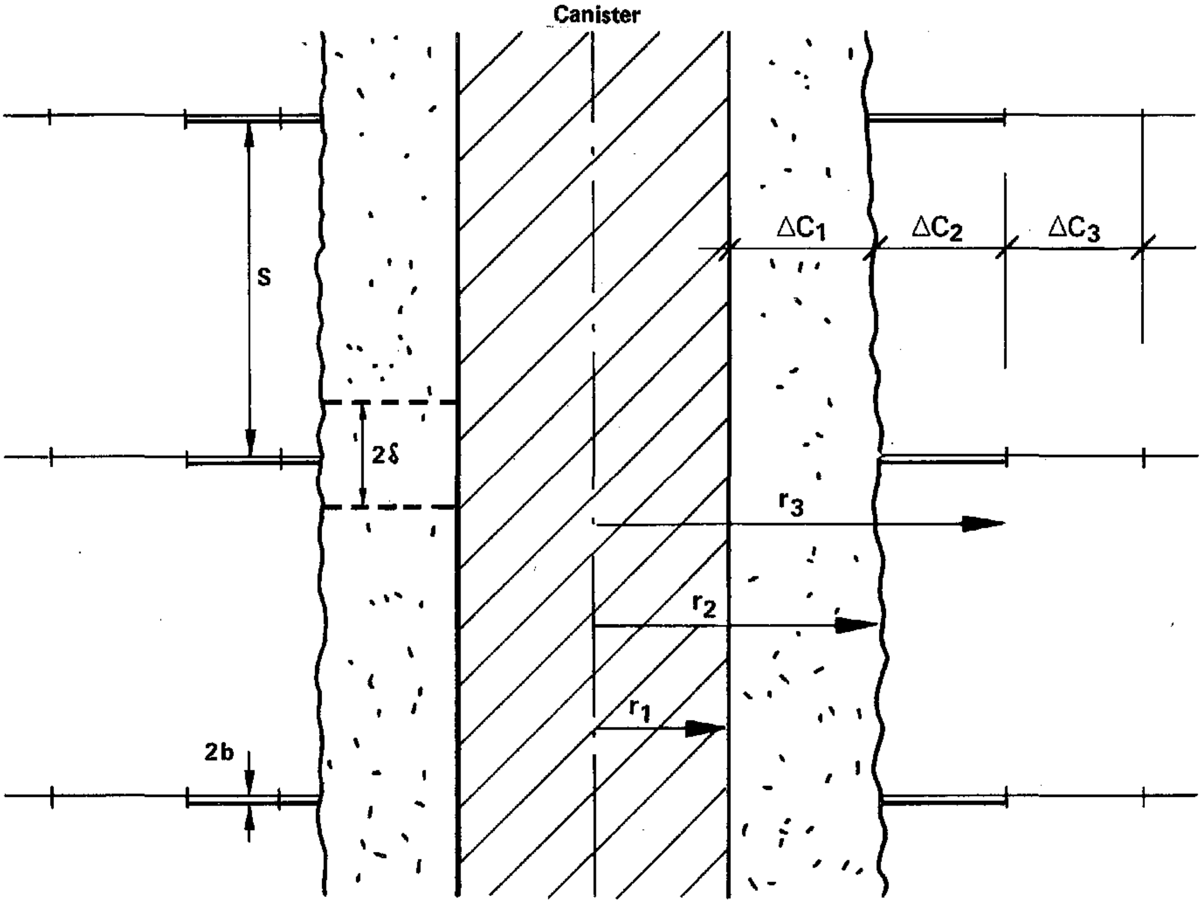

Fig. 4 Model for diffusion calculations according to Neretnieks (1).

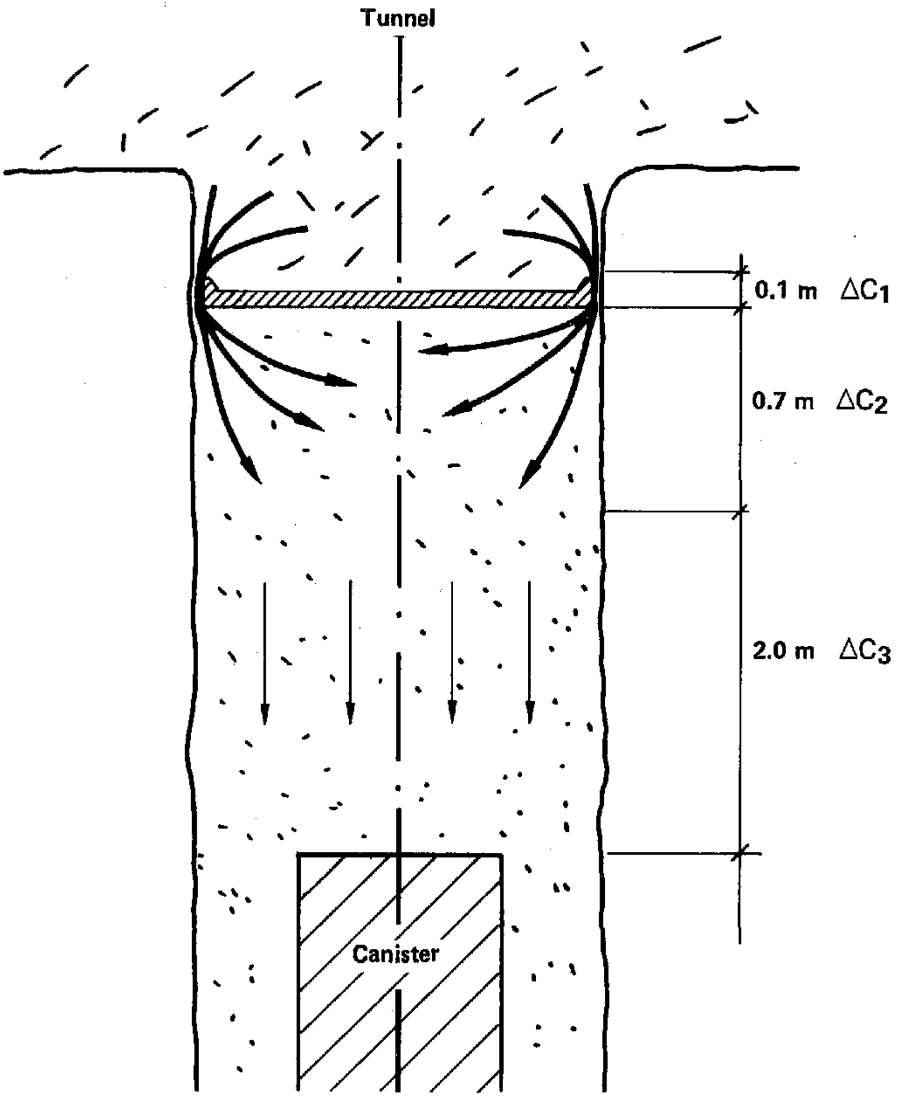

Fig. 5 Diffusion from tunnel past lid and canister.

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STATISTICAL EVALUATION OF COPPER CORROSION IN SOIL FROM TESTS CONDUCTED BY DENISON AND ROMANOFF

Certain results from studies by Denison and Romanoff have been analyzed in the current investigation of the durability of copper canisters for nuclear waste.

1. COMPLETED TESTS

In a large-scale investigation conducted in the USA, the corrosion of various metals in soil was studied. Exposure testing was started in the 1920s in a large number of different types of soil all over the United States. Exposure covered a period of 14 years. These tests were conducted by NBS, The National Bureau of Standards, and have been described in a report by Romanoff (1). The investigation included tests of copper and copper alloys, which are also dealt with in a special report by Denison and Romanoff (2).

The soils in which the tests were conducted are described in table 1. The results of the corrosion trials are summarized in table 2.

The empirical expression

$$P = kt^n \qquad /1/$$

was used in the report in an attempt to describe the time dependence of the corrosion penetration depth (P). The exponent n and the constant k were evaluated for both general corrosion and pitting. Table 3 presents a summary of the results in clays and loams. Results from soils of singular composition have not been included. In evaluating the corrosion rate according to the exponential expression, the logarithm of this expression has been taken and a linear regression has been made to the test values, as shown in fig. 1. As will be shown later, such a regression leads to an overemphasis of the corrosion attack after 2 years of exposure.

Four different copper grades were used for the evaluation, two of which were alloyed with low silicon contents. The spread in the individual results of penetration measurement was great, as is shown by Fig. 2. Small attacks were given as "< 6 mils" or as rough surface. As a result, the spread in the values for k and n in the empirical expression is relatively great.

2. DEPENDENCE OF CORROSION ON SOIL TYPE

The corrosion attacks varied widely from soil to soil. The report states that a correlation exists between various properties of the soils and the extent of the corrosion attack. With exceptions for extreme types of soil and soils with high chloride contents, however, it seems to be difficult to find a correlation between corrosion and soil composition, pH, aeration and temperature.

An attempt has been made to demonstrate a possible correlation between the properties of the soils and the extent of the corrosion by means of "pattern recognition." The correlation between the corrosion attack on the copper and all specified soil properties has been determined for 30 soils by means of a computer program at the University of Umeå (Appendix E1). No significant correlations have been found in the material.

3. DEPENDENCE OF CORROSION ON TIME

Denison and Romanoff (2) expressed the time dependence of the corrosion penetration by means of the empirical expression $P = kt^n$. The possibility of using this expression to calculate the corrosion attack on copper after a very long period of time has been discussed. Since the spread of k and n is great (3), however, the uncertainty involved in such an extrapolation would appear to be unacceptable.

In the reported evaluation, the values of the exponent n are given. These values vary between 0.12 and 0.57 for "normal" soils with a pronounced tendency to cause pitting (high pitting factor). With these values of the exponent n, the growth of the pits in depth will decrease with time. As is shown by figures 1 and 2 and the results of the measurements of maximum pit depth which are given in reference (2), the increase in maximum pit depth after 5.4 years of exposure is slight; in general, it lies within the normal spread of the test values. This indicates that pitting ceases sooner than would be indicated by the specified values for the exponent, i.e. the value of the exponent also decreases with time. A probable reason why Denison and Romanoff (2) found higher values for the exponent than would be expected may be that the linear evaluation of the log of the expression gives too much weight to the often immeasurable attack which follows upon two years of exposure. Another reason may be that pitting is preceded by a certain incubation period. An incubation period t_o can be introduced into the expression for pitting, which then will be

$$P = k\,(t - t_o)^n \qquad /2/$$

In order to study these factors more closely, an attempt was made to adapt the results obtained for pit depth to the empirical expression /1/ by means of linear regression of the logs of the values. The exponent n was calculated for a number of soils, on the basis of results from all five exposure times as well as after exclusion of the results for two years of exposure (4 values). As is shown by table 4, the exponent n decreases in all cases where the 2-year value is excluded. This clearly shows that the values of n are actually lower than the values calculated by Denison and Romanoff (2).

An attempt was also made to introduce an incubation period into the empirical expression in accordance with formula /2/. The incubation period was assumed to be one year. As is shown by table 4, the exponent n decreases in all cases with this modification as well and the correlation is improved. Apparently, pitting of copper in soil is preceded by a certain incubation period and then exhibits a strong tendency to decline with time.

Finally, in order to obtain a more correct evaluation of the test results, the results were subjected to computer processing using the least squares method at the Swedish National Defence Research Institute (see Appendix E2). Both unweighted and weighted values from different exposure periods and with and without the incubation period t_o were processed. The results are presented in table 5. As before, there is a clear tendency towards lower values of the exponent at a better fit. The incubation period t_o is around 2 years in most cases.

4. THE PITTING FACTOR

The tendency for pitting to occur is expressed by the pitting factor (P_f), which is the ratio of maximum penetration to average penetration. In the normal pitting process, an incubation period is followed by the formation of isolated pits which grow in depth (high pitting factor). The growth of these pits in depth eventually ceases, however, and new pits are initiated. As a result, the pitting factor decreases with time.

In Denison and Romanoff's study of the underground corrosion of copper, the pitting factor was evaluated and found to be 24 (tables 2 and 3). However, it is possible to obtain information on the change of the pitting factor with time from existing data by comparing the general corrosion rate with the pitting rate. If the former is larger it will become increasingly dominant with time and the pitting factor will decrease. This is illustrated by the following derivation:

$$P_f = \frac{P_{max}}{P_{med}} = \frac{k\ t^n}{k' t^u} = \frac{k}{k'}\ t^{n-u}$$

If u > n, the pitting factor will decrease with time. In table 3, (n - u) is given for the nine soils; averages have been used for n and u. In seven of the cases, the difference is negative, i.e. the pitting factor decreases with time. If the spread of the exponents is taken into consideration, four of the differences are still significantly negative, one is significantly positive and the others are indeterminant. As has been previously demonstrated, the exponent n decreases with time. This is not true for the exponent u, which can be proved by means of calculations analogous to those carried out for the exponent n. This is also illustrated in fig. 1. As a result, n - u is actually negative to a greater extent than would appear from Denison and Romanoff's original values (see table 3). The obtained results thus indicate that the pitting factor decreases with time. In any case, there is no evidence for the reverse.

