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Corrosion resistance of a copper canister for spent nuclear fuel

The Swedish Corrosion Research Institute
and its reference group

Stockholm , Sweden April 1983

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THE CORROSION RESISTANCE OF A COPPER CANISTER FOR SPENT NUCLEAR FUEL - FOLLOW UP

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A list of other reports published in this series during 1983 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17) and 1982 (TR 82-28) is available through SKBF/KBS.

The Swedish Corrosion Institute
Einar Mattsson
April 1983

Documents included in the report:

THE CORROSION RESISTANCE OF A COPPER CANISTER FOR SPENT NUCLEAR FUEL - FOLLOW-UP

Report from the Swedish Corrosion Institute Reference Group Einar Mattsson
(Chairman of the Reference Group)

1. Background

KBS Technical Report 90 (KBS 90) presents the Swedish Corrosion Institute's evaluation of copper as a canister material for spent nuclear fuel. The evaluation is made from the viewpoint of corrosion and applies to the concept and the premises defined by KBS in 1977.

In connection with the circulation of the copper concept for review and comment, certain viewpoints and questions concerning corrosion of the copper canister have emerged. Furthermore, KBS has commissioned a number of supplementary corrosion studies and even considered some modification of the concept. Under contract to SKBF/KBS, the Swedish Corrosion Institute has undertaken to update its evaluation in the light of the facts, viewpoints, questions and changes that have emerged since KBS 90 was published in 1978.

In order to discharge its undertaking, the Swedish Corrosion Institute has once again appointed a reference group of specialists mainly from the field of corrosion and materials technology. The meetings of the group have been attended by an observer from the Swedish Nuclear Power Inspectorate. The reference group has the following composition:

Professor E. Mattsson	Swedish Corrosion Institute	Chairman
G. Engström, Mining Engineer	Swedish Corrosion Institute	Secretary
L. Ekbom, Lic. Eng.	Swedish Defence Research	
Docent G. Eklund	AGA AB Innovation	
Professor I. Grenthe	Royal Institute of Technology	
Docent R. Hallberg	University of Stockholm	
Professor I. Neretnieks	Royal Institute of Technology	
M. Trolle, Mining Engineer	Swedish Nuclear Power Inspectorate	Observer
Professor N-G Vannerberg	Chalmers University of Technology	
Professor G. Wranglén	Royal Institute of Technology	

This report is a supplement to KBS 90. A detailed account has only been provided here with regard to new information and conditions. The judgments made in this report are based on the premises submitted by the client and on known facts concerning the reactions in question.

The reference group is unanimous in its opinion. Professor G. Wranglén, who submitted a special statement appended to the KBS 90 report, has motivated his concurrence with the opinion of the reference group expressed here in a supplementary statement (appendix 9).

2. Premises for the evaluation

In the main, the same premises as those described in KBS 90 apply. KBS has, however, pointed out certain discrepancies, which are reported in the following subsections.

2.1 Proposed method of storage

According to the original proposal, spent nuclear fuel from the reactor shall be enclosed in a canister made of unalloyed copper (fig. 1), known as "Oxygen Free High Conductivity Grade", OFHC (Swedish designation SIS 14 50 11). Now the question is asked what the consequences will be if phosphorus-deoxidized copper, PHC, with a low phosphorus content (max. 20 ppm) is used. This latter material is cheaper and more suitable with respect to canister fabrication.

According to the previous concept, the copper canister shall have a wall thickness of 200 mm. KBS now also wants an evaluation of the feasibility of reducing wall thickness to 10, 60 or 100 mm. In all alternatives, the outside diameter of the canister is to be 800 mm and its length 4 500 mm.

According to the premises in KBS 90, the canister's lid is to be applied by means of electron beam welding. KBS now asks whether the corrosion properties of the welded joint differ from those of the parent metal, both when the lid is joined by means of electron beam welding and when the lid is joined by means of diffusion welding through hot isostatic pressing.

According to the previous proposal, the fuel contained in the canister shall be embedded in cast lead. KBS now proposes as an alternative that this lead be replaced with hot-isostatically pressed copper powder.

The canisters are to be surrounded by a buffer mass of bentonite. KBS wishes to know how a layer of copper powder between the canister and the buffer would affect the corrosion conditions.

2.2 Composition of the groundwater

The groundwater's chemical composition and its redox status have been investigated at three different sites studied for their suitability as potential sites for the final repository, namely: Gideå, Fjällveden and Svartboberget (appendix 1) (1). The composition of the groundwater as a function of depth has been determined, generally in several boreholes on each site. A large quantity of measurement data have thereby been obtained. In view of these measurement data, the client has found reason to adjust the water analyses that were assumed in KBS 90 to apply for the evaluation. The adjusted water analysis premises are presented in table 1. The expected concentration intervals given there have served as a basis for the evaluations presented here; however, the fact that the chloride concentration can, in exceptional cases, be as high as 6 000 mg/l has been taken into consideration. The values given in table 1 for Eh are assumed to pertain to pH values within the stability range of the water.

2.3 Groundwater flow

In a special statement appended to KBS 90, G. Wranglén asserts that "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." This question has therefore been studied by KBS (2). The fractures in the rock that will surround the waste repository generally have a width that is less than 0.5 mm. Since the bentonite swells, it penetrates into the rock fractures around the borehole, the deeper the greater the fracture width. Calculations have shown a penetration depth of 2.8 m during a period of 10^6 years. Penetration of the bentonite into the fractures around the borehole during this period of time has been calculated to be equivalent to about 2% of the bentonite volume in the borehole, i.e. a negligible loss. This means that the bentonite can be expected on good grounds to remain in the borehole. The flow of water through the buffer will therefore be negligible and only diffusion through the water content of the buffer mass need be taken into account. In fact, penetration of the bentonite into fractures around the borehole is rather an advantage, since it counteracts ion transport to and from the canister.

According to new calculations carried out by Neretnieks et al (3), the annual inflow of species through the buffer to the canister surface is roughly equal to the species content of 0.1-3 litres of the groundwater that surrounds the storage hole. The volume figure depends on the fracturing of the rock on the storage site; a value of 1 has been deemed to be slightly higher than will probably be the case.

2.4 Buffer mass

The buffer mass that surrounds the canister in the repository consists of compacted bentonite that swells on contact with water. Each borehole contains about 17.4 tonnes of bentonite. Its volume is about 11.3 m^3. When the repository is sealed, it is estimated that each borehole will contain about 2 m^3 of air entrapped in the pores of the buffer mass etc.

The buffer is produced by precompacting sodium bentonite, which has been subjected to oxidation treatment prior to the compaction to reduce its contents of sulphide and organic matter. The remaining sulphide is said to be present in the form of pyrite (FeS_2). The sulphide content after oxidizing treatment is said to be no more than 200 mg S/kg, and the content of sulphate is said to be equivalent to max. 2 700 mg S/kg, i.e. 0.81% SO_4^{2-}. The organic matter content of the buffer is said to be less than 200 mg/kg, mainly poorly biodegradable matter.

The tunnel fill consists of a sand-bentonite mixture containing 15% bentonite, and each borehole corresponds to a tunnel section with a volume of about 80 m^3. Iron(II)phosphate (vivianite) may also be added to the tunnel fill in order to eliminate the oxygen present in the pores of the fill when the repository is sealed. Two cases will be evaluated: tunnel fill with and tunnel fill without addition of iron(II)phosphate.

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 relatively rapidly during the first 100 years.

For a canister containing spent nuclear fuel, the maximum temperature at the outer surface of the canister is stated to be 80°C; after 1 000 years, the temperature has dropped to 50°C. This applies in the case of a single-storey repository, i.e. a repository with canisters on only one level in the rock. In the case of a two-storey repository, it is estimated that it would take several thousand years for the temperature to have dropped to 50°C. 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 atomic radiation, radiolysis of the water may occur. This can lead to the formation of e.g. hydrogen and oxidants. If these radiolysis products are not removed, an equilibrium will soon be reached whereby the further production of hydrogen and oxidants ceases. If the radiolysis products are removed, however, for example by the hydrogen's diffusing away and the oxidants' reacting with copper and oxidizing it, the radiolysis can continue. Under the assumption that the oxidation of copper takes place rapidly, the radiolysis rate is determined by the rate at which the hydrogen diffuses away. The quantity of hydrogen transported away as well as hydrogen formed by radiolysis during different periods of storage has been calculated by Christensen and Bjergbakke (4). The results obtained for copper canisters of different wall thicknesses are presented in table 2. The radiolysis calculations for the wall thicknesses 10 and 60 mm pertain to the situation when the energy is assumed to be absorbed in 720 l of water containing 5 ppm Fe^{2+}. The calculations for 100 and 200 mm are very approximate, since the radiolysis in these cases is of a very small extent; the values in the two last-named cases are too high, however, since recombination of the radiolysis products has not been taken into consideration.

2.7 Canister life

KBS has expressed a wish for the following evaluations for copper canisters with a wall thickness of 10, 60, 100 and 200 mm, respectively:

- time to first corrosion penetration in worst case
- probable time to first corrosion penetration
- probable time function for occurrence of subsequent corrosion penetrations.

3. Corrosion of the copper canister

3.1 Oxidants for copper

In the presence of oxidants, copper can be oxidized and thereby be attacked. The effect of different possible oxidants is explored in KBS 90. The most obvious oxidant in this case is oxygen dissolved in the groundwater, this during the period immediately following sealing of the repository.

Other possible oxidants are e.g. sulphur(VI) in sulphate, hydrogen(I) in water and sulphide, sulphur(-I) in pyrite, nitrogen(V) in nitrate or iron(III) in various minerals. The oxidants sulphur(VI) in sulphate and hydrogen(I) in water are particularly important, since their concentration is relatively high in the canister's environment. KBS 90 particularly emphasized oxidation of copper by oxygen with the formation of copper oxides and by hydrogen(I) in the presence of sulphide with the formation of Cu_2S. It should be observed, however, that these two reactions cannot occur simultaneously as the former is possible only at high redox potentials above about 50 mV (SHE) and the latter only at low redox potentials, below about -200 mV (SHE). The effect of nitrate can be disregarded, since the nitrate concentration in the canister's surroundings is so low.

In KBS 90, it is asserted that the oxidation of copper by sulphate is negligibly low, even over geological periods of time, but can be catalyzed by sulphate-reducing bacteria. The reviewers have questioned whether it is not possible for copper to be oxidized by sulphate at a considerable rate even in the absence of micro-organisms.

The water analyses at certain potential storage sites have further indicated higher chloride concentrations than previously assumed. In view of this, it should be checked whether higher chloride concentrations can permit the oxidation of copper by hydrogen(I) in water.

The two questions mentioned above will be dealt with in this report. For further information the reader is referred to KBS 90.

3.1.1 Oxidation of copper by sulphate

The thermodynamic possibilities of oxidation of copper by sulphate have been elucidated in KBS 90. It was found that a direct oxidation of copper by sulphate according to the following formula is not thermodynamically possible:

$$8Cu(s)+SO_4{}^{2-}(aq)+H_2O \rightarrow Cu_2S(s)+3Cu_2O(s)+2OH^-(aq);\ \Delta G^o=+138{,}9kJ \quad [1]$$

Among thermodynamically possible reactions is the following:

$$2Cu(s)+SO_4{}^{2-}(aq)+2Fe^{2+}(aq)+H_2O \rightarrow Cu_2S(s)+Fe_2O_3+2OH^-(aq);$$

$$\Delta G^o = -\ 74{,}9\ kJ \quad [2]$$

The common denominator for these possible reactions is that they involve the participation of an Fe(II) species - in solid form or in solution - as a reducing agent.

Further research (appendix 2) has furnished additional evidence for the fact that these reactions in the absence of catalysts proceed so extremely slowly at temperatures below about 200°C that the oxidation is negligibly low even over geological periods of time.

However, micro-organisms can catalyze the reduction of sulphate, whereby the sulphide formed can react with copper:

$$2CH_2\cdot CHOH\cdot COOH(aq)+HSO_4{}^-(aq) \rightarrow 2CH_3\cdot COOH(aq)+HS^-(aq)+2CO_2(g)+2H_2O \quad [3]$$

As is reported in KBS 90, the micro-organisms require access to degradable organic matter for their life processes, so that with an excess of sulphate, the supply of such organic matter is determining for the reaction rate. In the calculations of the microbial formation of sulphide from sulphate in the borehole and tunnel fills, it has been assumed that 5.6 mg of organic matter gives rise to 1 mg of sulphide. Furthermore, organic matter in the groundwater has been assumed to give rise to an increase of the sulphide concentration by 1 mg S per litre, this through microbial reduction of sulphate.

The present standpoint is therefore that it must be regarded as highly improbable that copper will be oxidized to any appreciable extent by sulphate during the storage period, aside from the oxidation caused by the action of the micro-organisms.

3.1.2 Oxidation of copper by hydrogen(I) in the presence of chloride

The thermodynamic possibilities for the oxidation of copper by hydrogen(I) in the presence of chloride have been studied by Wallin (appendix 3). It has thereby been found that even at such a high chloride concentration as 35 000 mg/l, such a reaction is only thermodynamically possible at pH values less than 2. At such low pH values, the reaction can take place according to the following formula:

$$Cu(s)+H^+(aq)+Cl^-(aq) \rightarrow CuCl(s)+\tfrac{1}{2}H_2(aq) \qquad [4]$$

Since the groundwater on the repository site is estimated to have a pH of 7-9 and since the bentonite buffers the pH to 8-9, it is thus not thermodynamically possible for freely exposed copper surfaces to be corroded by hydrogen(I) in water with chloride concentrations of up to 35 000 mg/l.

Low pH values can occur locally in crevices, however, which could lead to the risk of crevice corrosion of copper in chloride-rich water. If there is a risk of groundwater with a high chloride content, great attention should therefore be paid to avoiding crevices on the outside of the canister, for example at joints. Any gap that might arise between the canister wall and the bentonite is not, however, expected to lead to crevice corrosion, since the bentonite prevents a low pH in the gap by virtue of its buffering effect.

3.2 Stress corrosion cracking

In KBS 90, the risk of stress corrosion cracking is deemed to be nil in canisters of OFHC copper. The reviewers have questioned, with reference to certain laboratory studies (5, 6), whether the risk of stress corrosion cracking can be completely ruled out in this case. Furthermore, as mentioned in section 2.1, KBS has proposed that the OFHC copper be exchanged for PHC copper, which is judged to have somewhat poorer resistance to stress corrosion cracking than OHFC copper. For this reason, KBS has had a stress corrosion cracking study of OHFC and PHC copper carried out, both in groundwater of the type that can be expected in the repository and in solutions with different concentrations of NO_2^-, which has been found to be capable of inducing stress corrosion cracking in pure copper. The studies, which have been carried out employing the constant strain method, have been conducted by Benjamin, Hardie and Perkins at the University of Newcastle-upon-Tyne (7).

The studies have shown that stress corrosion cracking is improbable both in OFHC and PHC copper in groundwater of the type concerned here, this both at room temperature and at 80°C. On the other hand, both of the copper types possess some sensitivity to stress corrosion cracking in nitrite-containing aqueous solution with a nitrite content of more than 69 mg/l. However, this only applies at high redox potentials (+344 mV, in the hydrogen scale at pH 8.5), which do not occur in the repositories in question here. In the studies, PHC copper exhibited slightly greater sensitivity to stress corrosion cracking than OFHC copper.

The studies have thus shown that stress corrosion cracking is improbable in canisters of OFHC copper or PHC copper under the specified storage conditions.

3.3 Oxidized quantity of copper

The quantity of copper that can be oxidized by oxidants formed through radiolysis is reported in table 2, where results are given for different values of canister wall thickness and exposure time.

The quantity of copper that can be oxidized by oxygen initially present in storage holes and tunnels (without the addition of vivianite) and supplied by the surrounding groundwater has been calculated (appendix 4). The results are given in table 3. The same applies to the quantity of copper oxidized by hydrogen(I) in the presence of sulphide. In both cases, it is assumed that the copper is oxidized to Cu(I).

As is evident from section 3.1.1, it is deemed highly unlikely that copper will be oxidized by sulphate to any appreciable extent during the storage period, beyond the oxidation mediated by the presence of the micro-organisms and taken into account in table 3. In this table, the quantity of copper that could theoretically be oxidized by SO_4^{2-} supplied is also given under the apparently unreasonable assumption that this reaction takes place. The calculations have been carried out by Neretnieks and are presented in appendix 5. They have taken into account the SO_4^{2-} content of:

- the bentonite in the borehole; 0.81% SO_4^{2-}
- the bentonite mixture in the tunnels, assuming that the SO_4^{2-} content of approx. 80 m^3 of tunnel fill reaches each canister and that the tunnel fill contains 15% by weight bentonite
- the surrounding groundwater, whereby it has been assumed that the SO_4^{2-} content of 2.4 l of groundwater with 15 mg SO_4^{2-} per litre reaches the canister every year.

The quantity of SO_4^{2-} that is supplied to the canister surface can be reduced by the following measures:

- By applying a granite plug in the mouth of the borehole; the granite plug should have a length of 1 m and such a diameter that the gap between the borehole wall and the granite plug is 0.5 cm. With such a plug, the supply of SO_4^{2-} from the tunnel to the canister surface is limited to about 1/6 of the values given in table 3.

- By exchanging the bentonite grade assumed in the premises (with 0.81% SO_4^{2-}) for sulphur-poor bentonite containing e.g. 0.027% SO_4^{2-}. The SO_4^{2-} quantities that can then be supplied to the canister have been calculated and are also given in table 3.

In addition, it should be taken into account that at an SO_4^{2-} supply above a given level, the thermodynamic possibilities of reaction between Cu and SO_4^{2-} are limited by the supply of Fe(II) species, which, according to section 3.1.1, are a fundamental prerequisite for the reaction. Fe(II) species can be supplied from the borehole and tunnel fills, from the borehole's rock wall and from the groundwater, which is assumed to contain max. 5 ppm Fe^{2+}. Approximate calculations have shown that the supply of Fe(II) to the canister surface is considerably less than the supply of SO_4^{2-} when bentonite with 0.81% SO_4^{2-} is used, all expressed in equivalent quantity of Cu according to formula 2 . A more thorough investigation is required for a quantitative determination of the limiting effect of the supply of Fe(II).

3.4 Form of the attack

The corrosion attack that can occur in the copper canister due to the action of the oxidants is only of importance if it has the character of local corrosion. Our prime concern here is for pitting. As is described in KBS 90, the relationship between pit depth (P) and time (t) can be expressed by means of the equation

$$P = A(t-t_o)^n,$$

where

t_o is the incubation time before pitting starts
A is a constant
n is a constant whose value is between 0 and 1.

In agreement with this equation, the time to corrosion penetration 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 then takes the form of a widening of existing pits and an initiation of new pits. After a very long time, the attack therefore assumes the character of a corroded surface zone with local variations in depth. The ratio between maximum pit depth and average penetration is usually called the pitting factor (P_f).

The maximum pit depth can be obtained by multiplying the average penetration by the pitting factor. In KBS 90, the pitting factor was set equal to 25, which was the largest value observed in Denison-Romanoff's large study of the corrosion of copper in different types of soil in the United States during an exposure period of 14 years (8). This value was regarded as conservative, since theoretical analyses in KBS 90 show that the pitting factor decreases with time. This is also confirmed by the Denison-Romanoff study.

In order to furnish further support for the estimate of the size of the pitting factor, KBS has commissioned a study of the pitting factor for:

- archaeological artifacts of copper material
- a piece of native copper from the United States
- three earth electrodes for lightning conductors

The archaeological artifacts and the native copper from the United States have been studied by Bresle et al (9). The archaeological artifacts consisted of bronze objects and copper coins. Conditions on the exposure site have been of a varying nature and have not, as a rule, been able to be defined exactly. The exposure time varied between 300 and 3 000 years. The largest pitting factor measured in this highly varying material is about 3. The piece of native copper, which had lain in the soil for at least 8 000 years, probably much longer, exhibited a pitting factor of 2-6.

The three earth electrodes, which consisted of copper plates, had been exposed in soil for 50-80 years. The earth electrode plates have been examined by Hallberg (appendix 6) and Sund (appendix 7), who have found a pitting factor of max. 5 in these cases.

It can be questioned with reason whether the investigated objects are representative of the copper canister in its bentonite environment 500 m below the surface of the ground. The fact nevertheless remains that in none of the cases did the measured pitting factor exceed or even come close to 25, which is the value used in the calculations reported in KBS 90. In view of this, and of the previously mentioned fact that the pitting factor can be expected on theoretical grounds to decline with time, the value of 25 may be regarded as very conservative. A more probable value is 5.

3.5 Growth of the attack

On the basis of the quantity of copper in each canister that, according to the calculations, can be oxidized (see tables 2 and 3), the depth of the attack caused by reactants supplied from the outside (table 4) and the average corrosion of the canister (table 5) have been calculated as a function of the exposure time, thus the time function of the depth of the attack has been determined, this under the assumption that the attack is uniformly distributed over the entire canister surface. However, as in KBS 90, the attack caused by reactants originating from the tunnel has been assumed to be concentrated to the top end of the canister, i.e. to 1/10th of its surface. The results for different wall thicknesses of the copper canister are reported in table 5.

The maximum pit depth can be calculated from the average penetration by multiplying by a pitting factor. The calculations for the probable case have been done using a pitting factor of 5, while the calculations for an extremely unfavourable case have been done with a pitting factor of 25, all in agreement with section 3.4.

Corrosion attack as a result of oxidation of copper by SO_4^{2-} has been deemed improbable. Nevertheless, the corrosion depth for the improbable case that such a reaction should take place has been calculated and is given in tables 6 and 7 for the following conditions:

- use of bentonite with 0.81% SO_4^{2-} without granite plug in mouth of borehole
- use of bentonite with 0.81% SO_4^{2-} with granite plug in mouth of borehole
- use of bentonite with 0.027% SO_4^{2-} without granite plug in mouth of borehole

In these calculations, the limiting effect of the supply of Fe(II) has not been taken into account, which means that the stated depths of attack are too large, in the first case far too large.

3.6 Weld corrosion

The question has been raised as to whether the welded joints have a corrosion rate that differs from that of the parent metal. In electrochemical studies of electron-beam-welded versus diffusion-welded copper, carried out by the Swedish Corrosion Institute, no such difference has been found. Metallographic etching studies carried out by Modin (appendix 8) have not furnished evidence for such a difference either. However, in the metallographic investigations, pores have been observed in the joints. Naturally, it is important that such defects be avoided wherever possible; this applies in particular to pores and crevices that are open to the canister's surroundings. In order to avoid such pores, every canister should undergo inspection of the welded joints.

In connection with diffusion welding by means of hot isostatic pressing, special measures should be adopted to avoid high oxygen concentrations in the welded joints. If the method is to be applied to the canister, it is proposed that the susceptibility of this type of weld to stress corrosion cracking should be checked by testing of a number of welded joints employing the constant strain method.

3.7 Effect of perforation of one canister on the corrosion of nearby canisters

If the canister wall is perforated due to corrosion, welding defects or the like so that water comes into contact with the enclosed nuclear fuel waste, alpha radiation from the waste causes radiolysis of the water. Hydrogen and hydrogen peroxide are thereby formed. Hydrogen peroxide is a powerful oxidant that alters the redox potential of the water in the surroundings from reducing to oxidizing conditions.

Neretnieks has calculated the movement of the redox front downstream along the fractures in the rock (10). The results show that the redox front under, judging from what is known, unfavourable conditions would be able to move 100 m during 10^6 years in rock of relatively low fracture content. These calculations have not, however, taken into consideration the fact that corrosion products formed in connection with corrosion of the waste inside the canister counteract the radiolysis and that a portion of the radiolysis products react with the copper and with the uranium oxide in the first perforated canister. The propagation of the redox front is therefore expected to be several orders of magnitude less. Since the canisters in the repository are intended to be spaced at a distance of 6 m, it would therefore probably take about 10^6 years before the radiolysis products from one perforated canister affect the corrosion of the canister located closest to it in the repository. The calculations must be regarded as highly approximate. Many of the factors that affect the propagation of the redox front are not well known. Investigations of the natural reactor at Oklo, Gabon, which was active about 1 800 million years ago, show that oxidizing agents have migrated only a metre or so from the uranium oxide. This confirms that the above calculations have given highly overestimated values.

3.8 Exchanging lead for hot isostatically pressed copper powder for embedding of the fuel rods in the canister

Embedding the fuel rods in the canister in hot isostatically pressed copper powder instead of casting them in lead is deemed to be favourable with regard to the rate of corrosion of the canister. The hot isostatically pressed copper cannot formally be credited with increased time for corrosion penetration of the canister, however, since the hot isostatically pressed copper zone is thin in places and since there is some risk of pores in this zone at the present state of the art.

3.9 Influence of a layer of copper powder between the canister and the bentonite

The question has been posed whether a layer of copper powder between the canister and the bentonite could act as a "corrosion buffer" and thereby prolong the life of the canister.

However, it is judged that such a layer of copper powder might lead to crevice corrosion in chloride-rich water (cf. section 3.1.2), for which reason it should not be introduced into the concept.

4. Conclusions

In view of the results of completed calculations, the following evaluation is made of the time to the first corrosion penetration for canisters with different wall thicknesses:

Wall thickness	Time to first penetration, years	
mm	Probable case	Pessimistic case
10	$>10^6$	10^5
60	$>10^6$	$>10^6$
100	$>10^6$	$>10^6$
200	$>10^6$	$>10^6$

Corrosion penetration will not take place simultaneously in all canisters; a considerable scatter can be expected due to variations in the fracturing of the rock, the tunnel fill, impurity of the bentonite etc.

Attacks caused by oxidation of copper by SO_4^{2-} in the presence of Fe(II) are thermodynamically possible but have been deemed improbable, since known evidence shows that the reaction is strongly inhibited. Even under the apparently unreasonable assumption that this reaction should take place rapidly, the time to corrosion penetration would be more than 10^6 for canisters with a wall thickness of 100 or 200 mm, provided that one of the following measures is adopted:

- the mouth of the borehole is blocked with a granite plug
- the assumed bentonite with 0.81% SO_4^{2-} is exchanged for a sulphate-poor grade with max. 0.027 SO_4^{2-}

This conclusion also applies in the pessimistic case when the pitting factor is 25. Beyond this, it should be borne in mind that the thermodynamic prerequisites for canister attack through oxidation by SO_4^{2-} are limited by the supply of Fe(II). This limitation appears to be significant, but has not yet been quantified. In order to eliminate all uncertainty concerning the effect of SO_4^{2-}, it is proposed that the reaction limitation represented by the supply of Fe(II) be studied more closely.

The addition of vivianite to the tunnel fill is judged to lead to only a marginal reduction of the canister attack and can therefore be avoided; the supply of Fe(II) to the canister should, after all, be limited as much as possible.

If the canister wall is perforated by corrosion, welding defects or the like so that water comes into contact with the nuclear fuel waste, alpha radiation from the waste causes radiolysis of the water, forming oxidants. According to completed calculations, however, it will take a very long time - probably on the order of 10^6 years - before these oxidants have reached and can influence the corrosion of the most closely located canister in the repository.

In order to avoid crevice corrosion in chloride-rich water, there should be no gaps or crevices, for example in the canister's welded joints. These welded joints should therefore undergo inspection.

According to completed investigations, stress corrosion cracking is improbable in canisters of OFHC copper or PHC copper under the defined storage conditions.

The corrosion rate in welded joints in copper of the type that will be present in the copper canisters does not appear to differ significantly from the corrosion rate of the parent metal. However, supplementary stress corrosion testing of welded joints produced by hot isostatic pressing is proposed.

Exchanging lead for hot isostatically pressed copper powder for embedding the fuel rods in the canister is deemed to be favourable with respect to the corrosion resistance of the canister.

Inserting a layer of copper powder between the canister and the bentonite can lead to the risk of crevice corrosion in chloride-rich water and should therefore be avoided.

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Table 1. Probable composition of deep granitic groundwaters (concentrations in mg/l).

	Expected intervals[a]	Simulated groundwater[b]
Conductivity, mS/m	22-30	
pH	7-9	8.2
Eh, V	0-(-0.45) >0.25[c]	
HCO_3^-	90-275	123
SO_4^{2-}	0.5-15	9.6
HPO_4^{2-}	0.01-0.2	
NO_3^-	0.01-0.05	
F^-	0.5-4	
Cl^-	4-15	70
HS^-	0-0.5	
Ca^{2+}	10-40	18
Mg^{2+}	2-10	4.3
Na^+	10-100	65
K^+	1-5	3.9
Fe^{2+}	0.02-5	
Fe(tot)	1-5	
Mn^{2+}	0.1-0.5	
Al^{3+}	0-0.02	
NH_4^+	0.05-0.2	
SiO_2(tot)	3-14	11
TOC[d]	1-8	

a) Probable interval for the majority of non-saline waters within which 90% of all measurement data fall. Locally, values outside of the interval may be encountered. Saline waters with total concentrations of up to 400-500 mg/l (Na^+, Cl^-) are occasionally found. Concentrations of up to 6 000 mg/l have been encountered on occasional sites (Finnsjön).

b) Artifical groundwater used as a reference system in sorption and solubility measurements etc.

c) Aerated systems.

d) Total organic carbon.

Table 2. Quantity of hydrogen formed through radiolysis as a function of time at different values of the wall thickness of the copper canister; equivalent quantity of copper oxidized to Cu(I) is also given

Wall thickness of copper canister, mm	Cumulative quantity of hydrogen (moles) formed through radiolysis during the following number of years				Maximum quantity of oxidized copper (kg) due to radiolysis during the following number of years			
	10^3	10^4	10^5	10^6	10^3	10^4	10^5	10^6
10	3	8	47	360	0.38	1.0	6.0	46
60	1	1	3	32	0.13	0.13	0.38	4.1
100*	1.50	3.20	9.0	69.0	0.19	0.41	1.1	8.8
200*	0.0051	0.0108	0.030	0.23	0.0006	0.0014	0.004	0.03

* In calculating radiolysis for these wall thicknesses, recombination of the radiolysis products has not been taken into consideration, making the tabulated values slightly too high.

0,13 kg

$3 \cdot 10^{-2} \cdot 1120 =$ 34 moler

34,

2,1 kg

Table 3. Quantity of reactants supplied to the canister surface, expressed in equivalent quantities of Cu(I) in kg.

Reactant	Exposure time, years			
	10^3	10^4	10^5	10^6
Oxygen				
Initially in deposition hole	4.8	4.8	4.8	4.8
From tunnel:				
- with vivianite addition	0	0	0	0
- without vivianite addition	0.30	0.38	0.38	0.38
From groundwater via fractures	0.002	0.019	0.19	1.9
Sulphide				
Initially in deposition hole with 0.02% S in bentonite	3.5	3.5	3.5	3.5
Formed through microbial activity in deposition hole	2.5	2.5	2.5	2.5
From tunnel:				
- with 0-0.02% S in bentonite	0.004	0.035	0.35	3.5
- formed through microbial activity	0.001	0.006	0.06	0.6
From groundwater via fractures	0.010	0.095	0.95	9.5
Formed through microbial activity in groundwater	0.010	0.095	0.95	9.5
Sulphate				
Initially in deposition hole:				
- with 0.81% SO_4^{2-} in bentonite	190	190	190	190
- with 0.027% SO_4^{2-} in bentonite	6.2	6.2	6.2	6.2
From tunnel:				
- with 0.81% SO_4^{2-} in bentonite	4.0	24	45	60
- with 0.027% SO_4^{2-} in bentonite	0.018	0.18	1.8	18
From groundwater via fractures	0.05	0.5	4.8	48

Table 4. Depth of attack (mm) caused by reactants supplied from the outside as a function of exposure time

Reactant	Exposure time, years			
	10^3	10^4	10^5	10^6
Oxygen				
Initially in deposition hole	0.04	0.04	0.04	0.04
From tunnel without vivianite addition	0.03	0.03	0.03	0.03
From groundwater via fractures	0.00	0.00	0.00	0.02
Sulphide				
Initially in deposition hole with 0.02% S in bentonite, incl. microbially formed sulphide	0.05	0.05	0.05	0.05
From tunnel with 0.02% S^{2-} in bentonite, incl. microbially formed sulphide	0.00	0.00	0.04	0.37
From groundwater via fractures, incl. microbially formed sulphide	0.00	0.00	0.02	0.17
Total, mm	0.12	0.12	0.18	0.68

Table 5. Total attack on the canister as a function of exposure time.

Canister wall thickness, mm	Reactant	Depth (mm) of attack during following exposure time (years)			
		10^3	10^4	10^5	10^6
10	Supplied from the outside according to table 4	0.12	0.12	0.18	0.68
	Radiolysis oxidants	0.00	0.01	0.05	0.42
	Average penetration, mm	0.12	0.13	0.23	1.10
	Max. pit depth, probable case (P_f=5), mm	0.6	0.7	1.1	5.5
	Max. pit depth, pessimistic case (P_f=25), mm	3.0	3.3	5.8	Perf
60	Supplied from the outside according to table 4	0.12	0.12	0.18	0.68
	Radiolysis oxidants	0.00	0.00	0.00	0.04
	Average penetration, mm	0.12	0.12	0.18	0.72
	Max. pit depth, probable case (P_f=5), mm	0.6	0.6	0.9	3.6
	Max. pit depth, pessimistic case (P_f=25), mm	3.0	3.0	4.5	18
100	Supplied from the outside according to table 4	0.12	0.12	0.18	0.68
	Radiolysis oxidants	0.00	0.00	0.00*	0.01*
	Average penetration, mm	0.12	0.12	0.18	0.69
	Max. pit depth, probable case (P_f=5), mm	0.6	0.6	0.9	3.5
	Max. pit depth, pessimistic case (P_f=25), mm	3.0	3.0	4.5	17
200	Supplied from the outside according to table 4	0.12	0.12	0.18	0.68
	Radiolysis oxidants	0.00	0.00	0.00	0.00
	Average penetration, mm	0.12	0.12	0.18	0.68
	Max. pit depth, probable case (P_f=5), mm	0.6	0.6	0.9	3.4
	Max. pit depth, pessimistic case (P_f=25), mm	3.0	3.0	4.5	17

* Estimated value

Table 6. Depth of attack (mm) caused by reactants supplied from the outside; improbable case

Reactant	Bentonite with 0.81% SO_4^{2-} without granite plug				Bentonite with 0.027% SO without granite plug			
	Exposure time, years				Exposure time, years			
	10^3	10^4	10^5	10^6	10^3	10^4	10^5	10^6
Oxygen								
Initially in deposition hole	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.0
From tunnel without vivianite addition	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.0
From groundwater via fractures	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.0
Sulphide								
Initially in deposition hole	0.03	0.03	0.03	0.03	0.00	0.00	0.00	0.
From tunnel	0.00	0.00	0.03	0.32	0.00	0.00	0.03	0.
From groundwater via fractures	0.00	0.00	0.01	0.09	0.00	0.00	0.01	0.
Sulphate								
Initially in deposition hole	1.73	1.73	1.73	1.73	0.06	0.06	0.06	0.
From tunnel	0.36	2.19	4.11	5.48	0.00	0.02	0.16	1.
From groundwater via fractures	0.00	0.00	0.04	0.44	0.00	0.00	0.04	0.
Total, mm	2.19	4.02	6.02	8.18	0.13	0.15	0.37	2.

	Bentonite with 0.81% SO_4^{2-} with granite plug			
	Exposure time, years			
	10^3	10^4	10^5	10^6
Oxygen				
Initially in deposition hole	0.04	0.04	0.04	0.04
From tunnel without vivianite addition	0.01	0.01	0.01	0.01
From groundwater via fractures	0.00	0.00	0.00	0.02
Sulphide				
Initially in deposition hole	0.03	0.03	0.03	0.03
From tunnel	0.00	0.00	0.01	0.05
From groundwater via fractures	0.00	0.00	0.01	0.09
Sulphate				
Initially in deposition hole	1.73	1.73	1.73	1.73
From tunnel	0.06	0.37	0.69	0.91
From groundwater via fractures	0.00	0.00	0.04	0.44
Total, mm	1.87	2.18	2.56	3.32

Table 7. Total attack on canister, improbable case

Canister wall thickness, mm	Reactant	Bentonite with 0.81% SO_4^{2-} without granite plug				Bentonite with 0.027% SO_4^{2-} without granite plug			
		Depth (mm) during following exp. time (years)				Depth (mm) during following exp. time (years)			
		10^3	10^4	10^5	10^6	10^3	10^4	10^5	10^6
10	Supplied from the outside according to table 6	2.19	4.02	6.02	8.18	0.13	0.15	0.37	2.64
	Radiolysis oxidants	0.00	0.01	0.05	0.42	0.00	0.01	0.05	0.42
	Average penetration, mm	2.19	4.03	6.07	8.60	0.13	0.16	0.42	3.06
	Max. pit depth (P_f=5), mm	Perf	Perf	Perf	Perf	0.7	0.8	2.1	Perf
	Max. pit depth (P_f=25), mm	Perf	Perf	Perf	Perf	3.3	4.0	Perf	Perf
60	Supplied from the outside according to table 6	2.19	4.02	6.02	8.18	0.13	0.15	0.37	2.64
	Radiolysis oxidants	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.04
	Average penetration, mm	2.19	4.02	6.02	8.22	0.13	0.15	0.37	2.68
	Max. pit depth (P_f=5), mm	11	20	30	41	0.7	0.8	1.9	13
	Max. pit depth (P_f=25), mm	55	Perf	Perf	Perf	3.3	3.8	9.3	Perf
100	Supplied from the outside according to table 6	2.19	4.02	6.2	8.18	0.13	0.15	0.37	2.64
	Radiolysis oxidants	0.00	0.00	0.00*	0.01*	0.00	0.00	0.00*	0.01*
	Average penetration, mm	2.19	4.02	6.02	8.19	0.13	0.15	0.37	2.65
	Max. pit depth (P_f=5), mm	11	20	30	41	0.7	0.8	1.9	13
	Max. pit depth (P_f=25), mm	55	Perf	Perf	Perf	3.3	3.8	9.3	66
200	Supplied from the outside according to table 6	2.19	4.02	6.02	8.18	0.13	0.15	0.37	2.64
	Radiolysis oxidants	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Average penetration, mm	2.19	4.02	6.02	8.18	0.13	0.15	0.37	2.64
	Max. pit depth (P_f=5), mm	11	20	30	41	0.7	0.8	1.9	13
	Max. pit depth (P_f=25), mm	55	100	150	Perf	3.3	3.8	9.3	66

* estimated value

Cont'd

Table 7. (Cont'd) Total attack on canister, improbable case

Canister wall thickness, mm	Reactant	Bentonite with 0.81% SO_4^{2-} with granite plug Depth (mm) during following exp. time (years)			
		10^3	10^4	10^5	10^6
10	Supplied from the outside according to table 6	1.87	2.18	2.56	3.32
	Radiolysis oxidants	0.00	0.01	0.05	0.42
	Average penetration, mm	1.87	2.19	2.61	3.74
	Max. pit depth ($P_f=5$), mm	9.4	Perf	Perf	Perf
	Max. pit depth ($P_f=25$), mm	Perf	Perf	Perf	Perf
60	Supplied from the oustide according to table 6	1.87	2.18	2.56	3.32
	Radiolysis oxidants	0.00	0.00	0.00	0.04
	Average penetration, mm	1.87	2.18	2.56	3.36
	Max. pit depth ($P_f=5$), mm	9.4	11	13	17
	Max. pit depth ($P_f=25$), mm	47	55	Perf	Perf
100	Supplied from the outside according to table 6	1.87	2.18	2.56	3.32
	Radiolysis oxidants	0.00	0.00	0.00*	0.01*
	Average penetration, mm	1.87	2.18	2.56	3.33
	Max. pit depth ($P_f=5$), mm	9.4	11	13	17
	Max. pit depth ($P_f=25$), mm	47	55	64	83
200	Supplied from the oustide according to table 6	1.87	2.18	2.56	3.32
	Radiolysis oxidants	0.00	0.00	0.00	0.00
	Average penetration, mm	1.87	2.18	2.56	3.32
	Max. pit depth ($P_f=5$), mm	9.4	11	13	17
	Max. pit depth ($P_f=25$), mm	47	55	64	83

* estimated value

Appendix 1
(51 571)

Composition of the groundwater

Ingmar Grenthe, Department of Organic Chemistry, Royal Institute of Technology

The Swedish Corrosion Institute's previous evaluation of the corrosion of copper in groundwater was based on information on the chemical composition and redox status of the groundwater (table 1 and appendix B). A more detailed body of analysis data from groundwaters from different sites is now available. These data will be used in the Corrosion Institute's new corrosion evaluation.

Three different sites - Gideå, Fjällveden and Voxna - have been investigated, in general with several boreholes on each site. The composition of the groundwater as a function of depth has been determined in each borehole. The number of measurement results is very large, and for the sake of simplicity, only maximum, median and minimum values of the different quantities for a given site are presented in the following tables.

All analyses have been performed on unfiltered water. Two different laboratories have been used, agreement between them is generally good. In certain cases, analysis results are obtained that differ greatly from other data. Faulty analysis or contamination of the sample cannot be ruled out here. It would have been desirable to check these data by means of a new water sample. This has not been possible due to the lapse of time between sampling and analysis.

The analysis data are tabulated in table 1.

The quantity of particulate matter is generally low. Table 2 shows an analysis of precipitation obtained by filtration through a 0.4 membrane filter. The concentrations are given as mg/l of water.

The concentrations of the different components agree well with previous data, with some important exceptions. The chloride concentration reaches considerably higher values than had previously been assumed, while the sulphide and sulphate concentrations are considerably lower.

Eh measurements have also been performed in the field. The results have not been finally interpreted, but indicate that reducing conditions exist at the depths in question. The redox potential can probably also reach such low values that reduction of sulphate cannot be ruled out for thermodynamic reasons. Redox data are tabulated in table 3.

Table 1

Analysis	Unit	Gideå			Fjällveden			Voxna		
		min	med	max	min	med	max	min	med	max
Conductivity	S/cm	22	-	128	18	-	79	22	-	25
pH		7	-	9.4	7.1	-	8.9	8.3	-	9.6
Total organic carbon (TOC)	mg C/l	0.6	3.9	10	1.9	7.8	58	1.4	5.0	80
Ca^{2+}	mg/l	9	10	66	9	20	34	1	18	26
Mg^{2+}		0.8	2.3	6	0.8	3.8	6	0.5	1.8	3.3
Na^{+}		5	49	200	25	42	138	21	35	54
K^{+}		0.6	2.3	7.6	0.7	2.2	3.7	0.6	0.8	1.9
Fe-tot		0.06	0.68	8.7	0.22	3.7	12	0.05	0.19	0.77
Fe^{2+}		0.03	0.30	7.4	0.02	2.7	10.3	0.02	0.13	0.46
Mn^{2+}		0.001	0.02	0.35	0.02	0.25	0.65	0.01	0.04	0.08
Al^{3+}		0.01	0.01	0.06	0.01	0.04	0.28	0.01	0.01	0.04
Cu^{2+}		0.005	0.005	0.03	0.005	0.005	0.02	0.005	0.005	0.02
Sr^{2+}		0.07	0.08	0.29	0.09	0.12	0.21	0.03	0.06	0.07
HCO_3^{-}		16	142	166	79	170	229	120	130	141
Cl^{-}		1.4	5.9	300	2.7	9.0	224	2	7.1	12
SO_4^{2-}		0.1	0.6	12	0.1	4	14	0.8	1.1	2.5
NO_3^{-}		0.01	0.035	0.065	0.01	0.04	4.6	0.02	0.04	0.3
PO_4^{3-}		0.01	0.022	0.085	0.01	0.04	0.26	0.001	0.08	1.1
F^{-}		0.8	2.6	5.6	0.2	1.4	5.7	2.1	4.5	6.5
SiO_2		0.9	20	25	4.6	8.3	14.5	6.0	8.6	13
$/HS^{-}/+/H_2S/$		0.01	0.02	0.23	0.01	0.04	0.20	0.01	0.01	0.07
NH_4^{+}		0.01	0.05	0.10	0.01	0.07	0.22	0.01	0.02	0.05
HO_2^{-}		0.002	0.004	0.045	0.002	0.005	0.05	0.002	0.002	0.005

Table 2. Analysis of particulate matter.
Data are given in mg/l of water

Analysis	Unit	Gideå			Fjällveden			Voxna		
		min	med	max	min	med	max	min	med	max
S	mg/l	0.0004,	0.0021	0.0034	0.002	0.015	0.05	0.0004	0.002	0.006
Fe	"	0.001	0.027	0.092	0.027	0.13	0.9	0.002	0.004	0.80
Al		0.001	0.025	0.24	0.04	0.17	0.67	0.002	0.08	0.27

Table 3. Experimental Eh measurements at different depths. The numbers indicate different boreholes.