5. CONCLUSIONS

The results from the corrosion tests on copper in various types of soil in the USA can be expressed by an exponential function: $P = kt^n$. There is a clear tendency towards lower values of n as the fit is improved. The low values of n which have been obtained indicate that the growth rate of the pits in depth declines sharply with time. But the spread of the obtained measurement values is too great to permit extrapolation over very long periods of time.

The soil corrosion tests on copper also show that the pitting factor in the introductory phase of the exposure does not exceed 25 and apparently decreases with time, so that a pitting factor of 25 must be regarded as conservative.

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(1978-03-17)

Table 1. Data for soils used in tests by Denison-Romanoff (2)

Soil No.	Soil Type	Location	Aeration [a]	Moisture equivalent	Apparent specific gravity	Resistivity at 60° F (15.6° C)	pH	Total acidity[b] (milligram equivalents per 100 g of soil)	Sulfide content [c]	Composition of water extract-milligram equivalents per 100 g of soil: Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
				Percent		*Ohm-cm*										
51	Acadia clay	Spindletop, Tex	P	47.1	2.07	190	6.2	13.2	+	10.27	15.55	5.03	0.00	0.56	5.75	22.00
53	Cecil clay loam	Atlanta, Ga	G	33.7	1.60	17,800	4.8	5.1	–	------	------	------	------	------	------	------
55	Hagerstown loam	Loch Raven, Md	G	32.0	1.49	5,210	5.8	10.9	–	------	------	------	------	------	------	------
56	Lake Charles clay	El Vista, Tex	VP	28.7	2.03	406	7.1	5.1	+	3.12	0.69	0.47	.00	.80	1.59	3.04
58	Muck	New Orleans, La	P	57.8	1.43	712	4.8	15.0	++	2.03	2.23	1.29	.00	.00	0.47	2.54
59	Carlisle muck	Kalamazoo, Mich	VP	43.6	------	1,660	5.6	12.6	+++	1.03	3.08	2.70	.00	.00	3.47	1.04
60	Rifle peat	Plymouth, Ohio	P	43.4	1.28	218	2.6	297.4	+++	2.91	10.95	2.86	.00	.00	0.00	56.70
61	Sharkey clay	New Orleans, La	P	30.8	1.78	943	6.8	4.9	+	0.73	0.68	0.33	.00	.71	.10	0.91
62	Susquehanna clay	Meridian, Miss	F	34.6	1.79	6,920	4.5	12.0	–	------	------	------	------	------	------	------
63	Tidal marsh	Charleston, S. C	VP	46.7	1.47	84	6.9	14.6	+++	33.60	6.85	4.00	.00	.00	12.70	36.60
64	Docas clay	Cholame, Calif	P	41.1	1.88	62	7.5	A	–	28.10	2.29	0.76	.00	.69	28.80	0.26
65	Chino silt loam	Wilmington, Calif	G	26.4	1.41	148	8.0	A	–	7.65	12.40	2.20	.00	1.30	6.05	16.90
66	Mohave fine gravelly loam.	Phoenix, Ariz	F	16.5	1.79	232	8.0	A	–	6.65	0.51	0.16	.00	0.73	2.77	2.97
67	Cinders	Milwaukee, Wis	VP	------	------	455	7.6	A	++	0.77	3.03	.53	.00	.55	0.08	2.69
70	Merced silt loam	Buttonwillow Calif.	F	24.7	1.69	278	9.4	A	–	8.38	0.38	.22	.02	1.87	1.12	5.57

[a] Aeration of soils: G, good; F, fair; P, poor; VP, very poor.

[b] A indicates absence of acidity because of alkaline reaction.

[c] –, Sulfides absent; +, sulfides present in low concentration; ++, sulfides present in moderate concentration; +++, sulfides present in high concentrati

Table 2. Copper corrosion as a function of time according to Denison and Romanoff (2)

Soil No.	Soil Type	Aeration	Penetration, Average: P_T=14 yr	$\overline{{}^aP_T=14\text{ yr}}$	k'	$\overline{{}^ak'}$	u	$\overline{{}^au}$	Penetration, Maximum: P_T=14 yr	$\overline{{}^aP_T=14\text{ yr}}$	k	$\overline{{}^ak}$	n	$\overline{{}^an}$	Pitting factor [b]: Copper	Pitting factor [b]: Plain iron and steel
			Mils	*Mils*	*Mils*	*Mils*			*Mils*	*Mils*	*Mils*	*Mils*				
65	Chino silt loam	Good	1.0	0.4	1.59	1.35	–0.18	0.40	16.0	4.3	3.51	1.8	0.57	0.26	16.0	5.3
51	Acadia clay	Poor	0.8	.3	0.63	0.45	.10	.36	4.7	0.7	1.73	0.46	.38	.14	5.9	------
55	Hagerstown loam	Good	.3	.02	.17	.02	.26	.04	7.2	.8	4.74	.96	.16	.10	24.0	15.8
59	Carlisle muck	Very poor	.3	.05	.11	.07	.36	.28	5.0	.5	2.35	.97	.26	.17	16.7	5.7
53	Cecil clay loam	Good	.5	.03	.15	.02	.45	.06	7.8	.9	2.69	.60	.40	.11	15.6	11.8
66	Mohave fine gravelly loam.	Fair	.9	.2	.26	.12	.45	.22	10.1	.9	7.43	1.6	.12	.11	11.2	4.5
67	Cinders	Very poor	15.1	8.6	4.40	5.4	.47	.52	64.7	21	31.7	21.0	.27	.32	4.3	------
62	Susquehanna clay	Fair	0.8	0.03	0.19	0.02	.54	.04	9.6	2.8	4.04	1.00	.33	.12	12.0	7.8
64	Docas clay	do	4.7	.9	.84	.29	.67	.17	15.1	7.1	7.04	2.0	.29	.14	3.2	1.6
61	Sharkey clay	Poor	1.0	.2	.14	.04	.69	.07	15.4	3.1	3.60	1.08	.55	.15	15.4	6.4
60	Rifle peat	do	8.6	5.8	.88	1.30	.86	.60	31.2	14.6	3.00	2.86	.89	.43	3.6	2.0
63	Tidal marsh	Very poor	9.9	.03	.95	0.05	.88	.03	11.2	2.6	1.83	0.88	.68	.23	1.1	6.8
56	Lake Charles clay	Poor	1.2	.2	.10	.03	.96	.16	4.9	1.0	1.68	.72	.37	.19	4.1	4.1
58	Muck	do	4.9	1.6	.09	.06	1.52	.31	19.0	3.0	1.28	.40	1.02	.16	3.9	6.0

[a] $P=k(k')T^{n}(^{n'})$, where P=average or maximum penetration at the time, T.

[b] Pitting factor $=\dfrac{\text{maximum penetration}}{\text{average penetration}}$.

Table 3. Extract from Denison and Romanoff's table over copper corrosion in soil (2).

Soil No.	Aeration xx)	pH	Total acidity mequiv. per 100g of soil	Average penetration x) um	Maximum penetration x) um	For average penetration		For max. penetration		P_f	(n - u)
						k'	u	k	n		
65	G	8.0	Alk	25±10	406±109	40.3	-0.18±0.40	89.1	0.57±0.26	16.0	0.75
51	P	6.2	13.2	20±8	119± 18	16.0	0.10±0.36	43.9	0.38±0.14	5.9	0.28
55	G	5.8	10.9	8±0.5	183± 20	2.5	0.96±0.16	120.4	0.16±0.10	24.0	-0.10
53	G	4.8	5.1	15±0.8	198± 23	3.8	0.45±0.06	68.3	0.40±0.11	15.6	-0.05
66	F	8.0	Alk	23±5	257± 23	6.6	0.45±0.22	188.7	0.12±0.11	11.2	-0.33
62	F	4.5	12.0	20±0.8	244± 71	4.8	0.54±0.04	102.6	0.33±0.12	12.0	-0.21
64	P	7.5	Alk	120±23	384±180	21.3	0.67±0.17	178.8	0.29±0.14	3.2	-0.38
61	P	6.8	4.9	25±5	391± 80	3.6	0.69±0.07	91.4	0.55±0.15	15.4	-0.14
56	VP	7.1	5.4	30±5	125± 25	4.3	0.96±0.04	47.8	0.37±0.19	4.1	-0.59

x) Calculated for 14 years of exposure

xx) G = good
F = fair
P = poor
VP = very poor

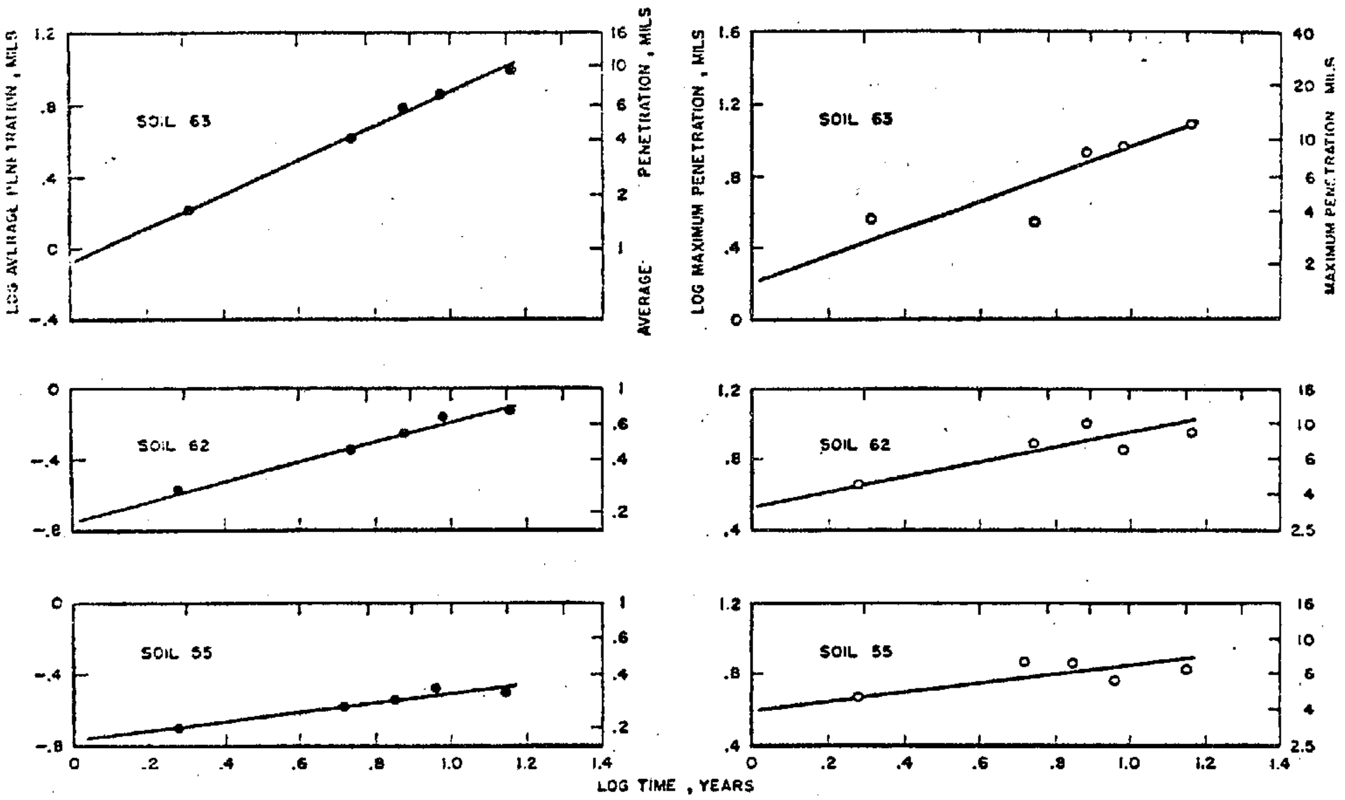

Fig. 1. Average penetration and maximum penetration for copper in various soils with logarithmic coordinates (2).
● Average penetration   o Maximum penetration