		E_h mV	
Gideå 2	178 m	-100	all measurement values decline with time
	328 m	- 85	
	400 m	- 90	
	544 m	- 90	
	602 m	-100	
Gideå 4	96 m	- 30	the measurement values decline with time
	222 m	-120	
	404 m	-120 - -200	
	512 m	- 180	
	616 m	-300 - -340	
Fjällveden 2	123 m	- 80	
	342 m	- 70 - -100	
	483 m	- 80 - -140	
	605 m	- 90 - -150	
Fjällveden 4	151 m	- 90	
	317 m	-110	
	410 m	-110	
	496 m	-170	

Appendix 2

(51 571)

Oxidation of copper by sulphate

R. Hallberg and I. Grenthe

Copper is the noblest (i.e. least reactive) of the common engineering materials and has been proposed as a material for canisters for spent nuclear fuel. A detailed discussion of possible corrosion mechanisms for copper has previously been presented in the main report from the Corrosion Institute and in the cited technical reports. The conditions under which metallic copper is thermodynamically stable are discussed in these reports. Published thermodynamic data show that copper can be oxidized in aquatic environments similar to those that may exist in a nuclear fuel repository.

Under the reducing conditions that prevail in groundwater at great depth, the most important of these oxidants is H^+ in combination with another electron acceptor, e.g. Fe(II).

The sulphide content of deep groundwaters is low in many places, less than 0.5 ppm (see appendix 1), while the sulphate contents are often a factor of ten to 100 higher. Relatively large total sulphur contents (around 0.2%) occur in the bentonite grade that is intended to be used as a buffer material in the waste repository.

The maximum corrosion of copper is determined by, among other things, the quantity of oxidants supplied; here, the quantity of sulphate is often dominant.

It is well known from the chemical literature that redox reactions that take place with the transfer of several electrons and a change of the chemical composition of oxidants or reductants are slow. The thermodynamically possible redox reactions of this kind are kinetically inhibited.

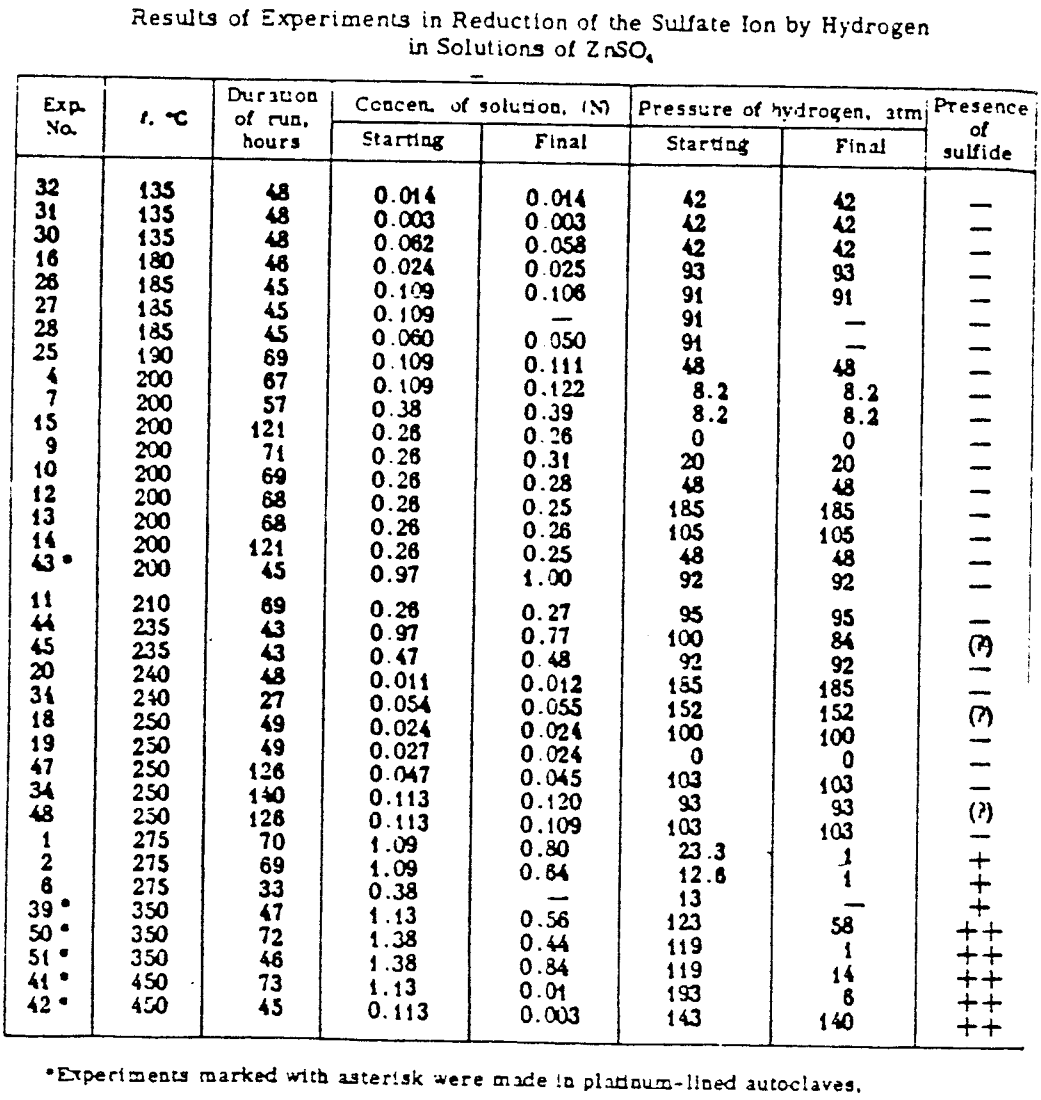
In the case of sulphate, the kinetic inhibition is so strong that no examples of inorganic reduction of sulphate in aqueous solution and at room temperature are known. The following quote from R. A. Berner's "Principles of Chemical Sedimentology", McGraw Hill, 1971, page 132, illustrates this: "The rate of nonbiological reduction of SO_4^{2-} to H_2S by geologically reasonable reducing agents at room temperature is immeasurably slow."

We have attempted to verify this claim with different kinds of literature data.

Reduction of sulphate by hydrogen

Malinin and Khitarov (1969) have carried out semiquantitative determinations of the reduction of SO_4^{2-} in solution with hydrogen at high pressures and temperatures. The authors conclude, op. cit page 1025: "The resistance of SO_4^{2-} to reduction at 200°C must be noted again: it remains stable despite the fact that low temperatures favour reduction from the thermodynamic point of view." Measurable reduction does not occur until at 275°C and at a hydrogen pressure of several tens of atmospheres. The following table presents the results of the experimental measurements:

Results of experiments in reduction of the sulphate ion by hydrogen in solutions of $ZnSO_4$



Results of Experiments in Reduction of the Sulfate Ion by Hydrogen in Solutions of $ZnSO_4$

Exp. No.	*t*, °C	Duration of run, hours	Concen. of solution, (N)		Pressure of hydrogen, atm		Presence of sulfide
			Starting	Final	Starting	Final	
32	135	48	0.014	0.014	42	42	—
31	135	48	0.003	0.003	42	42	—
30	135	48	0.062	0.058	42	42	—
16	180	48	0.024	0.025	93	93	—
26	185	45	0.109	0.106	91	91	—
27	135	45	0.109	—	91	—	—
28	185	45	0.060	0.050	91	—	—
25	190	69	0.109	0.111	48	48	—
4	200	67	0.109	0.122	8.2	8.2	—
7	200	57	0.38	0.39	8.2	8.2	—
15	200	121	0.28	0.26	0	0	—
9	200	71	0.26	0.31	20	20	—
10	200	69	0.26	0.28	48	48	—
12	200	68	0.26	0.25	185	185	—
13	200	68	0.26	0.26	105	105	—
14	200	121	0.26	0.25	48	48	—
43*	200	45	0.97	1.00	92	92	—
11	210	69	0.26	0.27	95	95	—
44	235	43	0.97	0.77	100	84	(?)
45	235	43	0.47	0.48	92	92	—
20	240	48	0.011	0.012	155	185	—
34	240	27	0.054	0.055	152	152	(?)
18	250	49	0.024	0.024	100	100	—
19	250	49	0.027	0.024	0	0	—
47	250	126	0.047	0.045	103	103	—
34	250	140	0.113	0.120	93	93	(?)
48	250	126	0.113	0.109	103	103	—
1	275	70	1.09	0.80	23.3	1	+
2	275	69	1.09	0.84	12.6	1	+
6	275	33	0.38	—	13	—	+
39*	350	47	1.13	0.56	123	58	++
50*	350	72	1.38	0.44	119	1	++
51*	350	46	1.38	0.84	119	14	++
41*	450	73	1.13	0.01	193	6	++
42*	450	45	0.113	0.003	143	140	++

*Experiments marked with asterisk were made in platinum-lined autoclaves.

Sulphur isotope data

Ohmoto (1972) has, after a survey of the literature (11 references), found reason to draw the following conclusion (page 576): ... "all suggests that the rates of both chemical and isotopic exchange reactions, particularly between the reduced and oxidized sulphur species, are extremely slow at temperatures below about 200°C."

Biologically catalyzed sulphate reduction

The reactions for sulphur can, however, be catalyzed by micro-organisms. This takes place with the aid of dissimilatorially sulphate-reducing bacteria.

$$HSO_4^- + 9H^+ + 8e^- \xrightarrow{\text{sulphate-reducing bact.}} H_2S + 4H_2O$$

The hydrogen sulphide formed is protolysed according to the following equation:

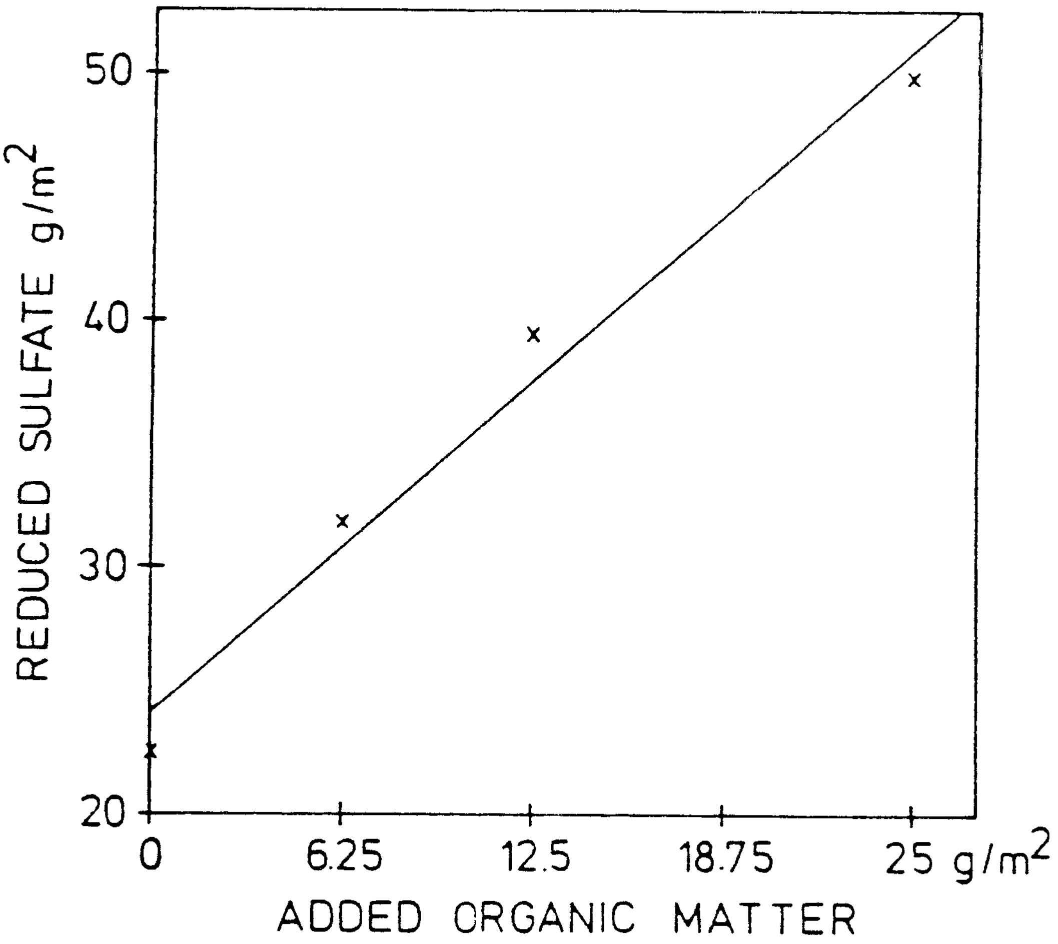
$$H_2S \rightleftharpoons HS^- + H^+ \quad pK = 6.9$$

Thus, both H_2S and HS^- will be present at the pH values that can be expected in the planned final repository. These substances can react either directly or via other metal sulphides with the copper canister and form copper sulphides. Copper as a canister material can thus be expected to corrode in a repository with groundwater at a depth where the water is oxygen-free, since such water usually contains sulphide ions as a result of the above bacterial process.

The quantity of hydrogen sulphide that can be formed is limited by the factors which in turn limit the bacterial process. These organisms are strictly anaerobic, i.e. they require an oxygen-free environment. In groundwater, oxygen is consumed quite soon through a number of processes, both inorganic and biological. We can therefore assume that this requirement is always fulfilled very soon after the closure of the repository.

Sulphate-reducing bacteria are heterotrophic, which means they require a source of organic carbon for their growth and reproduction. One of the most recent reviews of the bacteria of the S cycle and their nutritional requirements is a paper by Trüper (1982). Examples of suitable hydrocarbons for the sulphate-reducing organisms in question are acetate, formiate, propionate and fatty acids up to C_{18}. Thus, they normally require rather simple hydrocarbons, but for conservative reasons, we should assume that all organic matter that is supplied to the final repository is degradable.

In an experiment in a natural environment, Bågander (1977) has demonstrated a clear relationship between added quantities of organic matter (Chladophora detritus) and the quantity of reduced sulphate. The experiment lasted for 250 days at pH = 7 and Eh = -200 mV.



Goldhaber and Kaplan (1975) have carried out a number of model calculations of the rate of biological sulphate reduction in marine sediments. The calculations showed reduction rates down to 10^{-7} mol l^{-1} $year^{-1}$ (op. cit table 1 page 46). Biological sulphate reduction is expected to be many orders or magnitude faster than the inorganic process. The calculation method used is not without objection, but the authors nevertheless draw the following conclusion, op. cit page 45: "We believe that mathematical modelling gives a reasonable perspective on the variability in sulphate reduction rates between different sedimentary environments."

Geological evidence for inhibition of sulphate reduction

There are many thermodynamically possible redox reactions between SO_4^{2-} and Fe(II), for example the following:

$$9FeCO_3(s) + SO_4^{2-}(aq) + 8H_2O(l) \rightarrow FeS(s) + 4Fe_2O_3(s) + 9HCO_3^-(aq) + 7H^+$$

$$\Delta G^o = 85 \text{ kcal}$$

In groundwater with $pH = 8.5$ and $pHCO_3 = 2.7$; ordinary values in granitic groundwaters are:

$$pSO_4^{2-} - 9pHCO_3^- - 7pH = -62$$

i.e. $pSO_4^{2-} = 21.8$ at equilibrium.

Groundwater always has <u>much</u> higher sulphate contents than 10^{-22} M!

Siderite, which is a common fracture mineral, would be expected to have a surface coating of $Fe_2O_3(s)$ <u>if</u> the above reaction were not kinetically inhibited. Siderite does not normally have surface coatings of this type, which can be viewed as additional evidence for strong kinetic inhibitions of inorganic sulphate reduction.

Reduction of sulphate in the presence of native copper

The processes mentioned previously for the reduction of sulphate all took place without the simultaneous presence of copper. It is conceivable that the presence of metallic copper could catalyze the reduction of sulphate. But there is no evidence for such a hypothesis in the literature.

W. Lindgren, in "Mineral Deposits", 4th Ed. McGraw Hill New York 1933, describes the composition of groundwater from the Quincy Mine in the Lake Superior district, a mine which contains a great deal of native copper and very insignificant amounts of copper sulphide (this is a rule for all native copper deposits). The composition of the mine water is shown in the following table.

Table. Mine water from the 4 000 foot level in the Quincy Mine in the Lake Superior district.

Cl^-	176 g/l	SiO_2	0.02 g/l
Bi	2.2 g/l	$(Fe,Al)_2O_3$	0.01 "
Ca^{2+}	86.5 "	Mn	0.04 "
Na^+	15.2 "	Cu	0.016 "
K^+	0.41 "	Ni	0.006 "
SO_4^{2}	0.11 "	Mg	0.02 "

The water is extremely saline, which means that it is probably very old (Frape, S.K. and Fritz, P. TR-201, page 46 op. cit: "At present, we can only say that the Canadian Shield brines appear to be very old. The most likely age based in isotopic composition of ancient sea waters and tectonic evidence would be Devonian (350-400 million years)." Chemistry and Geochemistry - Proceedings of the Thirteenth Information Meeting of the Nuclear Fuel Waste Management Program", Pinawa, Manitoba, Canada, Vol. I, October 1982; see also Fritz, P, and Frape, S. K., Chemical Geology 36 (1982) 179) and has therefore not been in contact with the local and regional water circulation systems. This type of saline water is common at great depths in the Canadian Shield (Fritz, P. and Frape, S. K. Chemical Geology 36 (1982) 179).

The mineralization is surrounded by a relatively porous basalt containing around 10% Fe(II). This is the probable source of the iron in the mine water. The iron analysis is reported in the form of oxide, but the transport in the water has naturally taken place in the form of dissolved Fe(II). The almost total absence of sulphides in the mineralization indicates that the sulphate does not stem from a bacterial oxidation of sulphide.

The Quincy mineralization is a good example of a geological system where native copper has been in contact with water containing both sulphate and iron(II) without any appreciable quantities of Cu_2S forming. Both the geological formation and the groundwater are very old, furnishing additional evidence for the strong kinetic inhibition of redox processes with sulphate.

With the examples given above, we feel we have shown that the inorganic reduction of sulphate, with or without the presence of copper, takes place at such a low rate that sulphate does not have to be taken into account in calculating the life of copper canisters for radioative waste to any greater extent than the quantity that can be reduced with the aid of organic matter.

References:

Bågander L.E. 1977. Sulphur fluxes at the sediment - water interface - an in situ study of closed systems, Eh and pH. pH.D. thesis, Microbial Geochemistry. 1, 127 pp.

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Ohmoto H. 1972. Systematics of sulphur and carbon isotopes in hydrothermal ore deposits. Economic Geology. 67:5, 551-578.

Trüper H.G. 1982. Microbial processes in the sulphur cycle through time. (In: Holland H.D. and Schidlowski M., Mineral deposits and the evolution of the biosphere.) Dahlem Konferenzen 23, 5-30. Springer Verlag.

Appendix 3
(51 571)

THERMODYNAMIC ESTIMATES OF THE SOLUBILITY OF COPPER IN CONTACT WITH GROUNDWATERS OF DIFFERENT COMPOSITION

Tom Wallin

This report was commissioned by SKBF/KBS

1982-03-01

SUMMARY

Background

In a number of cases both in Sweden (e.g. in Finnsjön) and abroad, it has been observed that the composition of groundwater can deviate greatly from that which was assumed in the model calculations presented in KBS Report No. 90. The present report describes thermodynamic calculations carried out in an attempt to estimate the changes in the stability of copper and the changes in the total equilibrium concentration of dissolved copper species that occur in connection with different groundwater compositions.

Scope

The calculations have been carried out at 25°C for three groundwaters that deviate in different ways from the "normal water" that was assumed in KBS Report No. 90, Appendix B1:

I : Elevated chloride ion concentration (35 500 ppm) at pH = 8.5
II : Groundwater with the highest values of Cl^-, HCO_3^-, SO_4^{2-} and F^- concentrations that have been observed and at the lowest measured pH value = 6.3
III : Composition as II but with the highest measured pH value = 9.2

Results

- The total concentrations of dissolved copper species in equilibrium with metallic copper at different redox potentials (pe <0) will be completely determined in I, II and III by copper(I)chloride complexing. The total concentration increases at 35 500 ppm Cl^- by 4 powers of ten compared to "normal water". The relatively large changes in the equilibrium concentrations of the hydroxide, carbonate, sulphate and fluoride complexes do thus not affect the total concentration significantly at pe <0.

- When the pH decreases to 6.3, the stability range of the metallic copper is displaced towards higher pe values. At pH = 6.3, Cu(s) is stable up to pe = 1.66 (Eh = 98 mV). At pH = 9.2, the upper limit of the stability range is pe = -1.24 (Eh = -73 mV).

- At pH = 6.3 (II), $Cu(OH)_{1.5}Cl_{0.5}(s)$ is the stable phase at high pe values (in "normal water" CuO(s)).

- If $Cu_2S(s)$ can be formed, the total Cu concentration in the solution will be very low throughout its stability range. At pH = 6.3, $Cu_2S(s)$ is stable when pe <-0.40. Cu(s) is then stable only in the range -0.40 <pe <1.66.

INTRODUCTION

As a basis for the thermodynamic estimates of the highest total concentrations of dissolved copper species that can occur in equilibrium with metallic copper that were made in KBS Report No. 90, Appendix B (1.), a so-called "normal water" was used. The composition of this normal water is shown in table 1. Calculations have also been carried out for some minor deviations from this composition.

Since that time, measurements and analyses of groundwater have been carried out in situ at, among other places, Finnsjön, Kråkemåla and Sternö (2.). In addition, new data are available today on groundwater compositions from Canadian studies, among others (3.).

Large variations have been found in these studies in the composition of the groundwater, and in some cases large deviations from "normal water". This applies above all to chloride ion concentrations and pH, but higher sulphate, hydrogen carbonate and fluoride ion concentrations have also been measured.

The different concentrations change the equilibrium concentration of copper species in contact with metallic copper and shift the stability ranges for the solid phases.

In the present study, thermodynamic estimates have been made of the changes that could be caused by some observed extreme values of anion concentrations.