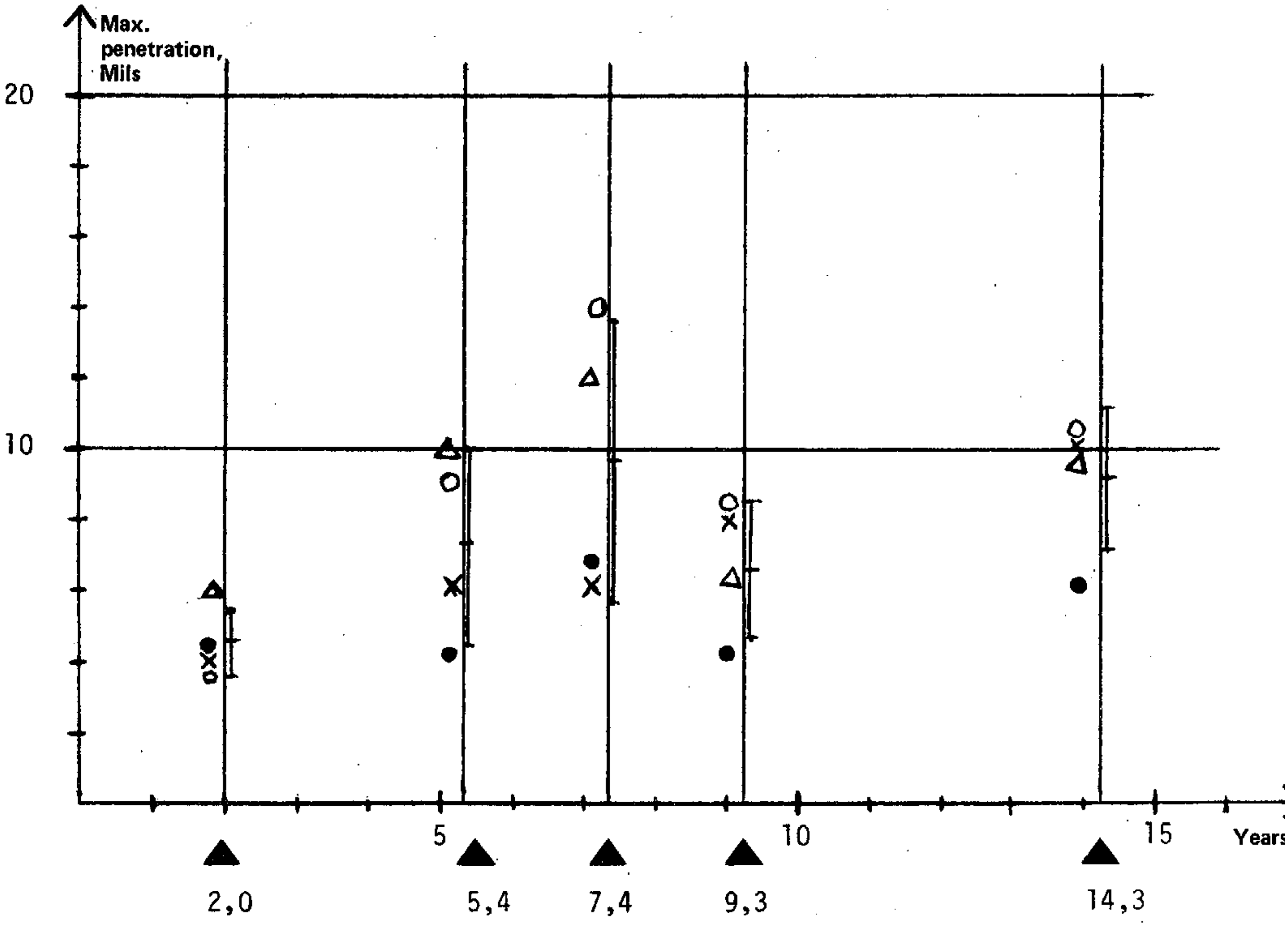

Fig. 2. Measured maximum penetration in four different copper grades in soil No. 62 according to (2).

Table 4 Calculated value of exponent n in different soils

Soil No.	Ref (2)	With 5 measurement values in Equation /1/		With 4 measurement values in Equation /1/	With 5 measurement values in Equation /2/, $t_0 = 1$ year	
	n	n	Correl. coeff.	n	n	Correl. coeff.
65	0,57	0,52	0,76	- 0,12	0,42	0,81
55	0,16	0,13	0,65	- 0,13	0,11	0,71
53	0,40	0,37	0,82	- 0,02	0,29	0,86
62	0,33	0,33	0,82	0,13	0,26	0,84
61	0,55	0,56	0,86	0,25	0,00	0,86
56	0,57	0,52	0,76	- 0,12	0,42	0,81

Table 5 Parameter estimates obtained using average values for copper grades, both with and without weighting and both with and without an incubation period t_o.

Soil No.	Adjustment by average values					
	unweighted			weighted		
	k	n	t_0	k	n	t_0
65	6,3	0,31	-	3,9	0,46	-
	10,0	0,12	2,0	9,9	0,11	2,0
53	3,5	0,28	-	3,5	0,33	-
	5,2	0,13	2,0	5,2	0,12	2,0
66	8,0	0,07	-	8,3	0,03	-
	8,5	0,05	2,2	8,5	0,04	2,3
62	6,1	0,33	-	3,6	0,33	-
	6,3	0,14	2,1	5,1	0,20	1,5
61	3,8	0,54	-	3,1	0,55	- x)
	4,2	0,51	0,2			

x) difficulty with convergence, t_o negative.

(1978-03-17)

Report concerning analysis of corrosion data for copper in various soils

Svante Wold, Chemometrics Group, University of Umeå,
March 22, 1978.

Data from the literature (Denison & Romanoff NBS RP2077, Vol 44, March 1950) concerning experiments in which copper specimens have been allowed to corrode over a longer period of time (approx. 20 years) in different soils in the USA have been analyzed by means of SIMCA analogy analysis.

Each soil was characterized by Denison and Romanoff with the aid of some 15 variables, such as resistivity, pH, presence of Na, Ca, Cl etc. In an initial analysis, the differences in these variables between two classes of soils were studied; soils where rapid corrosion of copper was noted and soils where slow corrosion was noted. No differences were found between these two classes, with respect to either individual variables or combinations of variables.

The soils were then classified on a geological basis by a geologist at the Swedish National Defence Research Institute. An analogy analysis was then carried out on each of the three geological soil classes in order to see whether the characteristic variables (the same 15) exhibited any systematic variation within each class. The results were negative here as well.

Since no characteristic pattern was obtained for the 15 variables within any soil class, it would be fruitless to attempt to relate the soil variables further to the observed corrosion rate of the copper.

The conclusion of the data analysis is that the studied soils comprise a much too disparate group to permit conclusions to be drawn regarding any correlation between soil characteristics and copper corrosion. If similar studies are done in the future, an attempt should be made to choose as homogeneous a group of soils as possible. Thus, a group consisting of at least 10 soils of very similar character should be selected and a number, say 3, of copper specimens should be allowed to corrode in these soils. Each soil should be characterized as accurately as possible, i.e. using a large number of variables, and these variables should be remeasured now and then, for example on the same occasions when the corrosion of the copper is measured.

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SWEDISH NATIONAL DEFENCE RESEARCH INSTITUTE
Section 213
Eva Elvers, Lars Björklund 1978-03-10

ESTIMATE OF COPPER CORROSION IN SOIL ON THE BASIS OF AN AMERICAN STUDY

Purpose

To estimate, using statistical methods, the corrosion of copper in soil over a long period of time on the basis of an experimental study conducted in the United States. The study involved a number of copper grades in different soils for a period of nearly 15 years (Denison & Romanoff, 1950).

A common prediction procedure

A common procedure in such a situation is to postulate a function $f(t;p)$ to describe the time dependence of the process (here corrosion). The letter t stands for time, and p stands for one or more parameters. These parameters may be dependent on, for example, the composition of the soil, and they may be time-dependent.

The parameters p are estimated on the basis of observed values. This can be done in different ways, for example by means of the least squares method. If the test results are associated with different uncertainties, weighted values may be used, whereby the weights should be inversely proportional to the individual variances. In this way, estimated parameter values p^* are obtained.

The corrosion at a given point in time T can be estimated by $f(T;p^*)$. This estimate is associated with some uncertainty. In the original observations, there were both measurement errors and random variations between individual specimens. These are propagated via p^* to the prediction $f(T;p^*)$. Moreover, the function which is chosen is, of course, just an approximative description.

Experimental data

The test results which are used here apply to pitting. Measurements are available for four copper grades (A, C, D, N) and for seven soils (65, 66, 61, 53, 55, 62, 56). The tests were conducted at five different points in time (after 2.0, 5.4, 7.4, 9.3 and 14.3 years - with the exception of soil 61, where 2.0 is replaced by 1.0). In general, an average value from 2 individual specimens is available. If the value for pitting is less than 6, it is not specified further.

If the four copper grades are ranked for each point in time and each soil, it is found that D has a tendency to be high, while A and C are low, although differences between these ranks are not great. If instead the averages of the results for the four copper grades are ranked with respect to soils, the same results, with only a few exceptions, are found for all points in time. Starting from the bottom, the ranking is 56, 53, 55, 62, 61, 66, 65. Thus, it may be advisable to deal with the soils separately, while it should be possible to use a common function for the copper grades.

It is noteworthy that the observations for all soils are lower at the fourth point in time than at the third. This indicates that the measurement procedure was not the same at all points in time, differing on at least one occasion.

How should the parameters be estimated? Small values are difficult to measure, while individual variations can be expected to increase with time. The logarithms of the values have previously been used (in order to get linear functions - see below). When this is done, early observations get relatively great importance.

Postulated functions

In their study Denison and Romanoff use a function of the type $f(t;p) = kt^n$ to describe the dependence of corrosion on time (both for general corrosion and for pitting, which is studied here). There are thus two parameters, k and n, which are generally dependent upon soil type and copper grade.

This function is not fully accurate, since a certain period of incubation can be expected before corrosion begins. Instead, it is possible to postulate, for example:

$$f(t;p) = \begin{cases} k(t-t_o)^n & \text{if } t > t_o \\ 0 & \text{if } t \leq t_o \end{cases}$$

We then have a function with three parameters to estimate, which is many in relation to the amount of data.

The last named function has the disadvantage of being equal to 0 all the way up to t_o. Another possibility is to refrain from postulating a function for low t values. For example, the results of the measurements at the first point in time (when there are, moreover, many unmeasurable values) can be excluded, and one of the two functions given above can be used from the time 5.4 years and on.

Some attempts at estimation

The measured pitting values have been used in a number of different ways to fit the above-specified functions. This has been done on a computer (DEC 10) with the aid of a program (MLAB) for least squares estimates. The test results have been used in the form of logarithms of basic values, logarithms of average values, basic values, average values, and average values with weights in relation to the variations for the four copper grades. The largest number of trials was carried out for soils 65 and 53, which had high n values when previous estimation trials were made. Some of the results are presented below.

When an incubation period t_o was included in the function f, the estimate was only occasionally less than 2 years, which is the time of the first measurement. There are two such cases in the table.

When the values from the 2-year measurement were excluded, the function f was tried both with and without an incubation period t_o. The results were significantly different in several cases. For soil 62 with weighted average values, for example, $n^* = 0.2$ when t_o was assumed to be 0, while $n^* = 0.7$ when t_o was included. The incubation period t_o was in this case negative, -18 years.

Parameter estimates should be the same when unweighted average values are used and when basic values are used. But in the case of soil 65, it was found that the standard deviations in the estimated values produced by MLAB differ widely (for example 0.2 instead of 0.4 and 0.6 instead of 0.1 for the parameters n and t_o, respectively). This means that the basic values are distributed in a manner other than that assumed by the estimation model.

Discussion

It has been described above how a function f(t;p) can be postulated with parameters p, how these can be assigned values p^* with the aid of the measurement results, and how $f(t;p^*)$ can be used for predictions. The results when this method was used for pitting were, however, discouraging.

The main problem is the choice of the function f. There are five measurement occasions with values that are fairly low on the first occasion and fairly even on all the other occasions.

However, the values on the next-to-last occasion are all low. The measured values can therefore not be used to verify a function postulated on theoretical grounds.

Individual variations should also be taken into consideration in making a prediction. Such variations can be expected to increase with time, but it is difficult to estimate the extent of this increase on the basis of the limited test results.

Conclusion

On the basis of existing measurement results for pitting and postulated functions, it would seem to be impossible to draw statistical conclusions concerning the corrosion of copper in soil over a long period of time.

Soil	Estimation using average values					
	unweighted			weighted		
	k	n	t_o	k	n	t_o
65	6.3	0.31	-	3.9	0.46	-
	10.	0.12	2.0	9.9	0.11	2.0
66	8.0	0.07	-	8.3	0.03	-
	8.5	0.05	2.2	8.5	0.04	2.3
61	3.8	0.54	-	3.1	0.55	-
	4.2	0.51	0.2			x)
53	3.5	0.28	-	3.5	0.33	-
	5.2	0.13	2.0	5.2	0.12	2.0
62	6.1	0.33	-	3.6	0.33	-
	6.3	0.14	2.1	5.1	0.20	1.5

x) difficulty with convergence, t_o negative.

Table Parameter estimates obtained using average values for copper grades, both with and without weighting and both with and without an incubation period t_o in the function f.

Special statement

by

Professor Gösta Wranglén
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concerning

"Copper as canister material for unreprocessed nuclear waste - evaluation with respect to corrosion"
(report from Swedish Corrosion Institute's reference group for canister material for nuclear waste)

Summary

1. According to a guiding principle in the international debate concerning waste from nuclear reactors, the long-term toxicity of the waste, after the fission products have decayed, should not be allowed to exceed the toxicity of the uranium ore from which the waste originally stems. In consideration of this principle, French and American researchers have found it to be "indispensable" to further separate plutonium from conventional high-level waste from reprocessing, from which 99.5% of the plutonium in the spent fuel has already been separated, so that only 0.01-0.05% of the original amount of plutonium remains.