CONCENTRATION VARIATIONS IN GROUNDWATER

The composition of the "normal water" used in the thermodynamic calculations in KBS No. 90 Appendix B (1.) is given in table 1. Table 2 contains data on the probable composition and maximum values for groundwaters at great depths as given in KBS No. 90 (1.). SGU's (the Geological Survey of Sweden) measurement results from the investigations at Finnsjön, Kråkemåla and Sternö have been reported in Ref. 2. An excerpt that shows examples of measurement results from Finnsjön is appended in table 3. The groundwater compositions in different bedrocks reported by the AECL (3.) are given in table 4.

Extreme values of pH, [Cl^-], [HCO_3^-], [SO_4^{2-}] and [F^-] from these sources have been compiled in table 5. It is evident there that the maximum concentrations measured by SGU for all ionic species significantly exceed those that were assumed in "normal water". Extremely high chloride and sulphate concentrations are given for saline groundwaters in the Canadian report.

MODELS FOR THE EQUILIBRIUM CALCULATIONS

The thermodynamic calculations have been carried out for 3 different groundwater compositions with extreme concentration conditions:

I : "Normal water" according to table 1, but with a high chloride ion concentration, Cl^- = 35 500 ppm = 1 M
II : Cl^- = 35 500 ppm
HCO_3^- = 400 ppm
SO_4^{2-} = 1 040 ppm
F^- = 7.0 ppm
pH = 6.3
III : As II, but with pH = 9.2

The calculations have been carried out using the same method as that employed in KBS No. 90, Appendix B1, which is also appended as an Appendix here. Thus, the activity ratios between different species within the system have been calculated at 25°C and at different redox potentials. The equilibrium constants have been taken from the Appendix. From the relative diagrams plotted in this manner, it has been possible to determine dominant species and stability ranges for the solid phases. Adding together the concentrations of the species that dominate in equilibrium with metallic copper then gives the total concentration of copper in the groundwater at different redox potentials.

RESULTS

Groundwater I

The redox diagram for copper in equilibrium with "normal water" is shown in Figure 1. In addition, lines have been plotted for the species that are affected by an increase in the chloride concentration to 100 mM (35 500 ppm). It can be seen that at pe values <-0.54 (Eh <-32 mV), metallic copper is stable and that $CuCl_2^-$, $CuCl_3^{2-}$ and $Cu_2Cl_4^{2-}$ dominate in the solution. No other ions contribute significantly to the total concentration of copper.

The thermodynamic stability of $Cu(OH)_{1.5}Cl_{0.5}(s)$ is so nearly equal to the stability of CuO(s) at the high chloride concentration that it is difficult due to the uncertainty in the equilibrium constants to determine which of them exists at high pe values.

Groundwater II

At pH = 6.3, carbonate occurs in the form of H_2CO_3 and in the form of HCO_3^-. At the given total concentration of carbonate, $pHCO_3^- = 2.51$.

For dissolved species, the concentration of hydroxide and carbonate complex will decrease substantially in relation to "normal water", while the fluoride and sulphate complexes will increase slightly. However, the copper(I) chloride complexes are completely dominant in groundwater II as well. In the redox diagram, the lines for $CuCl_2^-$, $CuCl_3^-$ and $Cu_2Cl_4^{2-}$ will be identical to those given for these species in Figure 1 at 1 000 mM Cl^-.

The pH reduction to pH = 6.3 leads to a widening of the stability range for Cu(s) all the way up to pe = 1.66 where $Cu_2O(s)$ is formed. At high pe values, $Cu(OH)_{1.5}Cl_{0.5}(s)$ is stable instead of CuO(s).

If it is assumed that $Cu_2S(s)$ can be formed, its stability range will also be shifted towards higher pe values. If the constant values given in KBS No. 90 are used, $Cu_2S(s)$ will be stable at redox potentials that are lower than pe = -0.40 (Eh = -24 mV) in groundwater II.

Groundwater III

At pH = 9.2, $pHCO_3^- = 2.21$. The concentrations of all dissolved complexes increase in relation to "normal water". As in Groundwaters I and II, however, the copper(I)chloride complexes will be completely dominant and thus determine the total concentration of copper.

In Groundwater III, Cu(s) will only be stable up to pe = -1.24, where $Cu_2O(s)$ is formed. If $Cu_2S(s)$ is assumed to be present, it is stable at pe values below -4.25 (Eh = -251 mV).

Total concentrations

The total concentration of dissolved copper species ($CuCl_2^-$, $CuCl_3^{2-}$ and $Cu_2Cl_4^{2-}$) in equilibrium with Cu(s) has been summarized in table 6. This is representative of all three groundwater compositions in the different parts of the pe range where Cu(s) is stable (For I below pe = -0.54, for II below pe = 1.66 and for III below pe = -1.24). In Figure 2, the total concentration line for 1 000 mM Cl^- has been drawn together with earlier calculations from KBS No. 90, Appendix B1. As can be seen, the total concentrations at equilibrium are about 10^4 times greater than in "normal water".

Calculations have also been carried out under the assumption that $Cu_2S(s)$ is formed and in consideration of the fact that $Cu_2O(s)$ becomes stable in some cases already at pe <0. The total concentrations of copper that are thereby obtained in the pe range -9 - 0 are shown in table 7.

The great concentration-reducing effect of $Cu_2S(s)$ is clear. It can also be seen that the oxidation to $Cu_2O(s)$ leads to a reduced concentration of copper species in the solution in the range above pe = -1 for the compositions I and III.

DISCUSSION

The parameters that determine both the existence ranges of the solid phases and the total concentrations of dissolved species at equilibrium in the investigated systems are redox potential, pH and chloride ion concentration. It has been assumed in the calculations that sufficient oxidant reaches the copper metal in order for the equilibrium concentrations to be reached. The other limitations in the calculations have also been the same as those given in the Appendix.

It nevertheless deserves to be mentioned that both the AECL work and the SGU measurements have reported nitrate concentrations that exceed those discussed in KBS No. 90, and that the SGU measurements have found some NH_4^+. The higher sulphate ion concentration should also be borne in mind in any further discussions of the probability of sulphate reduction. Temperature effects were not to be dealt with in this report.

REFERENCES

1. KBS Technical Report No. 90, 1978-03-31. "Copper as canister material for unreprocessed nuclear waste - evaluation with respect to corrosion."

2. "Grundvatten i kristallin berggrund" ("Groundwater in crystalline bedrock"), SGU, July 1981.

3. "The corrosion behaviour of copper under simulated nuclear fuel waste repository conditions", King P. J. et al, Proc 81CMC, Mainz, September 1981, p 1650.

Groundwater composition used in thermodynamic calculations in KBS No. 90 (Ref. 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 M
$[O_2]$	0	

Table 4.

Groundwater compositions, AECL (Ref. 3)

RANGE OF EXPECTED GROUNDWATER COMPOSITIONS

	Concentration in mg/L			
	Granite GGW	Basalt BGW	Saline WN1	Saline SCSSS
Na	8.3	30.0	1910	5 050
K	3.5	9.4	14	50
Mg	3.9	1.0	61	200
Ca	13.0	6.6	2130	15 000
Sr	—	—	24	20
Fe	—	—	0.6	—
HCO_3	—	58	68	10
Cl	5.0	16	6460	34 260
SO_4	8.6	24	1040	790
NO_3	0.6	—	33	50
F	0.2	0.8	—	—
pH	6.5±0.5	8.0±0.3	7±0.5	7±0.5

TABLE III

CORROSION OF COPPER IN WN1 SALINE SOLUTION AND BENTONITE AT 75°C

Time of Immersion (days)	Air Saturated		Air Free	
	Corrosion Current μa/cm²	Penetration Rate μm/yr	Corrosion Current μa/cm²	Penetration Rate μm/yr
1	—	—	0.7	8.0
2 (24 C)	1.0	12	0.21	2.4
3 (65 C)	1.0	12	0.08	0.90
4 (65 C)	—	—	0.040	0.45
5	3.5	40	0.082	0.95
8	6.3	75	0.055	0.63
9	9.1	105	0.044	0.50
10	8.6	100	0.044	0.50
11	14.4	165	0.047	0.55
125	14.4	165	—	--
15	17.2	200	0.047	0.55

TEST ENVIRONMENTS

Representative of	Temperature °C	Atmosphere	Test Type
Pre-closure early	75	Air, 1 atm	Electrochemical
Post-closure early	150	N_2, 10 atm	Immersion
Post-closure late	75	N_2, 1 atm	Electrochemical

TABLE IV

CORROSION OF COPPER IN WN1 SALINE SOLUTION AT 150°C, AIR FREE

Time of Immersion (days)	Average Penetration (μm)	Corrosion Rate (μm/yr)
No Bentonite		
7	0.10	5.2
10	0.26	9.5
40	0.35	3.2
50	0.36	2.6
80	0.46	2.1
90	0.60	2.4
With Bentonite		
20	0.20	3.6
50	0.43	3.1
100	0.38	1.4

Table 2.

Groundwater composition according to KBS No. 90 (Ref. 1)

Analysis	Units	Probable interval	Min. value[x)]	Max. value
Conductivity	S/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) Estimated probability for that the values will not be lower than the minimum or higher than the maximum is 95%

Table 3.

Groundwater analyses according to SGU report (Ref. 2)

Examples of analyses from Finnsjön

Site	Borehole	Depth	Date	Cond. lab. s/cm	Cond. field s/cm	pH lab.	pH field	MnO$_4$ demand	Total hardness Ca	Total org. carbon	SiO$_2$
3	2	385	771203	510	-	7.75	-	44	37	9.8	6.2
3	2	385	771207	520	-	7.65	-	40	36	9.8	6.0
3	4	152	791026	990	800	8.05	8.50	50	33	9.2	15
3	4	152	791030	950	700	7.90	8.45	42	32	8.6	14
3	4	152	791204	970	760	7.95	8.70	42	33	8.4	13
3	4	152	791212	940	710	7.95	8.80	46	39	10.0	14
3	4	247	800117	1200	980	8.00	9.15	40	52	8.6	14
3	4	247	800123	1600	1100	7.80	9.10	35	92	8.4	10
3	4	247	800229	780	660	7.80	8.00	38	31	10.0	16
3	4	368	800314	770	700	7.90	8.40	38	30	10.6	16
3	4	368	800328	760	590	7.90	8.10	38	30	9.0	17
3	4	368	800426	780	485	7.80	7.60	36	28	8.4	13
3	4	368	800429	770	500	7.80	7.70	37	28	7.8	15
3	4	534	800507	780	535	7.80	7.70	44	29	7.8	12
3	4	534	800514	780	645	7.80	7.80	44	29	7.8	13
3	4	534	800521	770	575	7.70	7.60	45	29	7.8	13
3	4	534	800528	770	570	7.80	7.65	43	29	8.0	14
3	5	141	790814	8300	-	7.50	-	20	800	3.6	8.6
3	5	141	790911	7600	6600	7.65	7.55	19	790	4.0	11
3	5	141	791003	7500	5500	7.65	7.70	32	744	4.2	12
3	5	141	791018	7500	5300	7.60	7.80	36	744	4.2	12
3	5	141	791206	7300	5350	7.55	8.40	34	745	3.8	10
3	5	205	800118	9600	7100	7.60	8.60	35	1140	4.3	5.0
3	5	205	800125	9500	6800	7.70	8.75	35	1090	3.7	10
3	5	205	800129	9400	6800	7.60	8.70	35	1060	3.9	9.0
3	5	205	800208	9100	5900	7.60	7.90	35	1100	3.8	10
3	5	205	800215	9000	6100	7.30	7.95	25	1080	3.6	9.5
3	5	297	800320	12500	7100	7.60	8.40	38	1605	3.0	9.5
3	5	297	800328	13000	7800	7.60	8.30	30	1615	2.8	11
3	5	297	800411	12000	7800	7.40	8.30	10	1660	1.9	11
3	5	297	800417	12000	6700	7.40	7.85	10	1615	1.9	11
3	5	297	800422	12000	6600	7.00	8.00	10	1615	1.9	7.0
3	5	297	800428	15500	5950	7.60	7.85	9	1630	1.6	11
3	5	384	800514	18000	5550	7.40	7.75	9	1935	1.2	12
3	5	384	800521	18500	4300	7.40	7.55	9	1955	1.0	11
3	5	384	800528	18500	4250	7.50	7.70	6	1940	1.2	12
3	7	123	800902	500	-	7.85	-	36	45	6.2	16

Table 18 cont'd.

SGU analyses con't.

Site	Borehole	Depth (m)	Date	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NH_4	NO_2	NO_3	PO_4	Fe^{2+}	Fe (total)	Mn	F
3	2	385	771203	30	4.5	92	4.4	24	2.1	325	0.11	<0.01	0.18	<0.01	-	6.6	0.14	1.5
3	2	385	771207	30	4	96	5.6	32	2.4	320	0.08	<0.01	0.22	<0.01	-	7.8	0.10	1.5
3	4	152	791026	23	6	180	2.9	136	47	383	0.18	0.02	0.04	0.09	-	2.4	0.05	3.3
3	4	152	791030	25	4	225	3.0	127	44	386	0.17	<0.01	0.08	0.07	1.8	1.8	0.04	3.5
3	4	152	791204	24	5.5	225	3.1	133	48	390	0.20	0.01	0.20	0.06	4.8	5.1	0.06	3.5
3	4	152	791212	23	9.5	210	3.1	124	46	389	0.17	0.01	0.10	0.05	3.3	3.4	0.05	3.5
3	4	247	800117	40	7	215	3	200	40	360	0.26	0.01	0.01	0.06	3.2	3.2	0.06	2.5
3	4	247	800123	76	10	275	4	360	51	335	0.29	0.02	<0.01	0.06	5.8	5.8	0.11	2.5
3	4	247	800229	24	4	170	2.8	74	30	390	0.20	<0.01	0.09	0.16	6.1	6.1	0.08	2.1
3	4	368	800314	23	4	165	2.7	72	30	388	0.21	<0.01	0.09	0.16	3.8	3.8	0.07	2.1
3	4	368	800328	23	4	165	2.8	70	28	387	0.20	<0.01	0.09	0.22	3.0	3.0	0.05	2.1
3	4	368	800426	22	4	165	2.8	72	25	397	0.24	<0.01	0.04	0.09	1.9	9.2	0.08	2.6
3	4	368	800429	22	4	165	2.7	72	29	395	0.23	<0.01	0.04	0.09	7.8	9.7	0.08	2.0
3	4	534	800507	22	4	165	2.9	75	29	395	0.23	0.03	0.02	0.09	7.3	8.0	0.08	2.2
3	4	534	800514	22	4	170	2.8	75	29	393	0.23	0.03	0.03	0.08	6.8	6.8	0.07	2.2
3	4	534	800521	22	4	170	2.8	75	19	393	0.22	0.03	0.03	0.09	2.4	7.9	0.05	3.0
3	4	534	800528	22	4	170	2.7	75	19	393	0.27	0.03	0.03	0.08	5.9	5.9	0.06	3.0
3	5	141	790814	650	89	900	10	2650	224	151	1.34	0.02	0.07	0.05	-	2.9	0.71	0.90
3	5	141	790911	640	89	900	10	2520	225	166	1.38	0.03	0.05	0.06	-	2.8	0.75	1.1
3	5	141	791003	641	62	875	9.1	2700	224	161	1.37	0.02	0.05	0.05	-	3.1	0.75	1.1
3	5	141	791018	643	79	900	9.1	2700	197	161	1.32	0.02	0.03	0.07	-	2.7	0.75	1.1
3	5	141	791206	630	70	1000	10	2580	236	161	1.40	0.02	0.11	0.10	7.4	9.2	0.74	1.2
3	5	205	800118	955	110	1100	10	3500	300	70	0.75	0.04	<0.01	0.13	3.2	3.7	0.59	0.74
3	5	205	800125	875	130	1100	10	3400	325	84	0.85	0.03	<0.01	0.13	2.9	3.1	0.65	0.90
3	5	205	800129	875	110	1100	10	3400	325	85	0.86	0.02	<0.01	0.14	3.0	3.0	0.66	0.86
3	5	205	800208	875	140	1100	10	3400	320	85	0.87	0.03	<0.01	0.14	2.7	3.1	0.67	0.82
3	5	205	800215	900	110	1100	9.4	3450	325	83	0.03	2.20	<0.10	0.13	3.4	6.2	0.67	0.74
3	5	297	800320	1440	100	1250	7.6	4580	325	39	0.21	0.02	0.10	0.16	3.5	3.5	0.41	0.74
3	5	297	800328	1450	100	1300	7.5	4700	330	39	0.21	0.03	0.10	0.18	2.9	3.1	0.44	0.75
3	5	297	800411	1530	80	1380	7.3	4500	288	38	0.20	0.01	0.02	0.16	2.2	2.5	0.46	1.2
3	5	297	800417	1500	70	1380	7.2	4650	300	39	0.21	0.01	0.04	0.15	2.4	2.4	0.47	1.3
3	5	297	800422	1500	70	1320	7.2	4650	300	33	0.20	0.01	0.02	0.39	2.5	7.0	0.50	1.3
3	5	297	800428	1500	80	1320	6.9	4750	300	39	0.21	0.01	<0.01	0.15	2.2	2.2	0.47	1.4
3	5	384	800514	1730	125	1480	8.0	5650	312	39	0.44	<0.01	0.02	0.16	2.5	3.0	0.70	1.1
3	5	384	800521	1790	100	1500	8.3	5650	324	44	0.44	<0.01	0.02	0.19	2.4	3.4	0.70	1.1
3	5	384	800528	1790	90	1460	8.2	5500	312	41	0.48	<0.01	<0.01	0.17	2.8	3.4	0.83	1.1
	7	123	800902	36	5.5	94	1.4	23	7	333	0.07	0.12	0.92	0.03	2.9	2.9	0.13	2.0

Table 5. Maximum concentrations of some ions in the groundwater

	KBS No. 90 "normal water" mg/l	KBS No. 90 max. values mg/l	SGU, max. measured (2.) mg/l	AECL (3.) max. values mg/l
Cl^-	500(5000)	100	5650	34280
HCO_3^-	120	500	395	68
SO_4^{2-}	100	50	330	1040
F^-	1.5	8	7	0.8
$NO_3^-+NO_2$	-	2.5	4.4(0.4)	50
NH_4^+		2	1.4	
pH	8.5(9.5)	9.0(7.2-8.5)	6.3-9.2	6.5-8.0

Figure 1.

Redox diagram for system
$Cu-H_2O-Cl^--CO_3^{2-}-SO_4^{2-}-F$

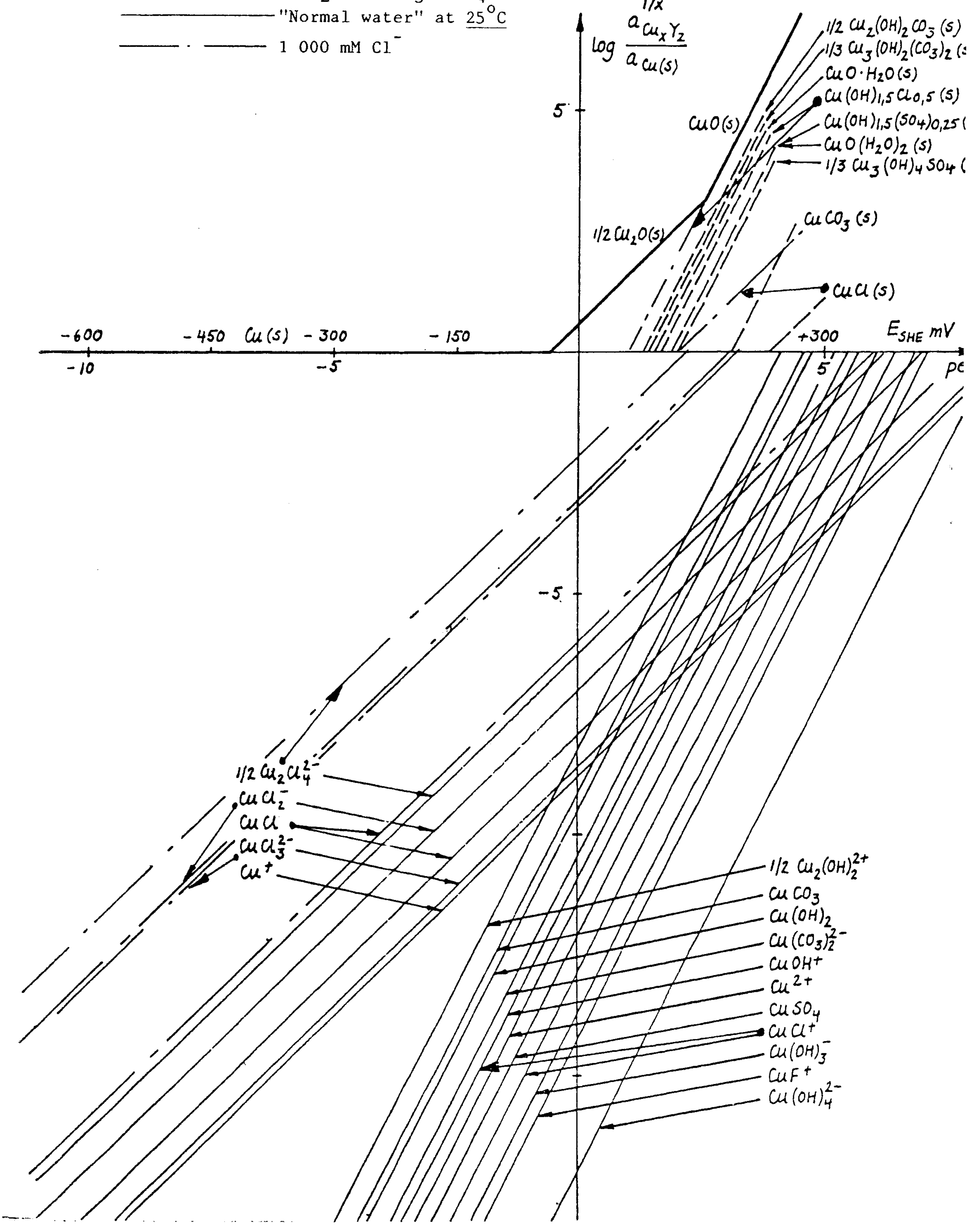

Figure 2.

Total copper concentration
for "normal water" in thermo-
dynamic equilibrium with metallic
copper at various T, pH and Cl^- .

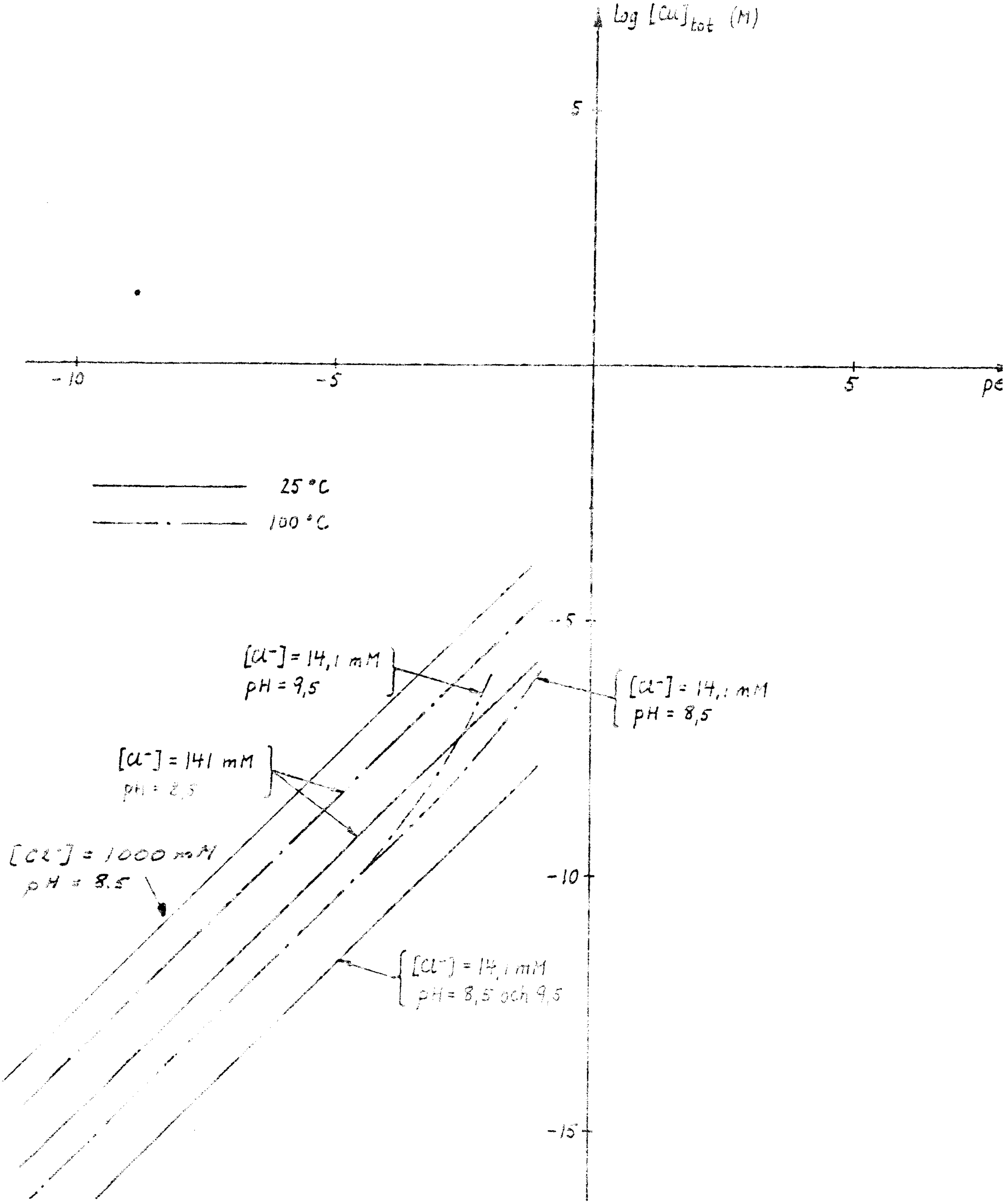

Table 6. Total concentrations of dissolved Cu species at equilibrium with Cu(s)

Groundwaters I, II and III

PE	E(SHE) MV	[CU]TOT M	[CU]TOT MG/L
-9	-532.4	1.4205E-12	.0000000902
-8	-473.3	1.4205E-11	.00000090267
-7	-414.1	1.4205E-10	.0000090267
-6	-354.9	1.4205E-9	.000090267
-5	-295.8	.000000014205	.00090267
-4	-236.6	.00000014205	.0090267
-3	-177.5	.0000014206	.090273
-2	-118.3	.000014213	.90318
-1	-59.2	.00014281	9.075
0	0	.0014965	95.097

Table 7. Total concentrations of dissolved Cu species at equilibrium with Cu(s), Cu_2S(s) and Cu_2O(s) for Groundwaters I, II and III

(Tabell)

PE	I M	II M	III M
-9	1.7078E-29	2.1011E-38	7.9881E-27
-8	1.7078E-25	2.1011E-34	7.9881E-23
-7	1.7078E-21	2.1011E-30	7.9881E-19
-6	1.7078E-17	2.1011E-26	7.9881E-15
-5	1.7078E-13	2.1011E-22	7.9881E-11
-4	1.7078E-9	2.1011E-18	.000000142
-3	.0000014206	2.1012E-14	.000001420
-2	.000014213	2.1023E-10	.000014213
-1	.00014281	.0000021123	.000082179
0	.0004316	.0014965	.000086115

Appendix B1

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 $Cu-H_2O-Cl^--CO_3^{2-}-F^-$ 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):

<u>Table 1</u> 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.

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

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

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. $pe = \frac{F}{RT\ln 10} \cdot E_{SHE}$ 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	100°C
$H^+ + OH^- \rightleftharpoons H_2O$	14.00	12.3
$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$	10.329	10.26
$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$	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
	$CiCl_3^{2-}$	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	-
	$1/sCu_2(OH)_2CO_3(s)$	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 Cy/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 = 5 000 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 production, 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 corrosion 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 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
$Cu\text{-}H_2O\text{-}Cl^-\text{-}CO_3^{2-}\text{-}SO_4^{2-}\text{-}F^-$
"Normal water" at 25°C

KBS report
770516
TW/DL

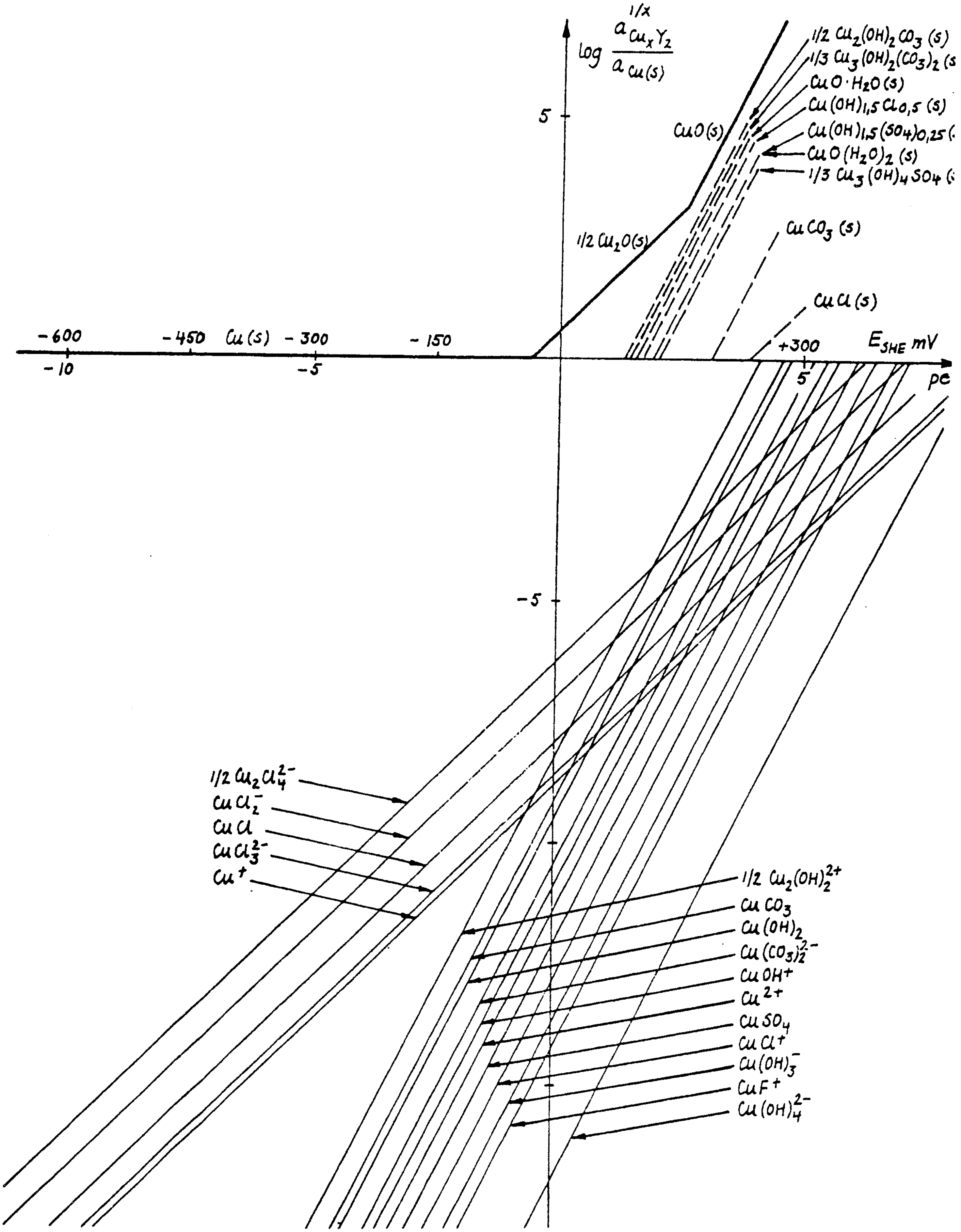

Figure 2

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

KBS report
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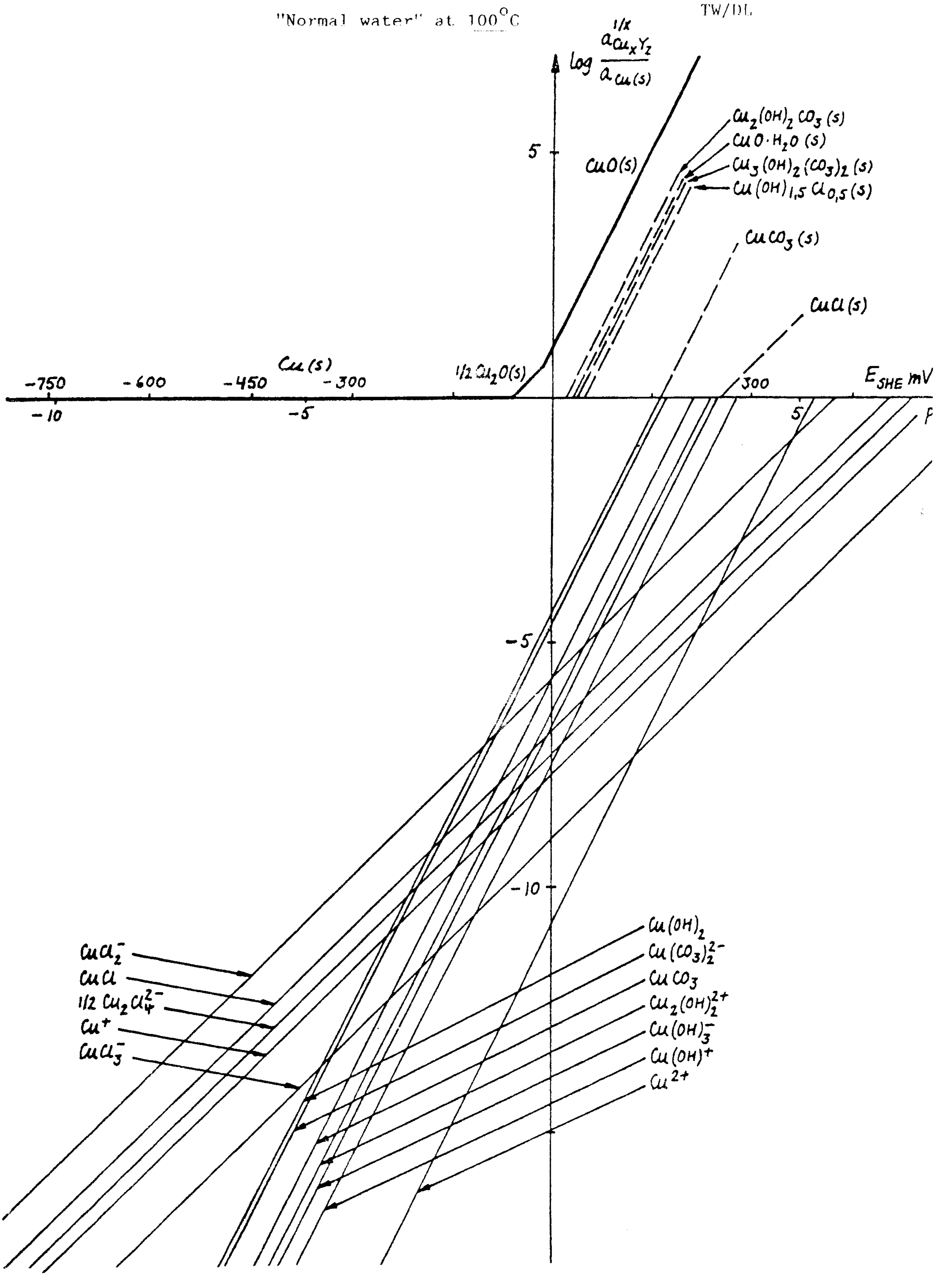

Figure 3

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

KBS report
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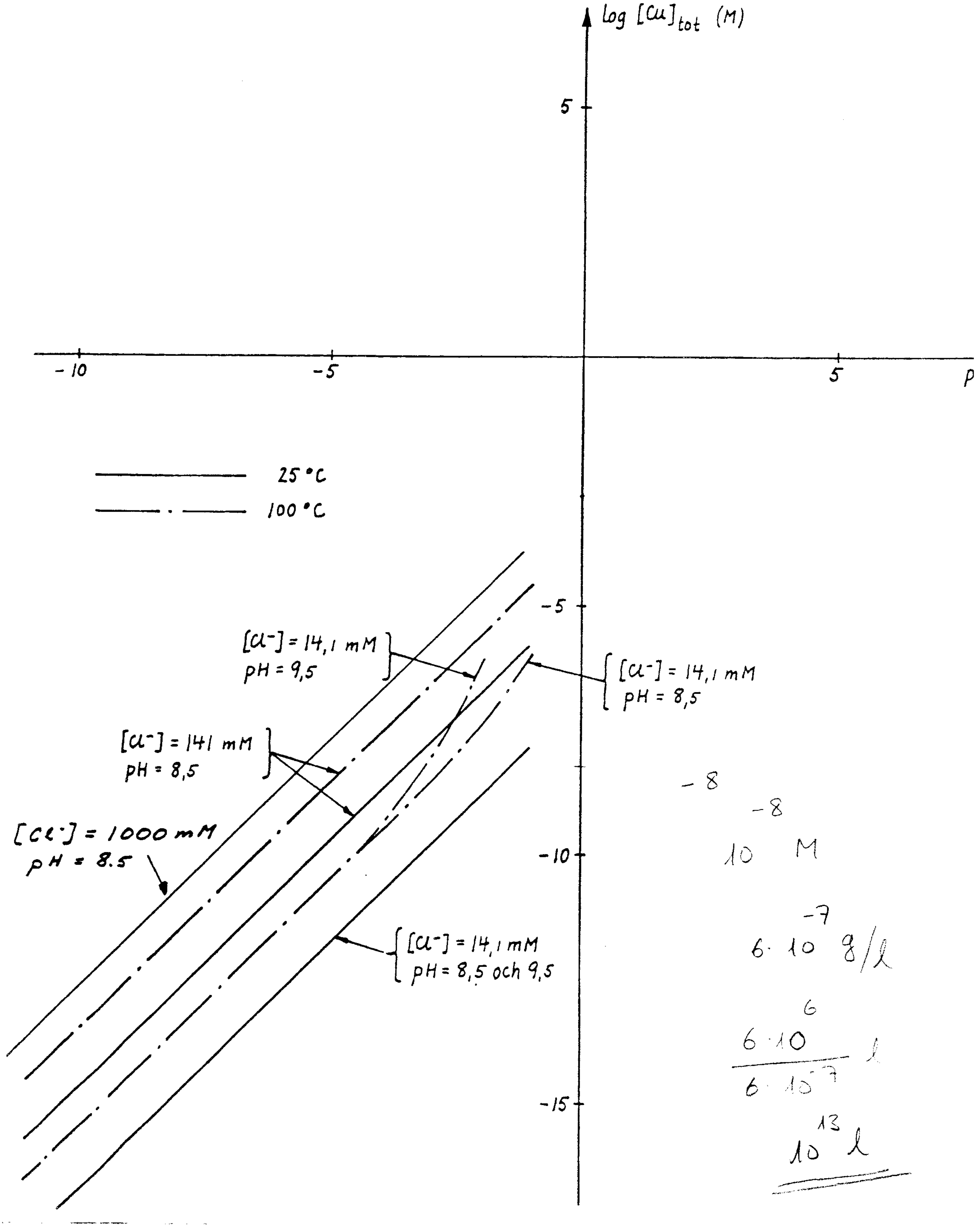

-8

10^{-8} M

$6 \cdot 10^{-7}$ g/l

$\frac{6 \cdot 10^{6}}{6 \cdot 10^{-7}}$ l

10^{13} l

Appendix 4
(51 571)

Approximate calculation of what happens with the oxygen that is entrapped in the repository at the time of its closure.

Contents:

83-02-02
Ivars Neretnieks

Summary

Oxygen that is entrapped with the air in a final repository for spent nuclear fuel can attack the copper canisters. For each copper canister, approx. 100 moles of oxygen are entrapped. This oxygen can diffuse down to the canister through the deposition hole and react with the canister, but it can also react with iron with oxidation number II (Fe(II)). Such iron is present in the clay in the buffer material in great excess - about ten times as much as is needed for all the oxygen. If the clay is burned in order to oxidize organic substances, the possibility cannot presently be ruled out that the iron will also be oxidized. The oxygen can then instead react with Fe(II) in the rock. The oxygen migrates more readily to the tunnel wall and diffuses a few mm into the rock than it diffuses down 2.5 m through compacted clay in the hole to the canister. Calculations show that max. 1.4 moles of the oxygen go down to and react with the copper and 101.6 moles react with Fe(II) in the rock. At the most, 0.5 kg of copper can be oxidized by the oxygen.

Background

When the repository is sealed, there is still air left in the buffer mass. The oxygen in this air can, when it dissolves in intruding water, attack the copper canister. However, the oxygen can also react with iron minerals in the rock that contain bivalent iron. In this approximate calculation, the rate at which the oxygen can be transported to and react with the copper is compared with the rate at which it can be transported to and into the rock.

Premises

The tunnel system consists of a 4 m wide and 3.7 m high tunnel. Every sixth metre, a deposition hole is drilled in the tunnel floor. The hole is 1.5 m in diameter and so deep that the top of the canister is 2.5 m below the floor. The tunnel is filled with a sand-bentonite mixture with a porosity of scarcely 30%. The hole is filled with compacted bentonite with a porosity of 25%. Thus, for each canister there is a tunnel volume 6 m long x 13 m^2 in cross-section = 78 m^3. This volume contains 0.3 x 78 m^3 = 23.4 m^3 of air and water, of which the water takes up more than half the volume. (Pusch 1983.) With the air in the hole, the total quantity of air is 12 m^3. Of this, 21% is oxygen = >2.52 m^3 O_2. This is equivalent to 103.1 moles of O_2.

The clay and the rock contain Fe(II)-containing minerals that react with oxygen. This has been measured by Allard (1983) in experiments with oxygenated water to which clay and crushed rock have been added. Allard found concentrations of between 0.8 and 7% by weight Fe(II). In clay (MX 80), Allard found 1.1% Fe(II).

In a rock with 1% Fe(II) and a density of 2 700 kg/m^3, the iron in 0.426 m^3 of rock is consumed in reacting with the oxygen according to the reaction:

$$4\ Fe^{2+} + 2H_2O + O_2 \rightarrow 4\ Fe^{3+} + 4OH^- \qquad (1)$$

With a tunnel area of 6 x (4 + 3.7) x 2 m^2 = 92.4 m^2, the rock will be oxidized to a depth of 4.6 mm if all the oxygen reacts with the rock.

The buffer material in the tunnel consists of 15% clay (MX-80) or the equivalent. This material has a density of about 1 800 kg/m^3 and contains about 270 kg of clay/m^3. 78 m^3 of buffer then contains 1.1% Fe(II) (232 kg). This is more than ten times the amount needed to react with all the oxygen.

If, however, this reaction should not take place for some reason (if the clay has been burned with air to oxidize organic matter), the oxygen can react with iron in the rock in competition with the copper.

The reactions are assumed to start when the clay has become saturated with water. This takes ten years or so, and the water saturation proceeds most rapidly in the deposition hole with the compacted bentonite. (Pusch 1983.)