2. The direct disposal of spent fuel would entail that all of the plutonium would be allowed to remain in the waste. As a result, it will be 10 million years before the hazard index for the spent fuel decreases to a value which corresponds to 30% uranium ore and which is therefore 1000 times higher than that of the Swedish Ranstad ore with 0.03% uranium.

3. The direct disposal of spent nuclear fuel would also entail the risk of criticality accidents, owing to the large quantities of plutonium which are stored. Following a canister failure, uranium can be dissolved by carbon-bearing groundwater and the plutonium thereby enriched so that an

uncontrolled nuclear reaction occurs, rapidly leading to additional canister failures and the escape of large quantities of radioactive material from the waste repository. The risk of criticality persists for some 100 000 years.

4. The conditions which prevail in a final repository - e.g. the fissure and water content of the rock and the composition, flow rate and flow direction of the groundwater - at the time of canister deposition cannot be expected to persist unchanged for all future time, particularly not during the next ice age, which geologists fear may occur as soon as within the next 1 000 - 10 000 years.

5. Under conditions which have been found to be likely by hydrogeological experts in the event of a future glaciation, a copper canister in contact with sulphur-bearing water for several thousand years could be converted to copper sulphide, which is the thermodynamically stable form in which copper generally occurs in the bedrock.

6. Copper cylinders for the encapsulation of spent unreprocessed nuclear fuel can therefore not be guaranteed to have a service life lasting hundreds of thousands of years or more. Under no circumstances can such a long service life be considered to be absolutely certain. Predictions which extend beyond the next ice age should in general be regarded as being completely meaningless.

7. The direct disposal of spent nuclear fuel would be a morally irresponsible act towards future generations and towards future life on earth in general.

8. It should be up to us, the generations now living, to destroy our own long-lived radioactive wastes, such as plutonium and other transuranium elements. This would appear to be possible by means of the reprocessing of spent

fuel with the separation of transuranium elements and their use as new fuel in breeder reactors. The storage problem is thereby limited to the storage of fission products for a relatively short period of time, 500-1000 years, which should be possible even from the point of of view corrosion.

1. Requirements on the service life of the canisters

a) With reference to the toxicity of the waste (hazard index)

No precise requirements concerning the service life of the canister material for the two alternatives of spent fuel and vitrified waste have been specified to serve as a guideline for the judgement of the reference group. But such requirements on service life can be derived from a principle which has long been a guiding one in the international debate concerning nuclear waste, namely that the long-term toxicity of the waste, after the fission products have decayed, should not be permitted to exceed the toxicity of the uranium ore from which the waste originally stems. The waste in question is vitrified waste with a low transuranium content, deriving from conventional reprocessing followed by the separation of transuranium elements. Swedish nuclear power specialists (1, 2), including the leader of the encapsulation group within the KBS project (2), have also backed up this principle. Such a safety requirement based on comparison with uranium ore has the advantage of being well-defined and unambiguous, something which cannot be said of the risk analysis (or safety analysis) practiced within the KBS project which was formerly used in the American space program and for nuclear reactors. A risk analysis can be of value in comparing similar systems or designs over relatively short periods of time. But making estimates of absolute risks over the long periods of time in question here is obviously a questionable approach. It has been found that the results can vary by several powers of 10, according to the assumptions which are made.

Figure 1, taken from a KBS report (3), is a comparison between the toxicity of spent fuel and that of uranium ore which shows how the hazard index for spent fuel decreases with time, whereby an index of 1 tonne of uranium in ore is chosen as the basic unit. This diagram gives the impression that the toxicity of the spent fuel has dropped to the level of the ore after only some 30 000 years. But this is grossly misleading, since the ore in the comparison is 100% uranium ore, while most uranium deposits only contain 0.2-0.3% uranium, and, for example, the Ranstad deposit in Sweden contains only 0.03% uranium. In a comparison of spent fuel with 100% ore, only the concentration of radioactivity in time by the nuclear power activities has been taken into account, not the concentration of radioactivity in space, which is the result of numerous enrichment processes in the fabrication of the fuel.

It is sometimes asserted that the toxicity of the fuel is determined solely by the total amount of radioactivity, not its concentration. It is thereby assumed that spreading the fuel out merely means that a larger number of individuals will be exposed to a radiation of weaker intensity, while the product of the number of doses times the dose strength will remain constant. It is easy to show that this line of reasoning is erroneous by means of a few examples.

Example 1: Relative toxicity of arsenic in the bedrock and in pure form.

The Swedish bedrock contains some 5 g of arsenic per m^3. Thus, down to a depth of 1 km, there are 5000 g of arsenic for every m^2 of ground surface, which if purified, would be sufficient to kill 1000 people. In the bedrock, however, the arsenic is completely harmless. Because it exists in a highly diluted and insoluble form, it is physically impossible to obtain a lethal or even a harmful dose.

Example 2. Waste (tailings) from uranium production.

The same is true of uranium and other radioactive materials. While the Ranstad ore, for example, can be considered to be harmless where it is, this is not the case with the uranium which is produced from it. An example of this is the tailings problem. Tailings are waste from uranium production whose uranium content is perhaps 100 to 1000 times higher than that of the ore and exists, moreover, in soluble and exposed form.

Example 3. Detoxifying high-level waste by dilution.

One method for detoxifying high-level waste is dilution in concrete or clay (4). Aside from the fact that the necessary quantities of material would be much too great, this proposal shows that concentration is an important factor in determining toxicity.

The importance of the concentration of the radioactivity in space is emphasized in a recently published work by French geologists (5), from which the following quote is taken: "But for the evaluation of the safety of a repository, it is important to notice that the effect of the geological disposal is to concentrate 3530 tons of natural radioactive material in about 0.26 ton of glass. Besides, an enormous dilution is necessary to meet the safety requirements. For instance, approximately 1/30 of all France's groundwater resources would be required to dilute the cumulated quantity of waste produced in the country up to the year 2000. The high density of radioactive material stored in a repository makes any comparison with natural radioactivity unacceptable until hundreds of thousands of years have passed, when radioactive decay will have reduced this density to natural levels in the ground." In this connection, criticism is levelled at the American nuclear physicist B.L. Cohen, who disregards the concentration effect and who furthermore is cynical enough to calculate the number of human lives which are saved over a period of 1 million years (!) due to the fact that the amount of uranium in the world is reduced by uranium fission in nuclear reactors (6).

Other foreign calculations of the hazard index of waste and ore have taken into account the high dilution of the uranium in the ore. One example is provided by figure 2 from Bond, Claiborne and Leuze (7). While the hazard index of the high-level waste, calculated as the volume of water of maximum permissible concentration per volume of waste, has dropped to the level of the hazard index for 100% uranium ore after some 5000 years, it has been found that the hazard index of the waste will never, not even after dilution in 10 times the amount of glass, be reduced to the level of the hazard index of 0.2% uranium ore. Since an intact and effective encapsulation cannot be guaranteed for all future time, the authors draw the conclusion that it is necessary to separate the heavy nuclides U, Np, Pu, Am and Cm from the waste. Based on the requirement that the hazard index for the undiluted waste after the fission products have decayed should not exceed the hazard index for 3% uranium ore, the following degrees of separation are necessary:

99.9% for uranium, americium and curium
95.0% for neptunium
99.95% for plutonium

A French study published one year ago (8) arrived at similar results. Based on the leaching rate for French waste glass, combined with the maximum permissible concentration (MPC) for different nuclides, an acceptable toxicity index has been calculated for waste glass: $3 \cdot 10^6$ m^3 H_2O/m^3 glass. As is evident from figure 3, it takes 10^7 years for conventional waste glass to decay to this value. From this, the conclusion is again drawn that it is necessary to separate the transuranium elements from the high-level waste so that the above-mentioned limit is reached after only 1000 years, which is a reasonable service life for an effective encapsulation. The following degrees of separation have been calculated:

99.5% for americium and curium
95.0% for neptunium
99.99% for plutonium

It is thus concluded in both of these studies that the disposal of conventional high-level waste glass is not possible, since the encapsulation materials do not have a sufficient life span. The solution is to separate long-lived nuclides, especially transuranium elements. Such a separation is termed in the French report to be "indispensable".

This French attitude is of special interest in view of the existing reprocessing agreement which Sweden has with France, under the terms of which French waste glass will be finally stored in Sweden. The fact that a country with such a positive attitude towards nuclear power as France takes such a hard line in the question of waste that they demand that 99.99% of the plutonium be removed from the waste makes the Swedish plans to allow all of the plutonium remain in the waste seem particularly heroic.

Up until a couple of years ago, even Swedish nuclear power specialists considered the direct disposal of spent fuel to be "entirely unacceptable", not only from the energy point of view but also in view of safety requirements (ref. 1, page 93). If it is nevertheless decided that it is desirable to try to dispose of spent fuel directly without first separating plutonium and other transuranium elements, then in order to meet the aforementioned requirements, it is necessary to make sure that the spent fuel is kept effectively encapsulated until its toxicity has declined to that of the original uranium ore. A glance at fig. 1 shows that this can never be possible. While the ore can be assumed to have contained 0.3% uranium (in the case of the Ranstad ore, 0.03%), the hazard index for the spent fuel after 10 million years has only decreased to a value corresponding to 30% uranium ore. Even after 10 million years, the toxicity index of the spent fuel is still 100 - 1000 times greater than that of the ore from which it was produced.

b) With reference to the risk of criticality

With the direct disposal of spent fuel, one doesn't have the extra safety barrier in the form of low solubility which can be obtained with vitrified waste. The following quote from the report of the Aka Committee (the Swedish Government Committee on Radioactive Waste), part II (10), pages 115-116 illustrates this:

"Naturally occurring uranium is effectively dissolved by oxidation by carbonate-containing groundwater, forming uranyl-carbonate complex. - Uranium concentrations of up to 1800 μg per tonne have been measured in the groundwater in bedrock with a high water content from the Masugnsby district in Norrbotten, where a single spring (7.2 m^3 water per hour) is estimated to precipitate more than 6 kg uranium per year."

Strongly oxidizing conditions resulting from radiolysis are automatically obtained in the event of a canister failure. Groundwater normally contains high levels of carbonate. Thus, Forsmark water from a depth of 450 m has been found to contain 400 ppm HCO_3^-, which is about 10 times higher than the level in surface water. In addition, the basically reacting clay (bentonite) in which the canister is proposed to be embedded contains some 2% organic matter, which will be radiolytically oxidized to carbonate. Carbonate solutions are, incidentally, used to leach uranium out of uranium ores. It even seems that the richest uranium ores in nature were formed by precipitation from carbonate solutions, which had taken up uranium on their passage through uranium-bearing bedrock. If the uranium, which makes up most (95%) of the spent fuel, is leached out, plutonium and other transuranium elements (combined about 1%) will remain in the form of a poorly soluble sludge. Under such circumstances, there is a definite risk that plutonium could accumulate in sufficient quantity to trigger a nuclear reaction. Only 0.5 kg of fissionable plutonium is required for this purpose (11). A suitable moderator, water, is always available. The risk of such criticality accidents in connection with the direct disposal of spent nuclear fuel is pointed out by the Aka Committee Report (9): "However, terminal storage of spent fuel places greater demands due to factors such as risk of criticality in the presence of plutonium." The Aka Committee Report pointed out the risk of criticality accidents during storage for the reprocessing alternative as well: "It would entail special problems if it became necessary in any situation to include large quantities of plutonium in the waste. In such a case, the risks of criticality in connection with storage over very long periods of time would have to be carefully examined" (ref. 10, page 99.) In the direct disposal of spent fuel, all of the plutonium is incorporated in the waste. A nuclear reaction in the middle of a waste repository would be a catastrophe with unforeseeable consequences. New canister failures could then occur in rapid sequence and large quantities of radioactive material could escape.

According to the direct disposal alternative proposed by the KBS project, each copper canister would contain 1.42 tonnes of uranium in the form of spent fuel. This would contain 0.7% or some 10 kg of plutonium-239. The time required for this to decay to 0.5 kg is some 100 000 years. Such a long period of time would certainly embrace one or more ice ages and would thereby entail unforeseeable conditions in the waste repository.

2. Thermodynamic aspects of the stability of copper in the bedrock

Copper would appear to be a promising canister material. It is, after all, a ductile material which does not crack and which is among the more noble (electrode-positive) of the metals. In actuality, copper is the noblest of the common constructional metals. The Aka Committee based its assessment on the assumption that copper is thermodynamically stable in the oxygen-free groundwater which can be expected to exist at great depths. This claim has also sometimes been made within the KBS project. It has thereby been noted that copper occurs in its uncombined (native) form in nature. But a closer analysis shows that copper is not thermodynamically stable in deep lying oxygen-free groundwater, if, as is often the case, the water contains sulphide ions.

If we first consider the geological argument, we can note that of the world's presently known copper deposits, 90% are composed of sulphides, 9% of oxides and less than 1% of pure, uncombined copper (mainly around Lake Superior in the United States). It would thus appear that metallic copper is thermodynamically stable in the bedrock only under special conditions. The copper ore at Lake Superior is, incidentally, largely impure on the surface. It is also noteworthy that a large number of metals occur in the uncombined form in nature under special and favourable circumstances (such as well-isolated inclusions in other minerals and rocks), many of which are less noble than copper. Among the latter, the Encyclopedia of Minerals (12) counts antimony, arsenic, lead and iron (both terrestrial and meteoric), nickel, tin and bismuth and even zinc. It must be assumed that many original deposits of uncombined metals have been destroyed and that only those which exist in a particularly favourable environment have survived. It would not seem to be possible that such a favourable environment could be guaranteed by technical means over a period of time which encompasses one or more ice ages.

It is generally known that the interior of the earth is high in sulphur content. Volcanoes (like hell!) have always been associated with sulphur and sulphur fumes. It has also been found that deep-lying groundwater often contains hydrogen sulphide (and is thereby also oxygen-free). Many health spas with hydrogen-sulphide-bearing water provide examples of this. It is probable that the hydrogen sulphide is sometimes formed when sulphide minerals in the upper, oxygen-rich and oxidizing soil strata decompose, forming sulphate, after which the sulphate is reduced to sulphide on its way down. The following reaction sequence is possible:

$$3Fe(OH)_2(aq) = Fe_3O_4 + H_2 + 2H_2O \; ; \quad \Delta G^o = -8.8 \text{ kcal} \qquad (1)$$

$$SO_4^{2-} + 4H_2 = S^{2-} + 4H_2O \; ; \quad \Delta G^o = -27.4 \text{ kcal} \qquad (2)$$

With regard to the first reaction, known as Schikorr's reaction[1], it is known that this reaction is catalyzed by copper, while the second reaction tends to take place bacterially.

Hydrogen-sulphide-bearing water can now react directly with copper as follows:

$$2Cu + H_2S\ (aq) = Cu_2S + H_2,$$

$$\Delta G^o_{react.} = -14.1 \text{ kcal} \qquad (3)$$

$$\Delta G^o_{mole} = -14.1 \text{ kcal/mole } Cu_2S$$

Rough calculations show that ΔG^o is negative, even at the H_2S concentrations and hydrogen gas pressures in question.

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1) Schikorr's reaction is the cause of the hydrogen gas formation which occurs in heat distribution systems and which necessitates the "bleeding" of radiators, whereby black magnetite particles and a characteristic hydrocarbon odour are observed. In the case of vitrified waste, Schikorr's reaction could lead to the destruction of the titanium canister due to hydrogen embrittlement.

According to equation (3), hydrogen ions are oxidizing. There are also a number of reactions with other oxidants (sulphate ions, iron oxides etc.) which lead to the formation of Cu_2S. Some such reactions are given as examples by Professor Grenthe (please see appendix B3):

$$8Cu + 3H_2S + SO_4^{2-} + 2H^+ = 4Cu_2S + 4H_2O \qquad (4)$$

$$\Delta G^o_{react.} = -112.4 \text{ kcal}$$

$$\Delta G^o_{mole} = -28.1 \text{ kcal/mole } Cu_2S$$

$$2Cu + SO_4^{2-} + 3Fe_2SiO_4 + 2H^+ = Cu_2S + 3Fe_2O_3 + 3SiO_2 + 2H_2O \qquad (5)$$

$$\Delta G^o_{react.} = -55.0 \text{ kcal}$$

$$\Delta G^o_{mole} = -55.0 \text{ kcal/mole } Cu_2S$$

$$4Cu + 2SO_4^{2-} = 9Fe_2SiO_4 + 4H^+ = 2Cu_2S + 9Fe_2O_3 + H_2O \qquad (6)$$

$$\Delta G^o_{react.} = -127.0 \text{ kcal}$$

$$\Delta G^o_{mole} = -63.5 \text{ kcal/mole } Cu_2S$$

$$2Cu + SO_4^{2-} + 6Fe_3O_4 + 2H^+ = Cu_2S + 9Fe_2O_3 + H_2O \qquad (7)$$

$$\Delta G^o_{react.} = -40.8 \text{ kcal}$$

$$\Delta G^o_{mole} = -40.8 \text{ kcal/mole } Cu_2S$$

$$4Cu + 4Fe_2O_3 + FeS_2 = 2Cu_2S + 3Fe_3O_4 \qquad (8)$$

$$\Delta G^o_{react.} = -19.8 \text{ kcal}$$

$$\Delta G^o_{mole} = -9.9 \text{ kcal/mole } Cu_2S$$

These reactions probably proceed electrochemically. Of special interest in this context is the fact that reactions which include sulphides normally take place at a rapid rate, since hydrogen sulphide and sulphide ions are very active catalysts for electrochemical processes, both anodic and cathodic. Metal sulphides possess high electrical conductivity, are highly electrode-positive and exhibit low overvoltages for electrochemical processes. The overvoltage of hydrogen on metal sulphides is often as low as on platinum. These circumstances explain the highly deleterious effects which sulphide slags and sulphur impurities have on the corrosion properties of metallic materials.

Figure 4 shows a number of electrode reactions which shed light on the stability of copper in groundwater containing sulphate and/or sulphide.

Besides the relevant electrode reactions for copper, the diagram includes the equilibrium between sulphide and sulphate ions and an equilibrium between oxides of bivalent and trivalent iron which generally seems to determine the redox potential in the soil. In oxygen-free soils, sulphide ions and thereby Cu_2S, are stabilized. Under less strongly reducing conditions, where sulphur exists in the form of sulphate, metallic copper is stabilized. Metallurgically, this corresponds to the fact that metallic copper is obtained from the properly regulated oxidation of Cu_2S:

$$Cu_2S + O_2 = 2Cu + SO_2. \qquad (10)$$

Except under highly reducing conditions, copper in the presence of the system S^{2-}/SO_4^{2-} is only stable in a narrow potential range between -0.20 V and +0.06 V. Trying to stabilize the potential within this range by the addition of a redox buffer would seem to be fruitless, since the natural redox buffer Fe(II)oxide/Fe(III)oxide would dominate in the long run and stabilize the potential within the existence range for S^{2-} ions and thereby for Cu_2S.

3. Data from the literature on the stability of copper in sulphide-containing solutions

The above thermodynamic observations concerning the stability of copper in sulphide-containing solutions are confirmed by data on the corrosion of copper in such solutions taken from widely-used corrosion handbooks:

Shreir, Corrosion, I (13):

4:54: "Hydrogen sulphide accelerates corrosion of most copper-base materials."
4:48: "Pitting is most likely to occur in polluted in-shore waters, particularly when hydrogen sulphide is present. In such contaminated waters non-protective sulphide scales are formed and these tend to stimulate attack."

La Que & Copson, Corrosion Resistance of Metals and Alloys (14)

"Copper is rapidly blackened in contact with moist hydrogen sulphide and sulphide salts. Generally, sulphide coatings are not protective, but in solutions low in sulphur such as gasoline, the attack is confined to tarnishing of the copper. Advantage is taken of the tarnishing of copper to determine the sulphur content of gasolines."

F. Ritter, Korrosionstabellen metallisher Werkstoffe (15):

"Kupfer Schwefelwasser   Starker Angriff"
stoff - feucht.

4. The importance of slow-acting and unknown material destruction processes and the lack of test results.

The long time perspective involved in the terminal storage of nuclear waste creates problems which were previously unknown in technical contexts. The long periods of time which are necessary for the waste to decay lead to a high degree of uncertainty in extrapolations of test results and experiences obtained over short periods of time. The entire history of science shows that scientific exploration normally begins with practical observations for which an explanation is then sought, in the beginning (in classical antiquity) by purely speculative means, later (after the breakthrough of the scientific method) by means of systematic experimental procedures, which have gradually been facilitated by an ever-growing theoretical understanding of certain fundamental phenomena. In many cases, this has made it possible for us to learn to master the problems which gave the impetus to the research work. In the case at hand, time does not permit this natural process of development. Even within, for example, the technologically highly advanced field of space exploration, it has been possible to work with both simulations and practical trials from which conclusions could be drawn for the continued work. But it is not possible to simulate or study by means of practical trials the effects of time spans which are far beyond those of human experience. In selecting materials and designs for waste canisters, it is patently impossible to take into account processes whose nature is unknown, but whose existence cannot rightfully be excluded. Allowance must be made, for example, for the existence of heretofore unknown processes of ageing and material destruction. The possibility cannot be excluded that a canister will, after a thousand years or so, begin to be destroyed by a slowly-acting ageing process XYZ, the nature of which, due to the necessarily long periods of time required for testing, may not have been elucidated until long after.

In the absence of test results and practical experiences, even fundamentally well-known phenomena and processes can easily be overlooked. Thus, the Aka Committee (9, 10) completely overlooked the radiolysis effect, which has since proven to be of fundamental importance for the entire disposal technique and is the reason why a wall thickness of 200 mm is proposed in the copper cylinder for spent fuel.

In the case of vitrified waste, the original proposal was a titanium canister with an "inner radiation shield" of 250 mm of steel, which, in the finally proposed version, was replaced by 100 mm of lead. With such wall thicknesses, penetrating radiation and thereby radiolysis effects are reduced to negligible levels.

5. <u>The importance of the next ice age (glaciation) for the corrosion environment</u>.

Within the KBS project, it is assumed that the environment around the canisters will remain unchanged for all future time with respect to such factors as the composition and flow rate of the groundwater. However, in view of the evaluations submitted by geological experts concerning the possible consequences of the next glaciation, the postulated constancy of the corrosion environment must be questioned.

In his comment (16) on the findings of the Aka Committee, Dr. Arne Bjerhammar, Professor of Geodesy at the Royal Institute of Technology in Stockholm, has the following to say: "Viewed in a longer time prospective, it is necessary to make allowance for the fact that the Scandinavian Peninsula will once again be subjected to a glaciation, whereby the outer portions of our rock massif may suffer heavy damage. By conservative estimate, this will occur in about 10 000 years, but more recent research does not exclude the possibility that another ice age may start approaching within 1000 years. - Even if the ice cap only peels off the top 50 or so metres of the surface of the bedrock, it is still possible that the canisters will suffer considerable damage. In the worst instance, most of the radioactive waste will accumulate in a "Baltic ice lake" of very limited volume."

The Quaternary geologist Dr. Nils-Axel Mörner of the University of Stockholm is very adamant in his contention that no extrapolations or forecasts can be extended longer than to the next ice age. The following extract is taken from his report, commissioned by KBS, entitled "Movements and instability in the Swedish bedrock" (17).

Extract from "Preface" to KBS report 18 (N-A. Mörner, ref. 17)

"First we threw garbage into the forest and believed that it hid everything and that no damage was done. Later we discharged sewage and chemicals into lakes, rivers and the sea and believed that it disappeared in this 'enormous' recipient - now it costs millions every year to try to restore better limnic and marine environments. We are now faced with the decision of storing nuclear waste in the bedrock in the belief that the bedrock is 'stable'. The principle of 'out of sight, out of mind' is still followed, but with more terrible material: from garbage in the forest via sewage and chemicals in rivers, lakes and the sea, to radioactive waste in the bedrock. Of course, it is madness to put nuclear waste in containers in the bedrock, seal them off and believe that nothing will happen with the containers over the centuries and millenia to come".

"It is quite clear that it is fundamentally madness to put radioactive waste in the bedrock and hope that nothing will come of it. But since we seem to live in a world that, to a great extent, is ruled by madness, I will present an objective geological evaluation of the Swedish bedrock and its movements during the past 20 000 years, which may serve as a basis for further evaluations of the feasibility of storing nuclear waste in the bedrock."

Extract from chap. "A: Background" from KBS report 18 (N-A. Mörner, ref. 17)

"The report of the Aka Committee (the Swedish Government Committee on Radioactive Waste) provides a very poor and inaccurate picture of the Swedish bedrock, its movements and its stability as a place for storing nuclear waste. Only a few months after the Committee had published its findings, experts had to be commissioned to submit separate evaluations (one of which is this report)."

"The Aka Committee report would have us believe that the Swedish bedrock' 'has been stable for hundreds of millions of years' (SOU 1976:30, p. 55 of the English version) and cites this assumed stability as an argument in a number of places in the study. As regards the groundwater flow in the bedrock for example, it is claimed that 'the stability of the bedrock provides essentially stable conditions during the storage period' (op.cit., p. 57). It is also concluded that 'this stability will provide the necessary precondition for terminal storage in bedrock free from surveillance'(op.cit., p. 56)."

"But is the bedrock really stable? And how much instability can be tolerated? As a geologist, I must point out that there is no such thing as stable rock. And that the stability of the Swedish bedrock is a myth which must immediately be dispelled. We must instead speak of the instability of the bedrock, although the Swedish bedrock is generally much less unstable than, for example, the Circum-Pacific-Mediterranean tectonic belt."

"Future forecasts and extrapolated average values are usually given for the next 100 000 or 1 million years, both in the Aka Committee report and in the Seismic Analysis of Sweden. This is grossly misleading."

"No processes which are measurable today can be extrapolated into the future farther than to the next ice age, which has either already begun (circa 500 BC) or will be upon us within 20 000 years. Forecasts covering longer periods of time must be disregarded (they serve only to mislead persons trying to evaluate the question)."