Calculation of the competing reactions between oxygen and Fe(II) and oxygen and copper

The reaction between oxygen dissolved in the water and Fe(II) in the rock is rapid, according to Allard's (1983) measurements. If we also assume that the reaction between oxygen and copper is rapid, the reactions will be limited by how rapidly the oxygen can be transported to the reaction zones.

a) Transport to the copper

We assume that the concentration of oxygen in the water-saturated clay is c at the mouth of the deposition hole in the tunnel floor and at the top of the copper canister 2.5 m farther down, the oxygen concentration is zero due to the reaction with the copper. The transport to the canister is determined by the diffusion in the clay.

$$N_k = \frac{D_l}{\Delta z_h} \cdot A_{hole} \cdot (c - o) \text{ mol/s} \qquad (2)$$

where D_l = the diffusivity in the clay

Δz_h = distance between canister and floor in tunnel (z_h = 2.5 m)

c = the concentration at the floor (this is assumed to be the same as in the tunnel, on the average)

b) Transport in buffer in the tunnel and in the rock

The transport to the rock wall where the concentration is assumed to be c_b can be described by an equation analogous to (2)

$$N_b = \frac{D_b \, A_b}{\Delta z_b} \; (c - c_b) \text{ mol/s} \qquad (3)$$

where D_b = the diffusivity in the buffer in the tunnel

A_b = the cross-sectional area for diffusion $\sim$ the tunnel's wall surface area

Δz_b = average diffusion distance to rock wall $\sim$ 1 m

$c - c_b$ = concentration difference between the water in the tunnel on the average -c- and the rock wall -c_b

When the oxygen has diffused to the rock wall, it proceeds further in the rock through the already oxidized layer with a thickness of x. The same quantity - N_b - is transported as in the buffer.

$$N_b = \frac{D_e \, A_b}{x} \, (c_b - o) \qquad (4)$$

D_e = the diffusivity in the rock

The concentration is 0 at the reaction front x m into the rock.

c_b can be eliminated from (3) with (4), whereby we obtain:

$$N_b = \frac{A_b \; c}{\dfrac{\Delta z_b}{D_b} + \dfrac{x}{D_e}} \tag{5}$$

The total amount of oxygen removed from the water in the tunnel is $N_b + N_k = N$

$$N = \left(\frac{D_L \; A_h}{\Delta z_h} + \frac{A_b}{\dfrac{\Delta z_b}{D_b} + \dfrac{x}{D_e}} \right) c \tag{6}$$

The oxygen that reacts with Fe(II) increases the depth of the reaction zone x.

$$\frac{dx}{dt} \cdot A_b \cdot q_o \cdot f = N_b \tag{7}$$

q_o = concentration of Fe(II) in the rock

f = stoichiometric factor in the reaction between Fe(II) and O_2 according to equation (1) $f = \frac{1}{4}$

The oxygen content of the water in the clay decreases according to:

$$\frac{dc}{dt} \cdot V_b \cdot \varepsilon_b = N \tag{8}$$

where V_b = volume of the tunnel m^3

ε_b = porosity of the buffer

Example

The solubility of O_2 in water at 25^oC and 10 bar is $0.2.10^{-3}$ m O_2/mole of water (Perry pages 3-98) (10 bar in the water pressure at a depth of 500 m x fraction of O_2 in air, 103 moles O_2, that dissolves in 23.4 m^3 of water ($1.35 \cdot 10^{-6}$ mol), (all pore volume consists of water when the buffer has been saturated) gives $0.076 \cdot 10^{-3}$ mol O_2/mol H_2O. In other words, all of the oxygen can dissolve in intruding water.

c_o = 4.40 mol/m^3 original oxygen concentration
D_1 = $4 \cdot 10^{-11}$ m^2/s (KBS TR 83 - 33) ← 82-29
D_b = $4 \cdot 10^{-10}$ m^2/s (KBS TR 79 1978)
D_e = $5 \cdot 10^{-14}$ m^2/s (KBS TR 82 - 12)
$A_{hole} = \frac{\pi \cdot 1.5^2}{4} = 1.77\ m^2$

Δz_h = 2.5 m
A_b = 92.4 m^2
Δz_b = 1 m
q_o = 967 moles of Fe(II)/m^3
$f = \frac{1}{4}$
$V_b \varepsilon_b$ = 23.4

While the tunnel is open for 40 years, oxidation of the rock takes place.

Equations (3) and (7) combined give

$$c_b \frac{D_e}{x} = \frac{dx}{dt} \cdot q_o \cdot f \tag{9}$$

c_b = constant when the tunnel is open and corresponds to the solubility at 0.21 bar

c_b = 0.22 mol/m^3

Equation (9) gives after integration

$$x^2 = \frac{2D_e\ c_b}{q_o \cdot f} = t$$

after 40 years, $x = 0.34 \cdot 10^{-3}$ m

i.e. x = 0.34 mm when the tunnel is closed.

Equations 2, 5-8 are solved with the data given above. This is done by means of numerical integration. It is hereby found that the resistance to transport into the rock wall is dominated by the diffusion resistance in the rock over the resistance in the buffer.

This is evident from the fact that the right-hand term in the denominator in equation (5) is larger than the left-hand term already at $x = 0.25$ mm.

If the transport into the rock is compared to the transport to the canister, this ratio varies with x.

The comparison is made by means of the ratio

$$N_b/N_k = \frac{A_b \qquad x_h}{\left(\frac{\Delta z_b}{D_b} + \frac{x}{D_e}\right) D_1 A_{hole}}$$

The smaller x is, the larger fraction of the oxygen goes to the rock.

Table 1 shows N_b/N_k and the integrated quantity that has gone to the rock M_b and the canister M_k as a function of time.

1.5% of the oxygen or 1.5 moles goes to the canister.

Trd	N_b/N_k	x	M_b	M_k	M_V
Year		mm	mol	mol	mol
100	81.6	1.90	43.7	0.28	59
1000	39.0	4.05	90.7	1.18	11.1
2000	35.9	4.43	98.9	1.41	2.59
3000	35.2	4.51	100.8	1.46	0.64
4000	35.03	4.53	101.3	1.48	0.16
5000	35.00	4.54	101.4	1.48	0.04

Table 1. Fraction of the oxygen that goes to the rock in relation to that which goes to the canister N_b/N_k and total quantity that has gone to the rock M_b and the canister M_k in moles at different times. M_v is the quantity of oxygen left in the water.

Results and conclusions

The oxygen entrapped with the air in the tunnel will react for the most part with bivalent iron in the clay in the buffer material, or if bivalent iron is not available in the buffer material, with bivalent iron in the rock. In the latter case, a scarcely 5 mm thick layer of the tunnel wall will have oxidized within a few thousand years. The copper canister will be reached by a few moles of O_2. This amount can oxidize less than 0.5 kg of copper.

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Appendix 5
(61 571)

APPROXIMATE CALCULATION OF CORROSION OF COPPER CANISTER CAUSED BY SULPHATE AND SULPHIDE ATTACK

Contents

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SUMMARY

In a final repository for spent fuel enclosed in copper canisters, sulphide in the buffer and water can attack the copper. Another thermodynamically possible corrodant is sulphate in the presence of bivalent iron. The sulphate reaction is very slow.

Calculations have been carried out in order to shed light on the consequences of the sulphate's reacting at a given rate as well as for the case when the reaction is very fast.

At time constants in the sulphate reaction of about 10^6 years and longer, this reaction decreases in importance in this context.

If the reaction is assumed to be very fast, it is limited by the supply of bivalent iron. The use of a sulphate-poor clay does therefore not reduce a possible sulphate attack very much.

The inward transport of sulphide and possibly sulphate from the tunnel could conceivably cause the attack to be concentrated to the top end of the canister. This inward transport can be reduced to less than 20% by inserting a rock plug above the canister instead of buffer.

It is estimated that the sulphide in clay will corrode approximately 4 kg of copper within 1 000 years. Sulphide supplied from the water in the rock contributes an additional corrosion of max. 10 kg over a period of one million years. A possible sulphate reaction should be able to multiply the attack by a factor of about 10.

1 BACKGROUND

In a conceived final repository for radioactive fuel, the fuel is encapsulated in a copper canister, which is deposited in a borehole in the floor of a tunnel at a depth of about 500 m in crystalline rock. The canister is surrounded by highly-compacted bentonite. See figure 1.

The tunnel is filled with a mixture of bentonite and quartz sand. The bentonite contains some sulphur in the form of sulphide and sulphate. The sulphide sulphur can react with copper. The sulphate sulphur is very slow to react. It also requires access to bivalent iron in order to react. There are three sources of sulphur:

2 SIMPLIFIED CALCULATION MODEL

The flowing groundwater can supply sulphur if the sulphur reacts with the copper, but might also conceivably carry away sulphur that is present in the tunnel and deposition holes if the concentration there is higher than the concentration in the flowing water. Figure 2 shows the transport paths for the sulphur. The transport to or from holes and tunnels can be estimated by the methods developed by Neretnieks (1982) and Andersson et al (1982). The methods are based on a calculation of how dissolved substances diffuse in the buffer and in the slowly flowing water in the fractures. The calculation results can be summarized in a quantity Q_{eq}, which stands for an equivalent flow that transports the dissolved substance.

The transport to (or from) the tunnel can be written:

$$N_t = Q^t_{eq} \cdot (C_\infty - C_t) \qquad (1)$$

C is the concentration in the water far away from the tunnel, C_t is the concentration in the water in the tunnel.

Q^t_{eq} is determined by calculating the diffusion transport in both the mobile water in the fractures and in the stagnant water in the pores in the clay. In the same manner, the transport to the clay in the actual deposition hole can be written:

$$N_h = Q^h_{eq} \; (C_\infty - C_h) \qquad (2)$$

C_h is the concentration in the water in the clay.

The transport between the tunnel and a point at depth Z_o down in the hole is determined by the diffusion through the compacted bentonite in the storage hole.

$$N_{th} = D_e \cdot A_h \cdot \frac{(C_t - C_h)}{Z_o} \qquad (3)$$

Where D_e is the diffusivity in the clay and A_h is the cross-sectional area of the hole.

Equations 1, 2 and 3 are to be regarded as highly simplified descriptions and are based on the following assumptions.

The concentration everywhere in the tunnel section that belongs to a storage hole is equal. This means that the diffusion resistance in the buffer is neglected compared to the transport to the fractures and to the hole. This assumption probably leads to overestimation of the transport to the hole, since the distance to the mouth of the hole is, on the average, longer than the distance to the fractures in the tunnel wall. In the storage hole, the concentration is assumed to be equal along the entire length of the hole. This is an approximation, since the hole is about 1.5 m in diameter and about 7 m long. By setting the transport distance from the tunnel to the canister as the distance to the top surface of the canisters (about 2.5 m) the attack on the canister is overestimated. The assumption that the concentration in the storage hole is equal in the radial direction is also fairly rough, but since the distance down to a point in the hole is considerably greater (>2.5 m) than the distance between the canister surface radially to the wall of the hole (about 0.38 m), the concentration at this level is also dominated by the supply from above.

The copper surface is assumed to react with the sulphur at a rate that is proportional to the concentration C_h. The quantity N_r that reacts per unit time is then

$$N_r = k''A_kC_h \tag{4}$$

k'' is the reaction rate constant between copper and sulphate. A_k is the area of the copper surface.

Figure 3 shows a simplified diagram of how the sulphur is transported to and reacts with the canister.

The quantity of sulphur that is transported to the storage hole either reacts with the copper or is enriched in (depleted from) the water in the pores in the clay (V_h).

$$N_{th} + N_h = N_r + V_h \cdot \frac{dC_h}{dt} \tag{5}$$

In the same manner, it is obtained that the sulphur that is transported to the tunnel either goes further to the hole or is enriched (depleted) in the water in the buffer's pore system (V_t).

$$N_t = N_{th} + V_t \frac{dC_t}{dt} \tag{6}$$

Equations 5 and 6 can be rewritten to

$$\frac{dm_h}{dt} = V_h \frac{dC_h}{dt} = \frac{D_e^h A_h}{Z_o} (C_t - C_h) + Q_{eq}^h (C_\infty - C_h) - k'' A_k C_h \tag{7}$$

The terms above stand for N_{th} + N_h - N_r

$$\frac{dm_t}{dt} = V_t \frac{dC_t}{dt} = Q_{eq}^t (C_\infty - C_t) - \frac{D_e^h A_h}{Z_o} (C_t - C_h) \tag{8}$$

The terms above stand for N_t - N_{th}

If the initial concentrations in hole C_{ho} and in tunnel C_{to} are known, equations 7 and 8 can be integrated from time t = 0 and forward in time.

The calculations are complicated slightly by the fact that both sulphide and sulphate have limited solubility, which means that the concentration C_h and C_t, respectively, is kept constant at the solubility limit until the solid phase has been consumed.

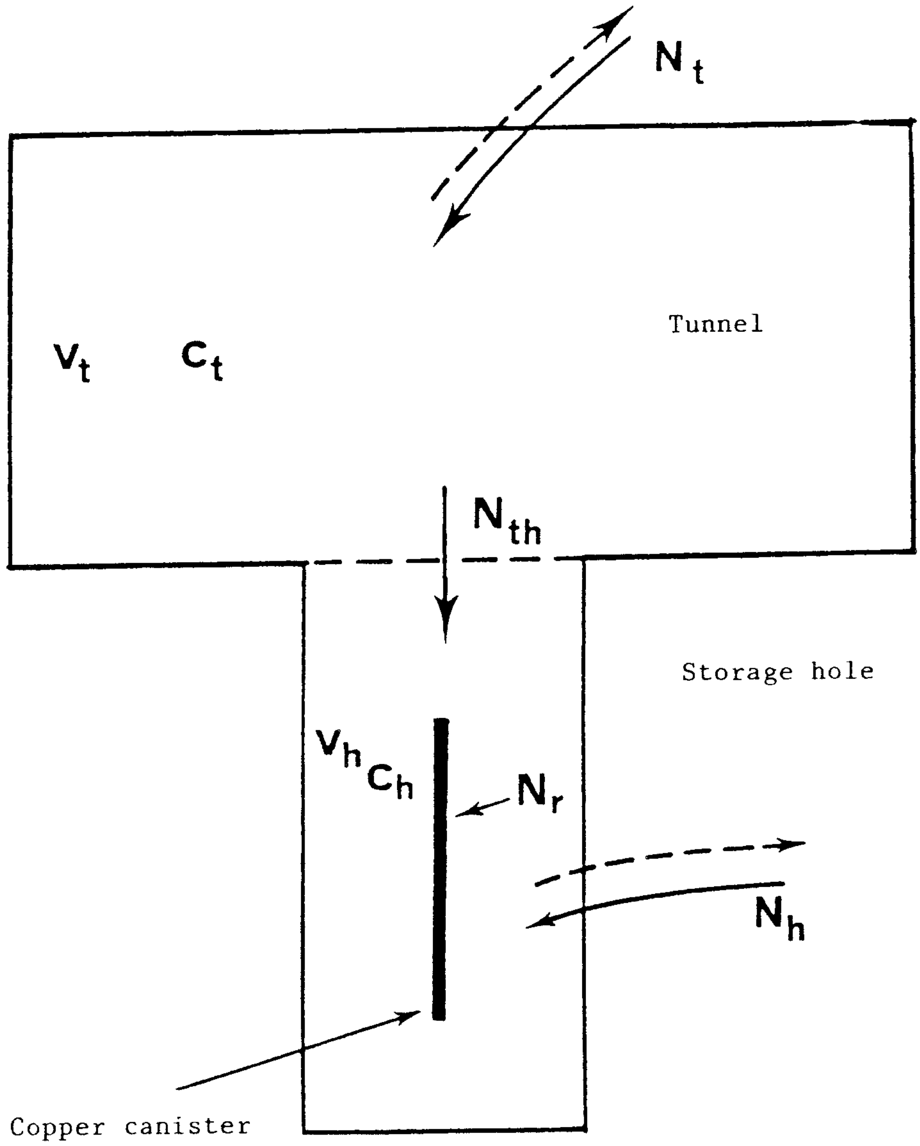

Figure 3

3 DATA FOR THE CALCULATIONS

The calculations are based on conditions that apply or can be estimated to apply to a final repository in crystalline rock with water flows and fracturing chosen within the limits that have been measured and calculated for a number of investigated sites.

Sulphide is assumed to react rapidly while sulphate reacts very slowly with copper (appendix 2). The reaction kinetics calculations are therefore carried out only for sulphate.

The concentration of sulphide and sulphate in the buffer and the compacted bentonite has been chosen on the basis of measured values. Tables 1 and 2 give the values used in the calculations.

U_o	water flow in rock	0.3 and 3 l/m^2, year
S	fracture spacing in rock	1 m
E_t	flow porosity of rock	10^{-4}
D_t	tunnel diameter	4 m
D_h	hole diameter	1.5 m
D_k	canister diameter	0.75 m
L_k	canister length	4.5 m
Z_o	distance between tunnel floor and canister	2.5 m
D_e^h	effective diffusivity for sulphate in compacted bentonite at 25°C (KBS TR 83-33)	0.3$^{\&}$ and 40.10^{-12} m^2/s
D_e^t	effective diffusivity in buffer (estimated)	1.5 and 200 $\cdot$ 10^{-12} m^2/s
V_t	water volume of tunnel	23.4 m^3
V_h	water volume of hole	3.8 m^3
M_t	quantity of bentonite in tunnel	23 000 kg
M_h^1	quantity of bentonite in hole	20 000 kg
$C^b_{SO_4}$	concentration of SO_4^{2-} in bentonite	0.81% by weight
M_t^s	quantity of SO_4^{2-} in tunnel	186.3 kg
M_h^s	quantity of SO_4^{2-} in hole	162 kg
m_{to}	initial concentration of SO_4^{2-} in clay in tunnel, figured per water volume	7.96 kg/m^3 *
m_{ho}	initial concentration of SO_4^{2-} in clay in hole	42 kg/m^3 *
C_{max}	maximum concentration of SO_4^{2-} in water, limited by $CaSO_4$ solubility	2 kg/m^3
C_∞	concentration of SO_4^{2-} in groundwater	0.01 and 0.1 kg/m^3
A_h	cross-sectional area of hole	1.77 m^2
A_k	surface area of canister	4.0 m^2
k"	reaction rate constant	$10^{-13\$}$, 10^{-14} m/s

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* Exceeds the solubility of $CaSO_4$ in water

& The lower value is expected to apply. It is based on measurement data for anions. The higher value is a ceiling value. It applies for uncharged, small molecules.

$ Considerably larger values of k" mean that the reaction will not be limiting. Considerably smaller values of k" mean that the reacted quantity will be very small.

Case	U_o $1/m^2 \cdot year$	D_e^h m^2/s	D_e^t m^2/s	Q_{eq}^h $1/year$	$(R_1/R_s)^h$	Q_{eq}^t $1/year$	$(R_1/R_s)^t$
1	0.3	$0.3 \cdot 10^{-12}$	$1.5 \cdot 10^{-12}$	0.063	29.6	0.23	5.3
2	3	$0.3 \cdot 10^{-12}$	$1.5 \cdot 10^{-12}$	0.064	51.2	0.26	16.7
3	0.3	$40 \cdot 10^{-12}$	$200 \cdot 10^{-12}$	0.94	0.12	1.42	0.040
4	3	$40 \cdot 10^{-12}$	$200 \cdot 10^{-12}$	2.4	0.38	4.1	0.125

Table 2. Equivalent water flow to tunnel and storage hole at different water flows in the rock and different diffusivities in buffer and clay. R_1/R_s is the ratio between the transport resistance in buffer or bentonite and the water in the fractures.

4 RESULTS OF THE SULPHATE REACTION CALCULATIONS

The results of the calculations are presented in table 3, where reacted quantity of sulphate at different times is given for several different combinations of other variables.

A low diffusivity in buffer and clay gives the highest reacted quantity. This is due to the fact that the sulphate then stays in the buffer and in the clay in the hole and can react with the copper. At higher diffusivities, it is transported away with the passing water; (lines 3-6). A high concentration of sulphate in the water (line 7) does not affect the results, since the reaction up to 10^6 years mainly takes place while the water in the hole contains sulphate at the solubility concentration 2 kg/m^3 and the flowing water only contains 0.1 and 0.01 kg/m^3, respectively, in the different calculation cases.

Case	k'' m/s	D_e^h m/s	D_e^t m/s	U_o $R/m^2 \cdot$ years	Reacted after 10^3	 10^4	 10^5	 10^6
						years		
1	10^{-13}	$0.3\ 10^{-12}$	$1.5\ 10^{-12}$	0.3 and 3	0.026	0.26	2.6	25
2	10^{-14}	$0.3\ 10^{-12}$	$1.5\ 10^{-12}$	0.3 and 3	0.0026	0.026	0.26	2.5
3	10^{-13}	$40\ 10^{-12}$	$200\ 10^{-12}$	0.3	0.026	0.26	1.96*	2.0
4	10^{-14}	$40\ 10^{-12}$	$200\ 10^{-12}$	0.3	0.0026	0.026	0.197*	0.2
5	10^{-13}	$40\ 10^{-12}$	$200\ 10^{-12}$	3	0.026	0.26*	0.8	0.9
6	10^{-14}	$40\ 10^{-12}$	$200\ 10^{-12}$	3	0.0026	0.026*	0.08	0.09
7	10^{-13}	$0.3\ 10^{-12}$	$1.5\ 10^{-12}$	0.3 and 3 C =100 g/m^3	0.026	0.26	2.6	25

Table 3. Summary of the different calculation cases. The four right-hand columns show how much SO_4^{2-} has reacted with copper at different points in time.

* The sulphate in the hole and the tunnel has mostly been transported away by this time.

5 CONSEQUENCES OF FAST CHEMICAL REACTION

If the reaction between sulphate and copper should be very fast, the consequence will be that all sulphate in the clay in the storage hole reacts as soon as it can be transported to the copper surface. This takes place within 400 years if the diffusion resistance in the clay is based on the higher diffusivity $D_e = 40 \times 10^{-12}$ m^2/s and within 54 000 years for the lower diffusivity $D_e = 0.3 \times 10^{-12}$ m^2/s. (These calculations are presented in section 6.) When the sulphate in the clay in the storage hole has been consumed, additional sulphate is supplied from the water and from the tunnel. The tunnel's sulphate content also decreases due to transport to the water flowing past the tunnel, so only a small fraction of the tunnel's sulphate reaches the canister.

Tables 4a, b show how much sulphate has reacted at different points in time when the reaction is fast. As can be seen from the tables, the initial quantity of sulphate in the tunnel is consumed after a few tens of thousands of years. Thereafter, a transport takes place to the tunnel and further to the hole. In addition, sulphate is supplied to the hole directly from the water that flows around the hole.

Reacted (kg) within 10^3 years at 0.81% SO_4^{2-}	142		
Supplied from	tunnel	water	tunnel + water
at time years			
10^3	3	0.07	3
10^4	18	0.37	18
10^5	34*	3.6	38
10^6	45	36	81

* The tunnel's sulphate has been carried away after about 60 000 years

Table 4a. Quantity of sulphate (kg) that has reacted at different points in time when the reaction is fast. High water flow in the rock (case 4 in table 2). Sulphate content in the water 15 mg/l. Sulphate content in the clay 0.81%.

Reacted (kg) within 10^3 years at 0.027% SO_4^{2-}		4.7	
Supplied from	Tunnel	Water	Tunnel + water
at time years			
10^3	0.2	0.037	0.2
10^4	1.1	0.37	1.5
10^5	2.2*	3.6	5.8
10^6	13	36	49

* The tunnel's sulphate has been carried away after about 25 000 years.

Table 4b. Sulphate quantity (kg) that has reacted at different points in time when the reaction is fast. High water flow in the rock (case 4 in table 2). Sulphate concentration in the water 15 mg/l. Sulphate concentration in the clay 0.027%.