Extract from chap. "G: Paleoclimate and future climate" from KBS report 18 (N-A. Mörner, ref. 17)

"We know that the paleoclimate fluctuated regularly between colder and warmer stages. Each stage lasted for about 10 000 - 12 000 years. The last interglacial period began about 130 000 BP and ended either about 118 000 BP or 96 000 BP. Paleoclimatologists disagree on this point."

"Everything depends on what actually happened during the period 118 000 to 107 000 BP. Was it a full glaciation or merely a somewhat colder stage? This is of decisive importance for our future forecasts, since we have obviously been in a similar climatic cycle since 500 B.C. that is to say, either we are already (for the past 2 500 years) heading towards a new glaciation period (the majority of American researchers think so) or this glaciation will not begin for another 18 000 - 20 000 years or so (I am personally of this opinion after having analyzed what is perhaps the finest climatic indicator on earth, a 19 m drill core from a lake in France). It is quite clear, however, that we, in the most favourable case, will have a glaciation within the next 20 000 years."

"All forecasts of the future must stop with this future glaciation. At this time, all effects of the deglaciation stage (faulting, fracturing, seismic activity) will be repeated and all stress factors will be multiplied many times over. During such a period storing nuclear waste canisters in bedrock is simply out of the question - this is quite clear."

Extract (in extenso) from chap. "H: Summary" from KBS report 18 (N-A. Mörner, ref. 17).

"(1) The Swedish bedrock is by no means "stable". Like all other bedrocks it is unstable.

(2) The Swedish bedrock has an old and rich tectonogeodynamic inheritance.

(3) The total uplift is about 830 m, 725 m of which is caused by the parabolic, purely glacio-isostatic factor, which died out some 2 000 - 3 000 years ago (the asthenosphere resumed its old position).

(4) The maximum instantaneous rate of uplift reached 50 - 5 cm/yr during a short period at around the time of deglaciation or the end of the Younger Dryas Stadial.

(5) The linear factor in the uplift seems to have been induced at about 8 000 BP and to have been caused by global cyclic changes of the geoid. The bend in the West Coast shoreline profile was formed by this change.

(6) Irregularities in the uplift in the form of shoreline bends and isobase irregularities have been established with the aid of ancient shorelines and geodetic data. They are as a rule all related to major fault lines and bedrock seams.

(7) Faulting, fracturing and seismic activity was shown to be linked to the deglaciation period (the maximum rate of uplift) and to be fairly frequently occurring.

(8) Major fault lines are generally related to old weak zones. Small fault lines (up to 2 m vertical displacement) and fracturing of the bedrock surface, on the other hand, are totally independent of these zones.

(9) Bouldery end moraines and bouldery ground in general record paleo-seismic activity (these areas must hence be excluded as possible sites for nuclear waste repositories in the bedrock).

(10) No extrapolation of presently measured mean values (e.g. for the seismic activity during the last decades) and no future predictions at all can be made beyond the next ice age.

(11) The next ice age is either on its way or will, under the most favourable circumstances, have begun 20 000 years from now (AP).

(12) During the next ice age, all the seismic and neotectonic effects of the deglaciation period will be repeated.

(13) During an ice age, nuclear waste cannot be stored in the bedrock.

(14) At each cyclic turning point, the linear uplift factor is likely to be linked to the same effects as those which were recorded for the period of about 80 000 BP (and maybe also those linked to the peak rates in the uplift).

(15) If one did succeed in finding a Precambrian bedrock unit within an area of smooth uplift, absence of recent earthquakes, the bedrock surface of which shows few fractures and no faultlines, and where the surroundings exhibit normal morain features and normal moraine composition, this area must still be evaluated with respect to what will happen and what may happen in connection with the next ice age and in connection with the cyclic gravitational changes in the present linear uplift."

Regarding the fissuring of the rock which can be expected to occur following a glaciation, the following is quoted from a statement by Professor Nils Hast (18):

"During the last ice age, and probably during a number of previous ones, the bedrock was under the burden of 3 000 metres of ice. This ice exerted an enormous horizontal pressure on the bedrock. When the ice melted, the rock could no longer propagate this pressure and was crushed."

Professor Hast (18) goes on to say:

"I don't think that it is possible to find fissureless rock in the Swedish bedrock. If such an area should be found, I would advise against locating a rock cavern there. The rock has not yet cracked, but the pressure in the rock is higher than normal and it will crack sooner or later".

Despite the fact that the KBS project commissioned Dr. Mörner's analysis (17), it is shocking to note that of all the objections he raises to the storage of radioactive waste in the bedrock, in view of the consequences of a future glaciation, not one line is mentioned, much less refuted, in the KBS report entitled "Handling of Spent Nuclear Fuel and Final Storage of Vitrified High-Level Reprocessing Waste" (19). Instead, concentration is centred on the peripheral question of whether recovery from the depression caused by the ice cap is still proceeding (Bjerhammar), or whether the current land uplift has other causes (Mörner). Even though no other authorities are cited concerning the effects of the next glaciation, the conclusion is nonetheless drawn that one more ice age cannot disturb a deep-lying rock repository. With respect to vitrified waste, the forecasts are projected 200 000 years ahead. Presumably, the forecasts for unreprocessed spent fuel will be extended even farther.

6. Groundwater flow around the waste canisters.[x]

In general, the calculations concerning the flow of the groundwater in and around a repository which have been carried out under the aegis of the KBS project must be characterized as being highly uncertain. Current knowledge concerning the permeability and fissure content of rock at such a great depth as 500 m is extremely limited, so that conditions even in virgin rock are difficult to assess. The situation is further complicated by the fact that the groundwater flow will be disturbed by the tunnel system and, during a transitional period, by the elevated temperature. Finally, and most important, are the unforeseeable conditions which will prevail during the next glaciation.

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x) This section has been examined without criticism by the Department of Land Improvement and Drainage at the Royal Institute of Technology (Head of Department: Professor Yngve Gustafsson).

Furthermore, in the models used for the calculations, it has been assumed that permeability has a low constant value or that it decreases rapidly with increasing depth. The influence of individual zones of permeability, which account for a large portion of the flow in the deeper parts of the bedrock, can therefore not be simulated by the models which are used. This is an obvious shortcoming, since it is known that zones of high water flow have been encountered in Swedish mines down to a depth of 900 m. There also seems to be some contradiction between different calculations. While J. Stokes (20) postulates that locally infiltrated water can penetrate down to a depth of thousands of metres, U. Lindblom et al. (21) posit a penetration of only a couple of hundred metres. Stokes (ref. 20, p. 10) further asserts that "it is not possible to draw definite conclusions concerning the flows at individual points" and that "the water transit times for adjacent points can vary over several orders of magnitude". Under such circumstances, it would seem to be impossible to make any predictions concerning the conditions which prevail in the repository during and after a new glaciation. It is therefore impossible to exclude the possibility that, despite all precautionary measures, the repository may, after a new ice age, come into contact with a heavily water-bearing "crush zone".

In this connection, I would like to quote some extracts from an American study which was presented at the special session on "Underground storage of nuclear waste" which was held in connection with "Rockstore 77", a conference held in Stockholm in September 1977, namely "Radioactive storage in argillaceous and crystalling rock masses" by P.A. Witherspoon, J.E. Gale and N.G.W. Cook of the Department of Geotechnics at the University of California at Berkeley, California, USA (22). (The main author, Professor P.A. Witherspoon, was, together with Professor Bo Lindell of the Swedish National Institute of Radiation Protection, chairman of the special session.)

"Thus we must be able to determine the rate and magnitude of the groundwater movement through a given rock mass. In addition we must be able to assess how the rock mass will respond to the thermal heads imposed by the decay of the waste material. It is possible that high thermal loads combined with the thermo-mechanical stresses may drastically alter the fluid flow characteristics of the rock mass."

"Unfortunately nearly all rock masses are fractured to depths greater than 1000 meters. These fractures (faults, shears, joints and solution channels) will represent the principal pathways by which radioactive material can reach the biosphere. The range of fractures that must be considered in radioactive waste storage include: (a) those related to the stress history of the rock, (b) those generated during mining, (c) those generated by stress relief after mining, (d) those generated by thermo-mechanical stresses due to heat generated by the waste and (e) those from future events such as glacial loads and major techtonic disturbances. It is important that we be able to define and assess the factors that control the flow of fluids through such discontinuities in rock masses".

The report does not end with any conclusions, but rather with a number of questions, which would seem to indicate that the situation is not at all as clearly understood as is sometimes implied in the KBS reports.

The uncertainty, not to mention the arbitrariness, in the flow calculations presented in the KBS project is also demonstrated by a comparison between the final results of the "Vitrified High Level Reprocessing Waste" project and a similar French investigation (5). While the Swedish study arrives at a maximum dose load after 200 000 years which is at a completely harmless level, the French study (at a depth of 500 m and a permeability of 10^{-8} m/s) finds a maximum after 20 000 years, when the concentrations of plutonium-239 and iodine 129 at ground level are several hundred times the maximum permissible concentrations (MPC). While the result for plutonium-239 can be explained by the use of different retardation factors (1100 in the Swedish study, 1 in the French), this is not the case for iodine-129, where both studies assume a retardation factor of 1. The difference, according to Dr. O. Brotzen (23), is that the French study has considered the possibility of an upflow, while the KBS project only considers the possibility of downward-flowing water in a repository. But even though the water might flow downwards at the time of the site survey or canister deposition, how do we know that the situation will be the same in a thousand years or during the next ice age?

The KBS project considers two different permeability values, namely those for

Impervious rock $k = 10^{-9}$ m/s
Crush zones $k = 10^{-5}$ m/s

The first value is remarkably low. Stokes, for example, postulates a mean value of around 10^{-7} m/s at a depth of 500 m.

An additional value will be considered in the following discussion, namely for:

Pervious rock $k = 10^{-6}$ m/s

If the hydraulic gradient (the slope of the water table) is assumed to be 0.05[x)], the following flow densities are obtained in the 3 cases:

Impervious rock $q=5\cdot 10^{-11} m^3/m^2$, $s=1.5\ l/m^2$, year
Pervious rock $q=5\cdot 10^{-8}\ m^3/m^2$, $s=1500\ l/m^2$, year
Crush zones $q=5\cdot 10^{-7}\ m^3/m^2$, $s=15000\ l/m^2$, year

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[x)] according to ref. 19 page 84.

It would not seem to be accurate to use the average permeability for impervious rock when estimating the risk of canister failure in the most unfavourably situated boreholes. In order to allow for local variations, higher values should be assumed for canisters in particularly unfavourable positions. The possibility of locally high permeabilities equivalent to those in crush zones cannot, in any case, be excluded during and after a coming ice age (without considering for the moment the possibility of any mechanical damage to the canisters). Furthermore, we must allow for a depression of the bedrock by some 1000 m (=amount of land uplift following most recent ice age). The tunnels might thereby collapse and/or serve as points of initiation for new fractures. If the permeability values are high, it is also necessary to consider the possibility that the buffer material (clay) will gradually be dispersed and carried away.

During the first 1000 years, the effects of the heat generated by the canisters on the pattern of groundwater flow in the boreholes and their immediate environment must also be taken into consideration. Even if the effects of the heating on the flow of the groundwater are generally small, for example as regards effects at the surface of the ground, this will probably not be the case with the local flow around each waste canister. This thermally generated flow could dominate locally during the first centuries (22).

7 Supply of oxidants

Oxidants are required for corrosion of the copper. At the intended depth of 500 m, the oxygen level should be negligibly low, around 10 ppb. Furthermore, with the intended thickness of the canister wall, the amount of oxygen produced by radiolysis will also be negligible. But one oxidant system which can never be discounted is the system H_2S/SO_4^{2-}.

Even if the waste repository is situated in an area where the sulphide content of the water is low, the possibility that water with a high sulphide content may enter the area at some point in the future, e.g. in connection with a glaciation, cannot be excluded.

In a report by Jan Rennerfelt, (24) of the engineering firm Orrje & Co. AB., the following groundwater analyses are presented in Appendix 3.

Sulphide and sulphate content of deep-lying groundwater

	Forsmark I 450 m 26.9.77	Forsmark II 450 m 5.10.77	Groundwater analysis, primary bedrock, probable analysis Range	 Max. value
SO_4^{2-}	10	9	20-40	100
HS^- ppm	5	5	0.2-5	10

The calculations are limited to reaction (3) on page 9, whereby H_2S can mean an equivalent quantity of FeS. According to reaction (3), 10 mg of HS^- are capable of converting 40 mg of Cu to Cu_2S. Assuming the above-specified values for pervious rock and crush zones, the following values are obtained:

Flow densities, supplied quantities of sulphur and oxidized quantities of copper for pervious rock and crush zones at 10 ppm HS^- in the groundwater. Hydraulic gradient = 0.05.

	Perme-ability k m/s	Flow density m^3/m^2, year	Supplied quantity of sul-phur g/m^2,year	Oxidized quantity of copper g/m^2,year	Oxidized quantity of copper in 1000 years kg/m^2	 in 10 000 years kg/m^2
Pervious rock	10^{-6}	1.5	15	60	60	600
Crush zones (during glacia-tion)	10^{-5}	15	150	600	600	6,000

The copper canister weighs 15 tonnes. Its outer surface area is about 12 m^2, so the copper weight per m^2 is about 1250 kg. Thus, even at a permeability of only 10^{-6} m/s, the copper canister could be corroded through after some 20 000 years, and at the highest possible permeability perhaps only a few thousand years (for example, from the start of a future glaciation). In the event of a glaciation, the possibility of an infusion of fossile saltwater of even higher sulphide content could not be excluded.

8 Conclusions

On the basis of what has been said above, the contention that copper cylinders for the encapsulation of spent unreprocessed nuclear fuel can be guaranteed to have a very long service life, hundreds of thousands of years and more, is hereby disputed. Under no circumstances can such a long canister life be considered to be an absolute certainty. In fact, any predictions which extend beyond the next ice age, which the consensus of geological opinion indicates is possible within the next 1 000-10 000 years, are completely meaningless.

In view of these considerations, the direct disposal of spent unreprocessed nuclear fuel must be regarded as a morally irresponsible action towards future generations and towards life on earth in general. We, the generations living today, should take it upon ourselves to destroy our own long-lived radioactive wastes, such as plutonium and other transuranium elements. This would appear to be possible by the reprocessing of spent nuclear fuel with the subsequent separation of transuranium elements and the use of these elements as new fuel in breeder reactors. The storage problem can thereby be limited to a storage of fission products for a relatively short, foreseeable period of time (500-1000 years) so that geological changes such as brought about by a new ice age do not have to be taken into account. It should be possible to guarantee absolutely safe encapsulation for such a short period of time, for example under supervised storage in dry rock caverns above the water table, whereby corrosion problems are virtually eliminated.

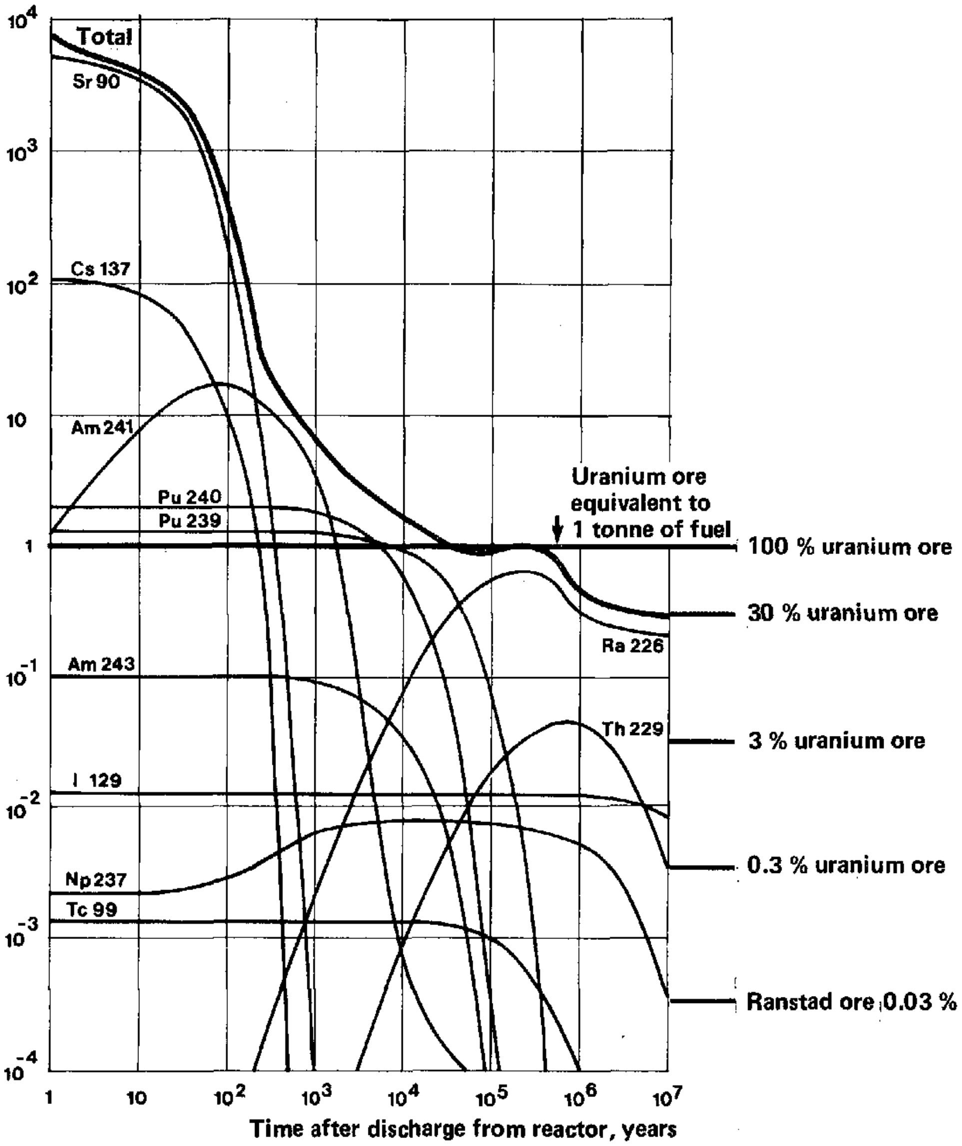

Fig. 1

Potential hazard index for different nuclides in 1 ton of spent fuel in relation to the quantity of uranium ore which is equivalent to 1 ton of fuel. Actual hazard is also dependent upon the exposure pathways of the elements to man (see chapter 6). The fuel has a burnup of 33 000 MWd(t)/tU, a power density of 34.4 MW(t)tU and an enrichment of 3.1% uranium 235.

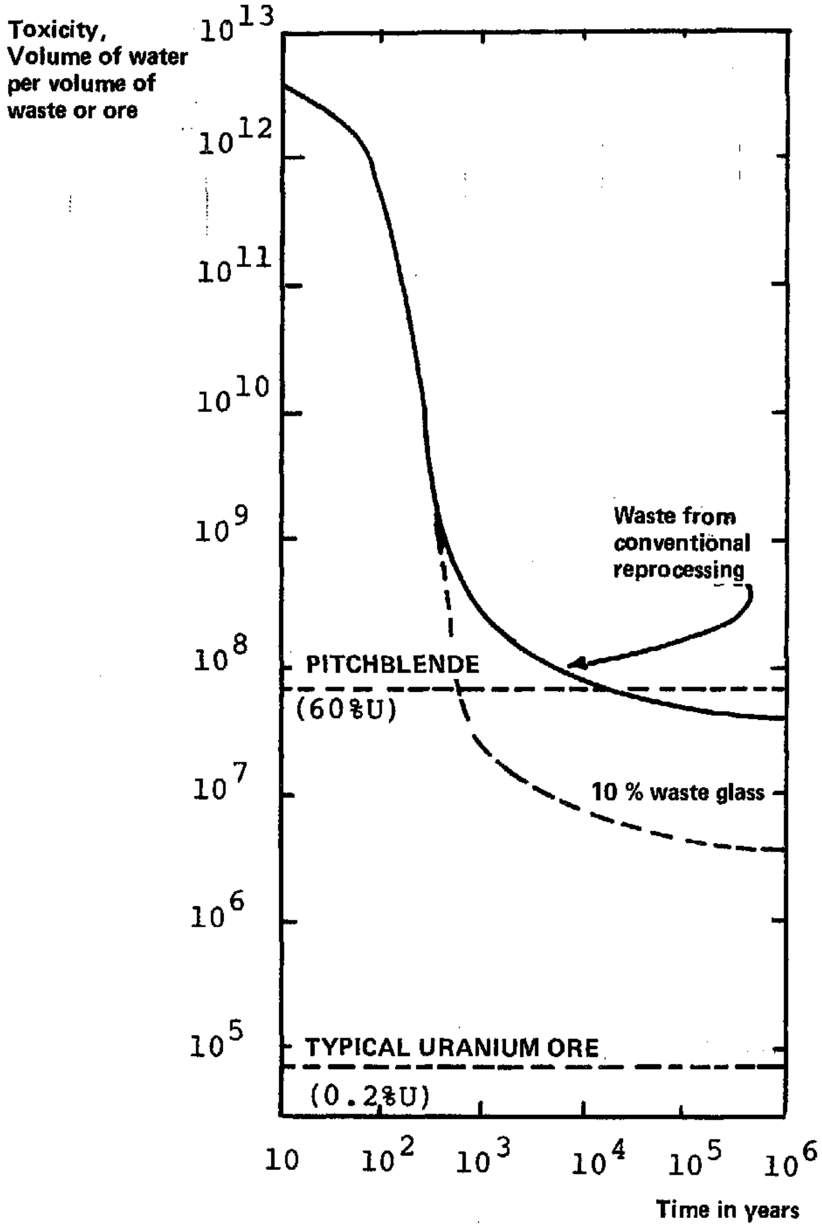

Fig. 2

Toxicity for high-level waste in comparison with uranium ore, from W.D. Bond, H.C. Claiborne and R.E. Leuze, Nuclear Technology 24 (1974) 362.

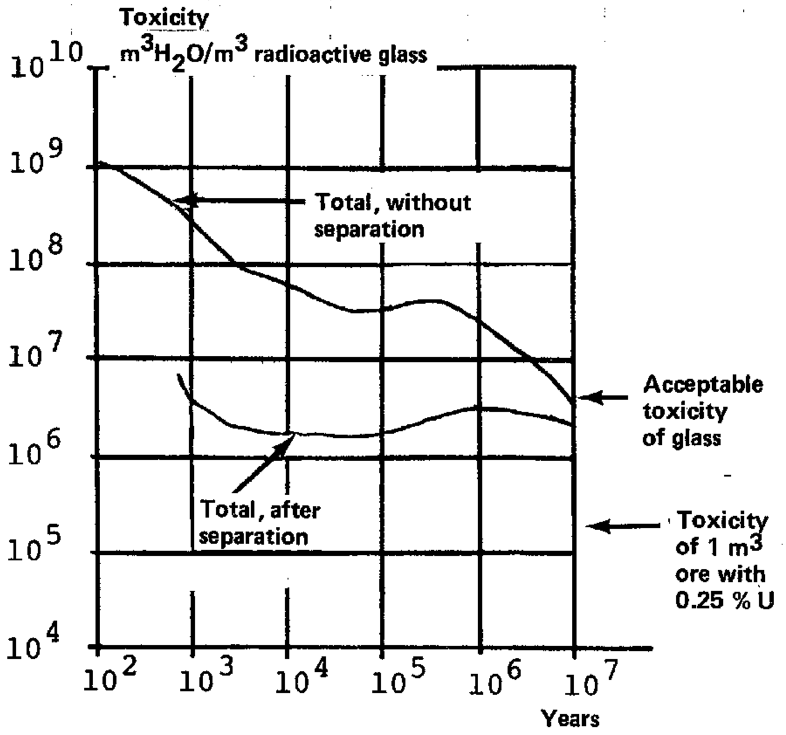

Fig. 3

Toxicity index of high-level waste glass in comparison with uranium ore, from B. Guillaume, B.I.S.T., CEA, No. 217. Sept. 1976, p. 31.