6 THE IMPORTANCE OF THE DIFFUSION RESISTANCE IN THE CLAY IN THE HOLE IN THE CASE OF FAST CHEMICAL REACTION

Figure 4 shows how the sulphide or the sulphate from the clay in the hole diffuses to the canister surface. The driving force for the diffusion is equal to the substance's solubility, since the concentration at the canister surface is assumed to be fast. The discussion below pertains to sulphate, but also applies to every substance limited by its solubility.

$$N = D_e \cdot A_{mean} \cdot \frac{Cmax}{\Delta r} \qquad (9)$$

C_{max} is the solubility of SO_4^{2-} in the water, where A_{mean} is a mean value of the cross-sectional area for diffusion. It is approximated with the largest area *. Out to the distance r from the canister surface, the clay has been depleted of solid sulphate. The area at this limit is, if end effects are neglected:

$$A = 2\pi L\ (r_k + \Delta_r) = A_{mean} \qquad (10)$$

r_k = canister radius

Since the concentration of sulphate in the water in the clay is low compared to the concentration of solid sulphate in the clay, the depletion is dependent on how fast the solid sulphate dissolves.

$$N = \frac{d(\Delta r)}{dt}\ A\ \rho_{bent} \cdot C^b_{SO_4} \qquad (11)$$

ρ_{bent} = the density of the bentonite in the hole and $C^b_{SO_4}$ is its content of solid sulphate.

Since the quantity of sulphate that reacts with the canister is taken from the clay, equation (9) = (11) and

* This approximation is made in order to avoid a numerical solution. Since the canister radius and the hole radius differ by a factor of about 2, the error with this approximation is no more than a factor of 2. The transport velocity is overestimated with this approximation.

$$\frac{d(\Delta r)}{dt} \cdot C^{b}_{SO_4} \rho_{bent} = \frac{D_e C_{max}}{\Delta r} \qquad (12)$$

which, after integration, gives

$$\frac{\Delta r^2 \cdot C^{b}_{SO_4} \rho_{bent}}{2 \cdot D_e \cdot C_{max}} = t \qquad (13)$$

for $\Delta r = 0.38$ m, $D_e = 40 \bullet 10^{-12}$ m^2/s,

$C^{b}_{SO_4} = 0.0081$ $\rho_{bent} = 1\ 750$ kg/m^3 and $C_{max} = 2$ kg/m^3, t is obtained as

$$t = \frac{0.38^2 \cdot 14.1}{2 \cdot 40 \cdot 10^{-12} \cdot 3.15 \cdot 10^7} = 402 \text{ years}$$

Thus, it takes about 400 years before all sulphate in the hole has reacted under these conditions. At the lower diffusivity $0.3 \cdot 10^{-12}$ m^2/s, t is obtained as = 54 000 years.

It is interesting to note that if the sulphur is instead present in the form of sulphide, the conditions are greatly changed.

The solubility of the sulphide is less than 1 g/m^3, i.e. about 2 000 times less than that of the sulphate.

At the same sulphur quantity, $C^{b}_{S} = 0.3\%$ by weight, equation 13 gives

$$t = \frac{0.375^2 \cdot 5.25}{2 \cdot 40 \cdot 10^{-12} \cdot 0.001 \cdot 3.15\ 10^7} = 0.29 \cdot 10^6 \text{ years}$$

At the lower diffusivity, we get

$$t = 39 \cdot 10^6 \text{ years}$$

Table 5 shows how much sulphide has reacted at different points in time if the higher diffusivity $D_e = 40 \cdot 10^{12}$ m^2/s is assumed to apply and the concentration of sulphide in the clay is 0.3%. Table 6 shows the results for a sulphide content of 0.01%.

$7 m^3 =$

38 kg

Time years	Reacted quantity of sulphide (kg)
10^3	1.4
10^4	4.7
10^5	17.5
334 000*	34.8
10^6**	52.5

140 kg Cu

93 kg

* All sulphide in the clay between the rock and the canister has reacted.

** All sulphide in the clay in the hole, including above and below the canister, has reacted.

Table 5. Reacted quantity of sulphide (kg) when the canister is 5 m long, $D_e = 40 \cdot 10^{-12}$ m^2/s, the sulphide's solubility is 1 mg/l and the sulphide content of the clay is 0.3%.

Time years	Reacted quantity of sulphide (kg)
10^3	0.29
10^4*	1.2
$>10^5$**	1.75

* All sulphide in the clay between the rock and the canister has reacted.

** All sulphide in the clay in the hole, including above and below the canister, has reacted.

Table 6. Reacted quantity of sulphide (kg) when the canister is 5 m long, $D_e = 40 \cdot 10^{-12} m^2/s$, the sulphide's solubility is 1 mg/l and the sulphide content of the clay is 0.01%.

Supply of sulphide or sulphate from water and tunnel

This supply can be calculated from equations 2 and 3.

$$N = Q_{eq}^{h} (C_{\infty} - C_{h}) + \frac{D_{e}A_{h}}{Z_{o}} (C_{t} - C\ ) \qquad (14)$$

if C_h is set = 0 (fast reaction)

and if it is assumed that $C_{\infty} = C_t$ = the concentration in the water in the rock, we obtain

$$N = (Q_{eq}^{h} + \frac{D_{e}A_{h}}{Z_{o}}) C_{\infty} \qquad (15)$$

For high water flows in the rock and high diffusivity in the clay (case 4 in table 2) and A_h and Z_o from table 1, we obtain

$$Q_{eq}^{h} = 2.4 \cdot 10^{-3} \text{ m}^3/\text{y}$$

$$\frac{D_e \cdot A_h}{Z_o} = 0.89 \cdot 10^{-3} \text{ m}^3/\text{y}$$

With C_{max} = the solubility of sulphide = 1 g/m^3, the supply from the water is

2.4 g sulphide per 1 000 years

and from the tunnel

0.89 g sulphide per 1 000 years.

For sulphate, the concentration C_{∞} = 15 g/m^3 and the supply is then about 15 times higher.

This supply is presented in table 7.

This supply is in addition to what has been reported in tables 5 and 6, counting from the time when the sulphide or sulphate in the hole has been consumed.

Time years	Quantity supplied (kg) from tunnel	 water
10^3	$0.89 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$
10^4	$8.9 \cdot 10^{-3}$	$24 \cdot 10^{-3}$
10^5	$89 \cdot 10^{-3}$	$240 \cdot 10^{-3}$
10^6	0.89	2.4

Table 7. Supply of sulphide (kg) to canister from water and from tunnel at "high" water flow and "high" diffusivity (case 4 in table 2) and at a sulphide concentration in the water C_{max} = 1 g/m^3.

$$\frac{De \cdot Ah}{z_0} \qquad \frac{3.2 \cdot 10^{-4} \cdot 1{,}77}{25} = 0{,}21 \cdot 10^{-3}\ m^3/a$$

$\underline{0{,}21\,g/1000\ år}$

$$HS^- + 2Cu \rightarrow 2CuS + \tfrac{1}{2}H_2$$

$$\frac{1 \cdot 10^{-3}}{32} = \frac{2 \cdot X}{64}$$

1 mg Cu

1.6

1.6 g/1000 år

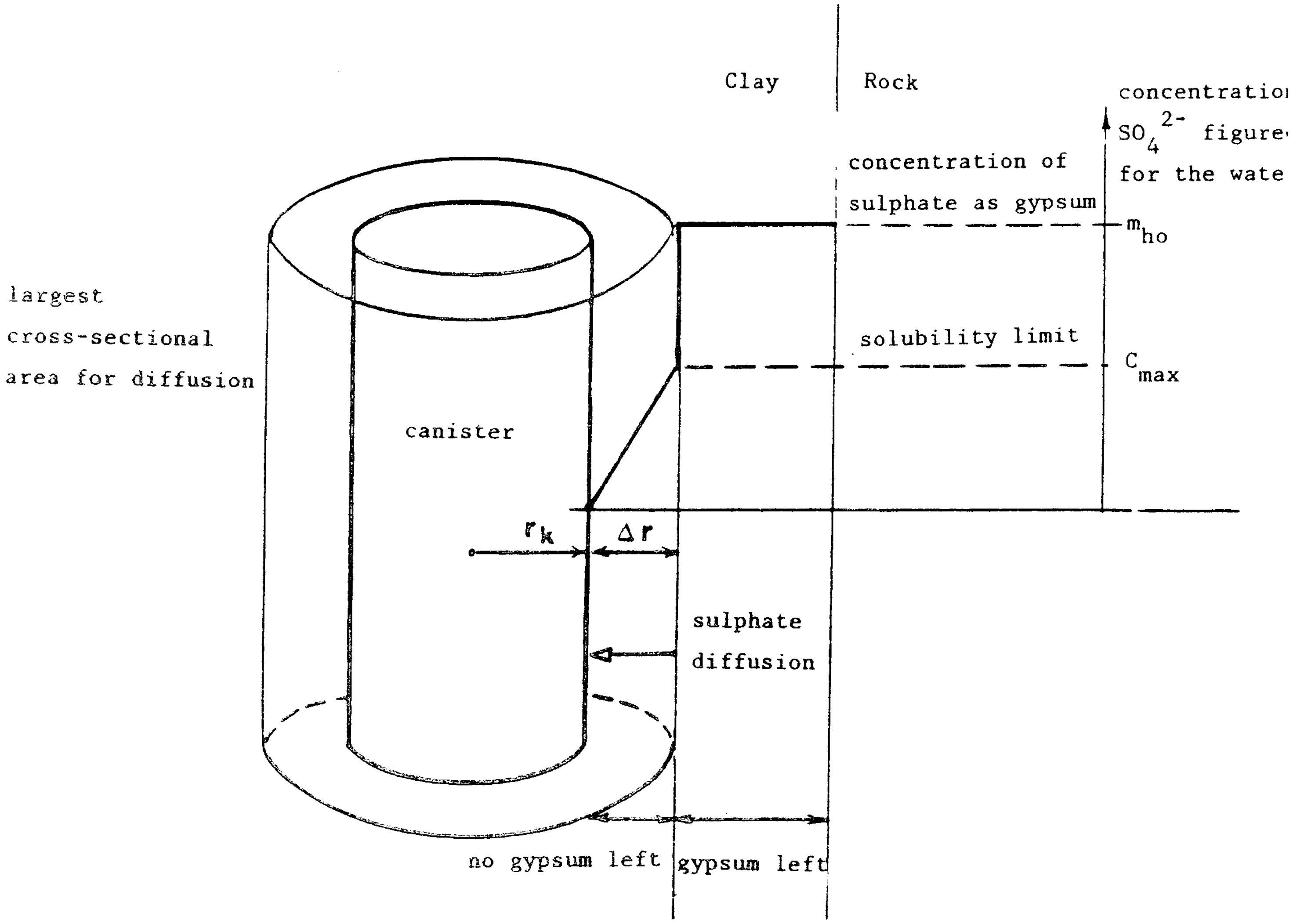
Clay
Rock
concentratio
SO$_4^{2-}$ figure
for the wate
concentration of
sulphate as gypsum
m_{ho}
solubility limit
C_{max}
largest
cross-sectional
area for diffusion
canister
r_k
Δr
sulphate
diffusion
no gypsum left
gypsum left

Figure 4

7 LIMITATIONS IN THE SULPHATE REACTION

In all the proposed reactions, it is necessary that a reductant, for example Fe(II), be present in order for the reaction to take place. A simplified formal way to view the reaction is

$$8\ H_2O + SO_4^{2-} + 2\ Cu + 6\ Fe^{2+} \rightarrow Cu_2S + 6\ FeOOH + 10\ H^+$$

The formula is only intended to show that 6 Fe(II) are required for each SO_4^{2-}, whereby 2 Cu are consumed.

The quantity of solid iron minerals in immediate contact with the copper canister is very limited. When these minerals have been consumed, in order for the attack to continue, iron must be transported to the canister in dissolved form. In the prevailing environment, bivalent iron has a solubility of less than 5 ppm.

The iron in the clay around the canister (0.3% by weight), about 50 kg, is enough to corrode about 120 kg of copper if excess sulphate is present. After that, the supply of bivalent iron from the groundwater and via the tunnel will limit the corrosion, since it is present at a lower concentration than the sulphate.

As before (equation 15), the supply of Fe(II) is:

from the tunnel $0.89^{*} \cdot C_{Fe(II)}$ g/1 000 years
from the water $2.4 \cdot C_{Fe(II)}$ g/1 000 years

where $C_{Fe(II)}$ = the solubility concentration of the iron = 5 mg/l.

Table 8 below shows how much iron is supplied at different times and how much copper this amount can corrode.

* If the same diffusivity is assumed for Fe(II) as for uncharged species.

Time years	From tunnel		From water	
	Supplied Fe(II) kg	Corroded Cu kg	Supplied Fe(II) kg	Corroded Cu kg
10^3	$4.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$12 \cdot 10^{-3}$	$4.6 \cdot 10^{-3}$
10^4	$45 \cdot 10^{-3}$	$17 \cdot 10^{-3}$	$120 \cdot 10^{-3}$	$46 \cdot 10^{-3}$
10^5	$450 \cdot 10^{-3}$	$170 \cdot 10^{-3}$	1.2	$460 \cdot 10^{-3}$
10^6	4.5	1.7	12	4.6

Table 8. Supply of Fe(II) and corresponding copper corrosion.

7.1 Supply of iron from clay and rock

The transport of dissolved bivalent iron to the copper surface can be calculated in the same manner as the transport of sulphide with equation 13. No measurement data are available on Fe^{2+} in clay, however. If the same values are used as for Sr^{2+}, Fe^{2+} is consumed (in an excess of SO_4^{2-}) within 10^3 years if the solubility of Fe^{2+} is set equal to 5 mg/l and the iron content Fe(II) to 0.3%.

The same type of calculation can be done to estimate how fast Fe^{2+} can be liberated from the rock matrix for further transport through the clay to the copper surface.

Diffusion data for Fe^{2+} are not available for crystalline rock either. High diffusivities have been measured for Cs^+ and Sr^{2+}.
$D_e \approx 2 \cdot 10^{-12}$ m^2/s. If this value is used, the following results are obtained, see table 9 below, when a solubility of 5 mg/l, an iron concentration of 2% and a rock density of 2 700 kg/m^3 are used.

Time Years	Depletion depth in rock m	Leached iron kg*	Corroded copper
10^3	0.0034	5.5	2.1
10^4	0.0108	17.5	6.6
10^5	0.034	55	21
10^6	0.108	175	66

* from the outer surface of the hole, 30 m^2.

Table 9. Possible supply of iron from the rock if the diffusion is "fast".

8 SUMMARY

When sulphide reacts with copper, 1 mole of S^{2-} is consumed for every 2 moles of Cu. In the reaction of sulphate with copper, 1 mole of SO_4^{2-} is consumed for every 2 moles of Cu. 3 moles of Fe are consumed for every 1 mole of Cu. Converted to mass, we get:

1 kg of S^{2-} is equivalent to 3.963 kg Cu
1 kg of SO_4^{2-} is equivalent to 1.324 kg of Cu
1 kg of Fe(II) is equivalent to 0.379 kg of Cu

The sulphate and sulphide quantities given in the previous tables are converted to copper quantities.

Five cases are treated, and it is assumed that both the sulphide and the sulphate reaction proceed rapidly.

Case 1	Sulphate concentration 0.81%	Sulphide concentration 0.02%
Case 2	Sulphate concentration 0.027%	Sulphide concentration 0%
Case 3	Sulphate concentration 0%	Sulphide concentration 0.3%
Case 4	Sulphate concentration 0%	Sulphide concentration 0.01%
Case 5	Sulphate concentration 0.81% or 0.027%, limited iron supply	

In all of the cases, the sulphide concentration in the water is assumed to be 1 g/m^3 and the sulphate concentration 15 g/m^3. Tables 10.1 - 10.5 present the different cases.

Table 10.1. Reacted quantity of copper (kg) at sulphate concentration 0.81%. Sulphide concentration 0.02% if iron is present in excess.

Corroded within 10^3 years by SO_4^{2-}	188
by S^{2-}	3.5
	192

Corroded through supply from	tunnel			water		
with at time (years)	S^{2-}	SO_4^{2-}	Total	S^{2-}	SO_4^{2-}	Total
10^3	0.004	4.0	4.0	0.01	0.05	0.06
10^4	0.035	24	24	0.095	0.5	0.6
10^5	0.35	45	45	0.95	4.8	5.8
10^6	3.5	60	64	9.5	48	58

Table 10.2. Reacted quantity of copper (kg) at sulphate concentration 0.027%. Sulphide concentration 0 if iron is present in excess.

Corroded within 10^3 years	by SO_4^{2-}	6.2
	by S^{2-}	-

Corroded through supply from	tunnel			water		
with at time (years)	S^{2-}	SO_4^{2-}*	Total	S^{2-}	SO_4^{2-}	Total
10^3	0.004	0.02	0.024	0.01	0.05	0.06
10^4	0.035	0.18	0.22	0.095	0.5	0.6
10^5	0.35	1.8	2.1	0.95	4.8	5.8
10^6	3.5	18	21	9.5	48	58

* equation 15

Table 10.3. Reacted quantity of copper (kg) at sulphate concentration 0, sulphide concentration 0.3%.

Corroded through supply from	tunnel			water and clay and in hole		
with at time (years)	S^{2-}	SO_4^{2-}	Total	S^{2-}	SO_4^{2-}	Total
10^3	-*	0.02	0.02	4.4**	0.05	4.4
10^4	-*	0.18	0.18	15.4**	0.48	16
10^5	-*	1.8	1.8	59**	4.8	64
334 000	-*			126**	15	141
10^6	0.6	18	19	142**	48	190

* the clay in the hole is still saturated with S^{2-}

** mainly from the sulphide in the clay

Talbe 10.4. Reacted quantity of copper (kg) at sulphate concentration 0, sulphide concentration 0.01%.

Corroded through supply from	tunnel			water and clay in hole		
with at time (years)	S^{2-}	$SO_4{}^{2-}$	Total	S^{2-}	$SO_4{}^{2-}$	Total
10^3	-*	0.02	0.02	0.95**	0.05	1
10^4	-*	0.18	0.2	4.2**	0.48	4.7
10^5	-*	1.8	1.8	5.4**	4.8	10.2
10^6	3.2	18	21	14**	48	62

* the clay in the hole is still saturated with S^{2-}

** mainly from the sulphide in the clay

Corroded within 10^3 years by

$SO_4^{2-} + Fe^{2+}$ in clay	20* kg at 0.81% SO_4^{2-} in the clay	6.4** kg at 0.027% SO_4^{2-} in the clay
S^{2-}	3.5 kg	0 kg

Corroded through supply from	tunnel				water and rock				
with	S^{2-}	SO_4^{2-} (0.81%; 0.027%)	Fe^{2+}	Total	S^{2-}	SO_4^{2-}	Fe^{2+}		Total
after (years)							from water	from rock	
10^3	0.004	$(4.0;\ 0.02)^*$	$0.002^{*\%}$	0.006	0.01	0.05^*	$(0.005)^\&$	$(2.1)^\&$	0.06
10^4	0.035	(24; 0.18)	0.017	0.052	0.095	0.5	(0.046)	(6.6)	0.6
10^5	0.35	(45; 1.8)	0.17	0.52	0.95	4.8	(0.46)	(21)	5.8
10^6	3.5	(60; 18)	1.7	5.2	9.5	48	(4.6)	(66)	58

* limited by Fe^{2+}

** limited by SO_4^{2-}

& maximum of Fe^{2+} from rock and water determines whether limitation comes into play

% only Fe from tunnel is assumed to react. An excess of Fe from the rock might possibly raise this level.

Table 10.5. Reacted quantity of copper (kg) at sulphate concentration 0.81% and 0.027%, respectively, in the clay, 15 mg/l in the water and Fe(II) concentration in the clay 0.3% by weight.

9 DISCUSSION AND CONCLUSIONS

Importance of reaction rate

The lower value for the diffusivity of SO_4^{2-} ions in bentonite may be assumed to apply when this gives the least favourable result. This value is also supported by measurements of the diffusion of other anions (I^-, Cl^-, SH^-). The reaction rate constant k" is based on the assumption that it is a surface reaction and that it is a first order reaction with respect to sulphate. If a homogeneous first order reaction is instead assumed, then

$$N_r = k'C_h \cdot V_h$$

and since V_h is numerically equal to A_k in equation 4, $k'A_k = k''V_h$ and $k' = k''$. This means that if we assume that the homogeneous reaction is rate-determining, k' will have the same numerical value as $k'' = 10^{-13}$ and 10^{-14} 1/s, respectively, or $3.2 \cdot 10^{-6}$ and $3.2 \cdot 10^{-7}$ 1/y, respectively.

This gives time constants for the homogeneous reaction of about $3 \cdot 10^5$ and $3 \cdot 10^6$ years, respectively. Since no reaction rate constants are measured for the heterogeneous reaction, no final conclusions can be drawn concerning the course of the reaction. However, decomposition of sulphate is a very slow process in nature, even when plenty of reducing species are available (Appendix 2).

The importance of the sulphate reaction decreases if the clay has a low sulphate content. This is evident from table 4. If it is assumed that the sulphate reacts rapidly, the initial quantity of sulphate in the clay in the storage hole will determine the attack for high sulphate concentrations, even over very long periods of time. A comparison between tables 4a and 4b shows that the sulphate supply from the tunnel is also of great importance at a high sulphate concentration.

Importance of diffusion resistance in clay

The sulphate is relatively easily soluble and can therefore be transported to the canister surface during a "short" period of time (about 400 years in the example with high sulphur concentration and high diffusivity). If the same quantity of sulphur is present in the form of sulphide, its solubility is at least a thousand times lower and it takes about 300 000 years for the sulphide to be transported to and react with the copper, even at the high diffusivity and sulphur concentration.

If the sulphur concentration is reduced to 0.01% S^{2-}, it takes at least about 10 000 years for all sulphide to react, but on the other hand there is only a total of 1-2 kg available for the reaction.

Importance of availability of bivalent iron

The availability of bivalent iron in the clay is of crucial importance for the initial reaction between copper and sulphate. If tables 10.1 and 10.5 are compared, it is seen that the corrosion initially declines from about 200 kg to about 20 kg. The supply of corrodants from the tunnel to the top part of the canister reduces the corrosion of the top part of the canister from 65 to 5.2 kg of copper. General corrosion is not altered appreciably, however, since it is assumed that iron can be supplied relatively rapidly from the rock.