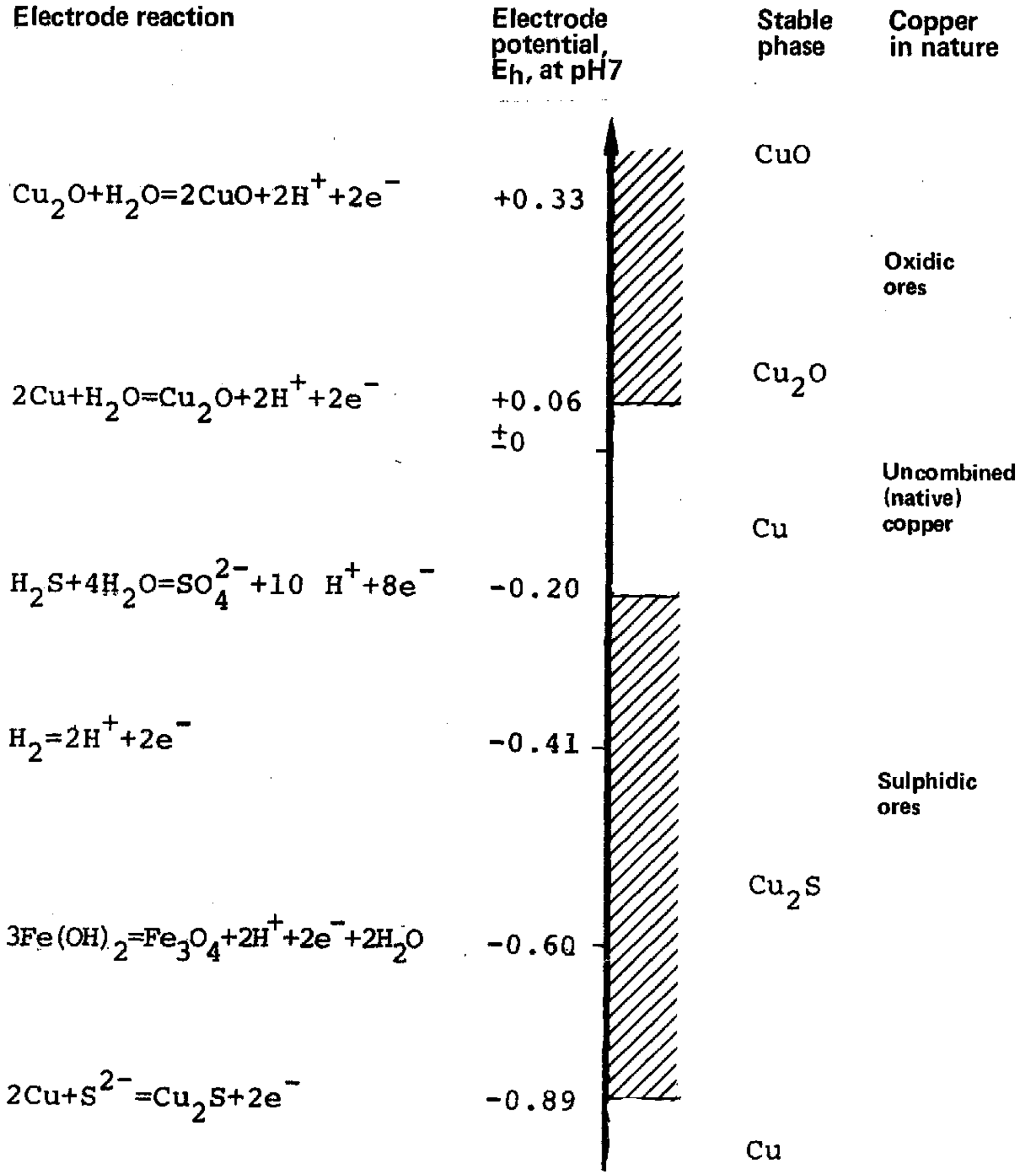

Figure 4. Potential diagram illustrating the stability of copper in sulphate-containing water at pH 7. Except at very negative potentials, metallic copper is stable in a potential range between the existence ranges for Cu_2O and Cu_2S. In sulphide-containing groundwater, copper is attacked with the formation of copper (I) sulphide, Cu_2S. Hatched areas in the diagram indicated corrosion.

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01 Källstyrkor i utbränt bränsle och högaktivt avfall
från en PWR beräknade med ORIGEN
Nils Kjellbert
AB Atomenergi 77-04-05

02 PM angående värmeledningstal hos jordmaterial
Sven Knutsson
Roland Pusch
Högskolan i Luleå 77-04-15

03 Deponering av högaktivt avfall i borrhål med buffertsubstans
Arvid Jacobsson
Roland Pusch
Högskolan i Luleå 77-05-27

04 Deponering av högaktivt avfall i tunnlar med buffertsubstans
Arvid Jacobsson
Roland Pusch
Högskolan i Luleå 77-06-01

05 Orienterande temperaturberäkningar för slutförvaring i berg
av radioaktivt avfall, Rapport 1
Roland Blomquist
AB Atomenergi 77-03-17

06 Groundwater movements around a repository, Phase 1, State of
the art and detailed study plan
Ulf Lindblom
Hagconsult AB 77-02-28

07 Resteffektstudier för KBS
Del 1 Litteraturgenomgång
Del 2 Beräkningar
Kim Ekberg
Nils Kjellbert
Göran Olsson
AB Atomenergi 77-04-19

08 Utlakning av franskt, engelskt och kanadensiskt glas med
högaktivt avfall
Göran Blomqvist
AB Atomenergi 77-05-02

09 Diffusion of soluble materials in a fluid filling a porous medium
Hans Häggblom
AB Atomenergi 77-03-24

10 Translation and development of the BNWL-Geosphere Model
Bertil Grundfelt
Kemakta Konsult AB 77-02-05

11 Utredning rörande titans lämplighet som korrosionshärdig kapsling för kärnbränsleavfall
Sture Henriksson
Kjell Pettersson
AB Atomenergi 77-08-24

12 Bedömning av egenskaper och funktion hos betong i samband med slutlig förvaring av kärnbränsleavfall i berg
Sven G Bergström
Göran Fagerlund
Lars Rombén
Cement- och Betonginstitutet 77-06-22

13 Urlakning av använt kärnbränsle (bestrålad uranoxid) vid direktdeponering
Ragnar Gelin
AB Atomenergi 77-06-08

14 Influence of cementation on the deformation properties of bentonite/quartz buffer substance
Roland Pusch
Högskolan i Luleå 77-06-20

15 Orienterande temperaturberäkningar för slutförvaring i berg av radioaktivt avfall
Rapport 2
Roland Blomquist
AB Atomenergi 77-05-17

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Stockholm augusti 1977

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Stockholms Universitet augusti 1977

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Herbert Henkel
Sveriges Geologiska Undersökning september 1977

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Rutger Wahlström
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Högskolan i Luleå 1977-08-22

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A model study
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Stockholm augusti 1977

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Kjell Pettersson
AB Atomenergi 1977-08-25

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Sven Knutsson
Högskolan i Luleå 1977-09-20

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Ove Stephansson
Högskolan i Luleå 1977-09-28

30 Retardation of escaping nuclides from a final depository
Ivars Neretnieks
Kungliga Tekniska Högskolan Stockholm 1977-09-14

31 Bedömning av korrosionsbeständigheten hos material avsedda för kapsling av kärnbränsleavfall. Lägesrapport 1977-09-27 samt kompletterande yttranden
Korrosionsinstitutet och dess referensgrupp

32 Egenskaper hos bentonitbaserat buffertmaterial
Arvid Jacobsson
Roland Pusch
Högskolan i Luleå 1978-06-10

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Roland Pusch
Högskolan i Luleå 1977-10-19

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Folke Sandelin AB
VBB
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Institutet för metallforskning
Stockholm november 1977

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Saint Gobain Techniques Nouvelles, October 1977

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Jan Rennerfelt
Orrje & Co, Stockholm 1977-11-07

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Hans Fagerström, VBB
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Stockholm oktober 1977

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Arne Finné, KBS
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Ulla Bergström
Sverker Evans
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Christina Gyllander
Siegfried F Johnson
Stig Rolandson
AB Atomenergi och ASEA-ATOM 1977-10-13

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Ann-Margret Ericsson
Kemakta Konsult AB november 1977

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Tibor Lakatos
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Roland Blomquist
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Roger Thunvik
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Graham Swan
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Hans Carlsson
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Göran Blomqvist
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H Gjöystdal
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Royal Norwegian Council for scientific and industrial research oktober 1977

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H Häggblom
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Chalmers tekniska högskola 1977-10-15

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Part 1 Conduction heat transfer
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Part 1 Permeability perturbations
Part 2 Inflow to repository
Part 3 Thermally induced flow
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Ulf Lindblom et al
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Heino Kipatsi
Jan Rydberg
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Berggrundvattenförhållanden i Finnsjöområdets nordöstra del
Carl-Erik Klockars
Ove Persson
Sveriges Geologiska Undersökning januari 1978

61 Permeabilitetsbestämningar
Anders Hult
Gunnar Gidlund
Ulf Thoregren

Geofysisk borrhålsmätning
Kurt-Åke Magnusson
Oscar Duran
Sveriges Geologiska Undersökning januari 1978

62 Analyser och åldersbestämningar av grundvatten på stora djup
Gunnar Gidlund
Sveriges Geologiska Undersökning 1978-02-14

63 Geologisk och hydrogeologisk grunddokumentation av Stripa försöksstation
Andrei Olkiewicz
Kenth Hansson
Karl-Erik Almén
Gunnar Gidlund
Sveriges Geologiska Undersökning februari 1978

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Sten G A Bergman
Stockholm november 1977

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Göran Carleson
AB Atomenergi 1978-01-27

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Fred Nilsson
Kungl Tekniska Högskolan Stockholm februari 1978

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3 st tekniska PM
Sture Henrikson
Stefan Poturaj
Maths Åsberg
Derek Lewis
AB Atomenergi januari-februari 1978

68 Degraderingsmekanismer vid bassänglagring och hantering av utbränt kraftreaktorbränsle
Gunnar Vesterlund
Torsten Olsson
ASEA-ATOM 1978-01-18

69 A three-dimensional method for calculating the hydraulic gradient in porous and cracked media
Hans Häggblom
AB Atomenergi 1978-01-26

70 Lakning av bestrålat UO_2-bränsle
Ulla-Britt Eklund
Roland Forsyth
AB Atomenergi 1978-02-24

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Roland Pusch
Högskolan i Luleå 1977-11-16

72 Värmeledningsförsök på buffertsubstans av kompakterad bentonit
Sven Knutsson
Högskolan i Luleå 1977-11-18

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Roland Pusch
Högskolan i Luleå 1978-02-25

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Roland Pusch
Högskolan i Luleå 1978-02-25

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Roland Pusch
Högskolan i Luleå 1978-03-02

76 Experimental determination of the stress/strain situation in a sheared tunnel model with canister
Roland Pusch
Högskolan i Luleå 1978-03-02

77 Nuklidvandring från ett bergförvar för utbränt bränsle
Bertil Grundfelt
Kemakta Konsult AB, Stockholm 1978-08-31

78 Bedömning av radiolys i grundvatten
Hilbert Christensen
AB Atomenergi 1978-02-17

79 Transport of oxidants and radionuclides through a clay barrier
Ivars Neretnieks
Kungl Tekniska Högskolan Stockholm 1978-02-20

80 Utdiffusion av svårlösliga nuklider ur kapsel efter kapselgenombrott
Karin Andersson
Ivars Neretnieks
Kungl Tekniska Högskolan Stockholm 1978-03-07

81 Tillverkning av kopparkapsel för slutförvaring av använt bränsle
Jan Bergström
Lennart Gillander
Kåre Hannerz
Liberth Karlsson
Bengt Lönnerberg
Gunnar Nilsson
Sven Olsson
Stefan Sehlstedt
ASEA, ASEA-ATOM juni 1978

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Bengt Lönnerberg
Alf Engelbrektson
ASEA-ATOM, VBB, KTH juni 1978

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Alf Engelbrektson
VBB Stockholm april 1978

84 Tillverkning och hantering av bentonitblock
VBB
ASEA
ASEA-ATOM
Gränges Mineralprocesser
Juni 1978

85 Beräkning av kryphastigheten hos ett blyhölje innehållande en glaskropp under inverkan av tyngdkraften
Anders Samuelsson

Förändring av krypegenskaperna hos ett blyhölje som följd av en mekanisk skada
Göran Eklund
Institutet för Metallforskning september 1977 - april 1978

86 Diffusivitetsmätningar av metan och väte i våt lera
Ivars Neretnieks
Christina Skagius
Kungl Tekniska Högskolan Stockholm 1978-01-09

87 Diffusivitetsmätningar i våt lera Na-lignosulfonat, Sr^{2+},Cs^{+}
Ivars Neretnieks
Christina Skagius
Kungl Tekniska Högskolan Stockholm 1978-03-16

88 Ground water chemistry at depth in granites and gneisses
Gunnar Jacks
Kungl Tekniska Högskolan Stockholm april 1978

89 Inverkan av glaciation på en deponeringsanläggning belägen i urberg 500 m under markytan
Roland Pusch
Högskolan i Luleå 1978-03-16

90 Koppar som kapslingsmaterial för icke upparbetat kärnbränsleavfall - bedömning ur korrosionssynpunkt
Lägesrapport 1978-03-31
Korrosionsinstitutet och dess referensgrupp

91 Korttidsvariationer i grundvattnets trycknivå
Lars Y Nilsson
Kungliga Tekniska Högskolan Stockholm september 1977

92 Termisk utvidgning hos granitoida bergarter
Ove Stephansson
Högskolan i Luleå april 1978

93 Preliminary corrosion studies of glass ceramic code 9617 and a sealing frit for nuclear waste canisters
I D Sundquist
Corning Glass Works 78-03-14

94 Avfallsströmmar i upparbetningsprocessen
Birgitta Andersson
Ann-Margret Ericsson
Kemakta Konsult AB mars 1978

95 Separering av C-14 vid upparbetningsprocessen
Sven Brandberg
Ann-Margret Ericsson
Kemakta Konsult AB mars 1978

96 Korrosionsprovning av olegerat titan i simulerade deponeringsmiljöer för upparbetat kärnbränsleavfall
Sture Henrikson
Marian de Pourbaix
ABB Atomenergi 1978-04-24

97 Colloid chemical aspects of the "confined bentonite concept"
Jean C Le Bell
Ytkemiska Institutet 1978-03-07

98 Sorption av långlivade radionuklider i lera och berg Del 2
Bert Allard
Heino Kipatsi
Börje Torstenfelt
Chalmers Tekniska Högskola 1978-04-20

99 Lakning av högaktivt franskt glas
Lägesrapport 1978-06-01
Göran Blomqvist
AB Atomenergi 1978-06-19