The iron transport calculations from the rock are highly uncertain, since no measured diffusivities in rock are available.

Importance of inward transport of corrodants from tunnel

The corrodants that come from the tunnel react preferentially with the copper surfaces located nearest the tunnel. The inward transport along this path can be sharply reduced by, for example, inserting a "plug" of e.g. rock. A 1 m long plug with a diameter 1 cm less than that of the hole reduces the cross-sectional area for diffusion to 1.3%. If the fact that the clay that can be used to fill the gap has a higher diffusivity (5 times), but that the plug is only about 40% of the distance between the tunnel floor and the canister, is taken into account, the transport resistance is 6 times greater than if this space were filled with compacted clay. Such an arrangement would reduce the inward transport of corrodants to the top surface of the canister by a factor of 6.

General

The availability of bivalent iron notably reduces possible corrosion due to the sulphate reaction. It would therefore appear to be advantageous to convert the sulphide in the clay to sulphate. Corrosion will then be less, even if the sulphate reaction is fast. A low-sulphur clay can scarcely reduce the attack further.

In terms of engineering measures, a rock plug in the hole above the canister can contribute considerably to reducing the attack on the top part of the canister.

10 REFERENCES

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Appendix 6
(51 571)

CORROSION OF COPPER FROM LIGHTNING CONDUCTOR PLATES

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Stockholm 1983-02-10

The Cu concentration dropped very rapidly, and only 3 cm from the plate, only background concentrations were found, about 0.05 mg Cu/cm^2 per plate in all cases. The results are presented in table 2.

The quantity of copper that has diffused out into the surrounding soil is, per 1 cm^2 of plate:

Gyttorp	1.25 mg
Trollhättan	1.24 mg
Lyrestad	0.41 mg

These values are equivalent to the following thicknesses of the copper layer:

Gyttorp/Trollhättan	1.3 µm
Lyrestad	0.5 µm

Four earth electrode plates for lightning conductors have been investigate The sites have been Gyttorp, Trollhättan, Lyrestad and Högsätra. No Cu plat was found in Högsätra, despite searching with metal detectors and digging i three different places with positive indications of metal objects.

At the three first sites - Gyttorp, Trollhättan and Lyrestad - Cu plates w found and recovered. Facts on the find sites are given in table 1. For t exact geographical location, consult Christer Bolin, Åskskyddskonsult (+46-18-320633).

The plates have been uncovered with the aid of an excavator. For this reas the soil layers on top of the plate have been disturbed. There has also b a risk that the corrosion products on the top side of the plate would scraped away. For this reason, all measurements of pH and Eh as well taking of soil samples have been done in the soil layers just below the pl after the plate has been carefully lifted out. In the case of Lyrestad, excavated hole quickly filled with water, so sampling and measurement had be done on the clay that had adhered to the plate in large lumps and taken up with it. The plates were not cleaned, but immediately transported Stockholm for further transport to the Swedish Corrosion Institute.

Two different types of soil samples were taken. One for analysis of Cu one for determination of bacterial activity.

Cu determination

Soil samples were taken with a plexiglas cylinder that was pushed down the soil layers so that a sediment core was obtained. This core, which h diameter of 5 cm, was sliced in 1 cm thick slices. Each slice was numbere consecutive order, and in cases where several sediment cores were taken, were designated 1:1, 1:2, 1:3 and 2:1, 2:2, 2:3 etc. The slices were fre dried and homogenized. 0.5-1 g of sediment from each slice was leached 10 ml of 5 M HNO_3 for one hour in an autoclave at 120°C. The sample washed and filtered through a 0.45 µm membrane filter. It was then dilute 50 g with Milli-Q water. The analysis was performed on Varian AA- 324.7 nm.

Table 1

Place	Date of recovery	Buried	Position	Depth cm	Soil type	pH	Eh mV
Gyttorp	820913		Horizontal	120	silt	6.0-6.9	+50 - -100
Trollhöttan	821022	1908 or 1932	Horizontal	150	stiff clay	4.7-5.2	+300 - +150
Lyrestad	821126	1922	Horizontal	330	clay	7.4-7.6	+250 - +150

Table 2

Sample designation		$\frac{\text{soil (g)}}{\text{cm}^2\text{ plate}}$	Cu $^{o}/_{oo}$	$\frac{\text{mg Cu}}{\text{cm}^2\text{ plate}}$		
Gyttorp	1:1	0.66	1.49	0.99		Quantity Cu/cm^2 plate = 1.25 mg
	1:2	0.76	0.21	0.16		
	1:3	0.84	0.053	0.06		
	1:4	0.99	0.039	0.04	1.25	
Trollhättan	1:1	0.59	1.42	0.84		Average quantity Cu/cm^2 plate = 1.24 mg
	1:2	1.25	0.46	0.57		
	1:3	1.56	0.04	0.06	1.47	
	2:1	1.33	1.10	1.46		
	2:2	1.42	0.03	0.04	1.50	
	3:1	0.94	0.55	0.52		
	3:2	1.31	0.14	0.18		
	3:3	1.42	0.04	0.06	0.76	
Lyrestad	1:1	1.02	0.42	0.43		Average quantity Cu/cm^2 plate = 0.46 mg
	1:2	1.02	0.03	0.03	0.46	
	2:1	1.40	0.20	0.28		
	2:2	1:69	0.04	0.05	0.33	
	3:1	1.16	0.47	0.55		
	3:2	1.22	0.025	0.03	0.58	

Activity of sulphate-reducing bacteria

Sampling

Soil samples were taken in connection with the recovery of Cu plates. The samples were taken in sawn-off syringes and kept sealed up to the time of analysis.

Analyses

The water content is calculated as weight loss upon drying in oven at 105°C and specified as % of wet weight.

Organic matter is weight loss on burning of dry sample at 500°C, 1 h.

Total sulphur calculated on sample burned in induction furnace (Leco) and titration of SO_2.

Determination of bacterial S reduction

The soil sample was furnished with a glass rod prepared with $^{35}S\text{-}SO_4{}^{2-}$ by pushing the glass rod through the entire sample (10 ml of soil), after which the sample was incubated for 3 hours. The sample was transferred to a digester and HCl was added. The mixture was boiled for 3 hours and the evolved gases were driven from the digester to three collection traps connected in series by means of a N_2 gas stream. The volatile sulphides were retained in the first trap, which contained 5 M NaOH. The two subsequent traps contained DTNB (= Ellman's reagent 5.5^1-dithiobis-2-nitrobenzoic acid), which binds sulphides but serves in the analysis more as reserve traps.

After the digestion scintillator counts were made on all solutions from the traps as well as from the filtered solution in the digester, the latter as a check to make sure that the non-reduced quantity of $^{35}S\text{-}SO^{2-}$ was still present after the digestion (Skyring et al, 1979). SO_4 analysis was carried out turbidometrically on the filtered solution in the digester.

Calculations of the activity of the sulphate reduction were carried out from the formula

$$\text{Rate} = \frac{[SO_4{}^{2-}] \cdot ({}^{35}S\text{-}H_2S) \cdot \alpha}{({}^{35}S\text{-}SO_4{}^{2-}) \cdot t} \quad g\ SO_4{}^{2-} \cdot cm^{-3} \cdot day^{-1}$$

$[SO_4{}^{2-}]$ = sulphate concentration cm^{-3} soil

$({}^{35}S\text{-}H_2S)$ = radioactivity of sulphides in counts per minute (cpm)

$({}^{35}S\text{-}SO_4{}^{2-})$ = total radioactivity of ${}^{35}S\text{-}SO_4{}^{2-}$ added in cpm

t = incubation time in days

α = natural isotope fractionating factor for bacterial sulphate reduction value used: 1.022 (Hallberg, unpublished values)

<u>Results</u>

	nmol $SO_4{}^{2-}$ cm^{-3} day^{-1}	org mat % d.w.	H_2O % w.w.	mg SO_4 / ml sample	% S d.w.
Gyttorp	21	2.2	26	0.56	0.015
Trollhättan	25	0.6	33	0.96	0.005
Lyrestad	33	0.7	39	0.39	0.011

In comparison, it can be mentioned that the activity in a surface sediment in Limfjorden was:

10μmol $SO_4{}^{2-}$ cm^{-3} day^{-1} (Bo B. Jörgensen 1978)

(960 μg $SO_4{}^{2-}$)

in a Baltic Sea sediment from Askö

4.9 μmol $SO_4{}^{2-}$ cm^{-3} day^{-1}

(428.6 μg $SO_4{}^{2-}$)

References

Jörgensen Bo B. 1978: A comparison of methods for the quantification of bacterial sulphate reduction in coastal marine sediments. Geomicrobiology Journal, Vol. 1, No. 1, 11-27.

Skyring G. W., Oshrain R. L., Wiebe W. J. 1979: Sulphate rates in Georgia marshland soils. Geomicrobiology Journal, Vol. 1, No. 4, 3-9-400.

Phase analysis

Identification of the crystalline corrosion products has been done using X-ray diffraction.

Lyrestad: Cu_2S (traces of CuS)
very well crystallized.

Trollhättan and Gyttorp: Cu_2O, very fine crystals.

A metallographic examination of plate samples that had been encased in plastic and polished perpendicular to the two-dimensional plane by means of light microscopy, scanning electron microscopy (SEM) and microprobe has also been utilized to permit the attacks to be followed in greater detail. Several products in addition to those already mentioned have been observed, but are X-ray amorphous or much too fine-grained.

The corrosion products from the Lyrestad plate were analyzed by means of X-ray diffraction, the first time 12 days after they were dug up.

Two weeks later, another similar analysis was performed and the results were slightly different. Copper sulphides were recorded both times.

The finding is that an analysis must be performed as soon as possible after recovery with subsequent preparation of the object in order to gain better insight into the corrosion mechanism involved in relation to the surrounding environment.

Gyttorp

Assume that the mean thickness of the oxide layer is 6 mm on the figures. This is equivalent to 12 µm, and translated to a uniformly thick copper layer, this would mean about 7 µm.

The basic data used in the calculations are as follows:

Formula	Density g/cm^3	Unit cell volume, Å^3	Number of formula units per unit cell
Cu	8.9	47	4
CuO	6.4	82	4
Cu_2O	6.0	78	2

The unit cell volumes for the oxides are virtually the same and about 1.7 times greater than metallic copper.

Trollhättan

The mean thickness of an oxide layer is assumed to be 1 mm on the figure, which is equivalent to 2 µm. The equivalent metallic layer is then 1 m.

Lyrestad

The figure shows no general corrosion or pitting.

Gyttorp

Calculation of pitting frequency

From a photo with a magnification of 500 X, a cone radius is assumed of r = 15 mm and h = 15 mm. This is equivalent to a cone volume of $V = 3 \cdot 10^{-5}$ mm^3.

The polished specimen shows 12 cones over a distance of 16 mm.

Assume that these etching pits are uniformly distributed (hexagonal dense packing). This gives 84 per cm^2.

This volume per cm^2 is then $2.4 \cdot 10^{-3}$ mm^3.

Uniformly distributed over 1 cm^2, this is equivalent to a layer thickness of ~ 0.02 µm Cu.

This layer is negligible in comparison to the layer of corrosion products on the surface and the quantity of Cu that has diffused out into the soil layers.

Calculation of pitting factors

	Pitting depth µm	Cu (soil analysis) µm	Cu (corrosion layer) µm	Pf
Gyttorp	30	1	7	5
Trollhättan	12	1	1	5
Lyrestad	0	0.5	0.5	0

Reservation

In connection with these chemical analyses, we have been able to observe that the sampling and preparation methodology employed to date unfortunately does not provide a correct and representative answer. A large fraction of the corrosion layers, and especially the fraction that is bound to the metal surface owing to a comparatively plastic consistency, are not recorded in the soil analysis. Nor are they clearly observed in the polished specimens, since these have been prepared several weeks after recovery. In the meantime, the objects have dried and the unstable layers have "peeled" due to, among other things, differences in the volume of the different materials (in connection with drying).

Some idea of these phenomena can be gained from photographs; Trollhättan, where the corrosion front is not flat, as it is in Gyttorp. In the Trollhättan sample, certain layers have been lost during handling and cannot be calculated at the present time. This also applies to the Lyrestad plate, where it is possible after drying to pick off thin layers of sulphidic composition.

Summary

The quantity of Cu that has diffused from the plate out into the soil layers is of the same order of magnitude for all three plates. The statistical errors are too great to permit significant differences to be given between Gyttorp (G) and Trollhättan (T), while the Lyrestad (L) values are significantly less than G and T.

Most of the corroded copper has been converted to corrosion products on the surface of the plate. Light micrographs clearly show that G has been subjected to the greatest corrosion, followed by T and L. The pitting factor for G and T is less than 5, while L does not exhibit any pitting. L appears to be virtually unaffected.

The chemico-mineralogical relationships, physical measurements on the site versus formed products, are not clear-cut. The Eh-pH diagram in figure 1 shows an environment for G that is more reducing than for the other two earth electrodes. The corrosion products that are formed are, on the other hand, primarily oxides, while L has primarily sulphides. L was situated below, while G was above, the groundwater table in what appears to be a well ventilated sediment. The redox environment has therefore probably fluctuated more for G than for L. It should be emphasized, however, that Eh and pH are intensity measures that do not measure the chemical capacity of the system. It is therefore probable that the measured values for L have been affected by oxidative water that seeped in from overlying layers.

The activity of sulphate-reducing bacteria is extremely low. This indicates that the sulphides in the L case were formed during an earlier period when more nutrients were available for the bacteria.

The determination of the corrosion time for the different plates is not completely certain in the G and T cases. In the T case, a Cu plate was buried in 1908. It was connected to a pole in a power transmission line.

This line was restored in 1932. There is no record of the plate's having been replaced at this time. The engineer from the Swedish State Power Board who participated in the field work was of the opinion, based on his experience from line restoration, that it is not probable that the plate was replaced. It is therefore most probable that the time of burial is 1908 and not 1932. In the G case, the plate was buried some time before 1920, and investigations are underway to establish the time more exactly.

Cu plates used as earth electrodes for lightning conductors are comparatively good objects for determining Cu corrosion.
The material is pure Cu.
They have been buried in the earth for 50-80 years.
The find site can be documented with regard to chemistry.
However, it should be possible to improve the results based on the experience we have gained in this study.

For example: A plate that is to be recovered must have a carefully recorded time of burial. The sampling procedure should be supplemented with a tool that drills out a piece of the plate so that both plate and soil (3-4 cm) are included in the same sample. This sample should be encased in plastic and sectioned in such a manner that an intact corrosion picture (plate, corrosion products and nearest soil layer) can be obtained.

Claes Ålinder of the Geological Survey of Sweden in Uppsala assisted in certain instrument analyses.

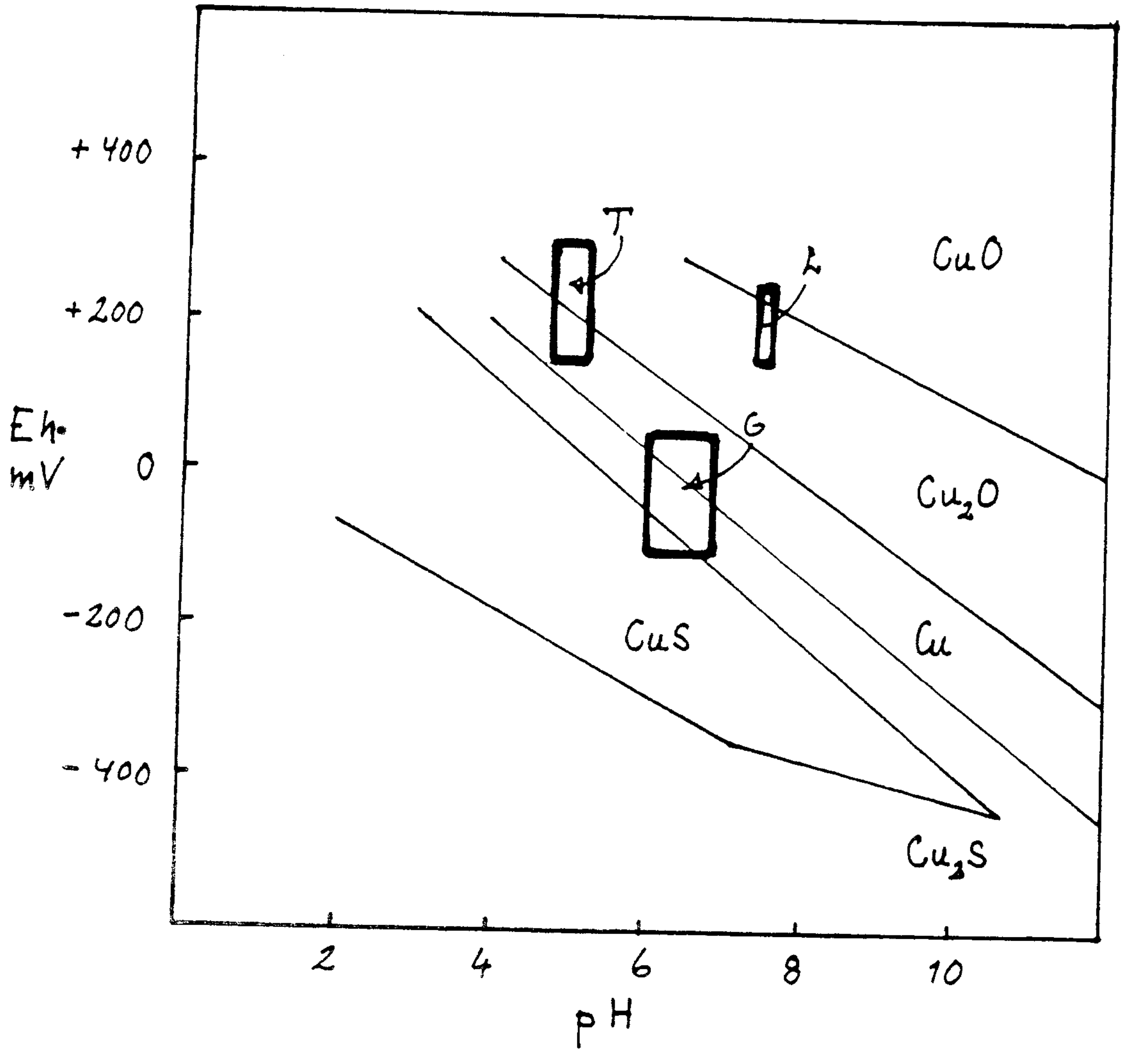
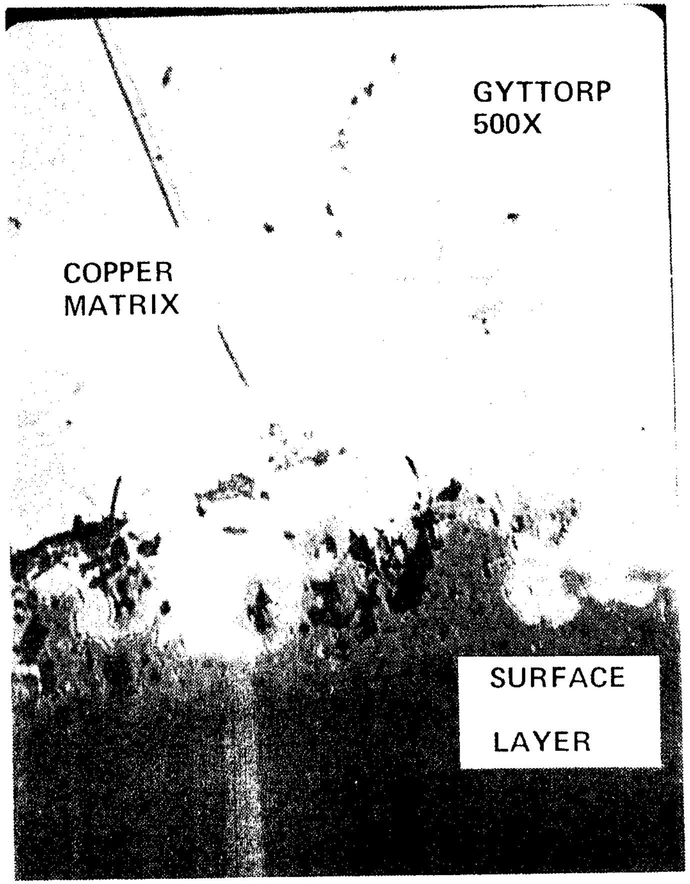
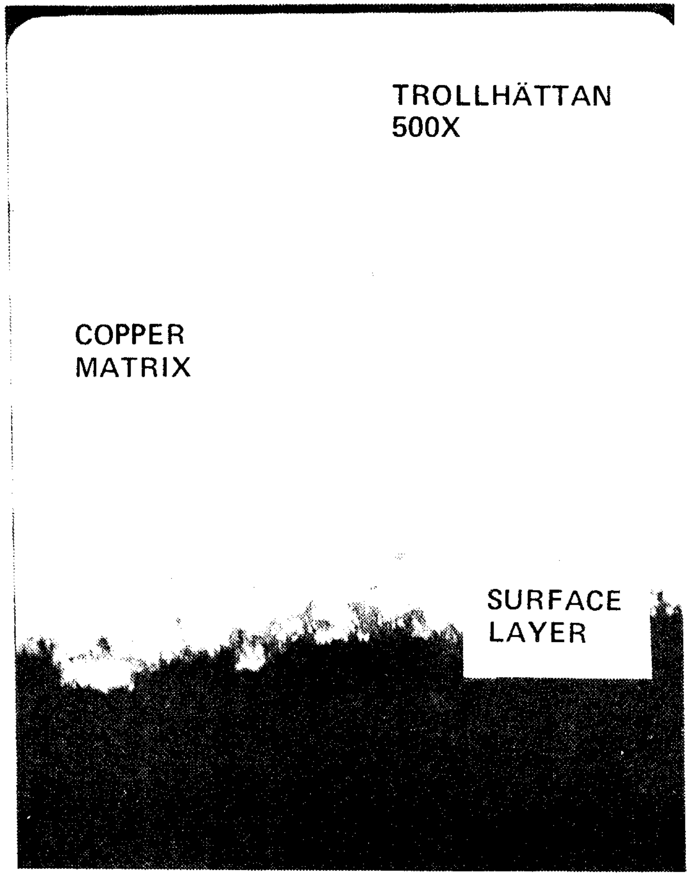
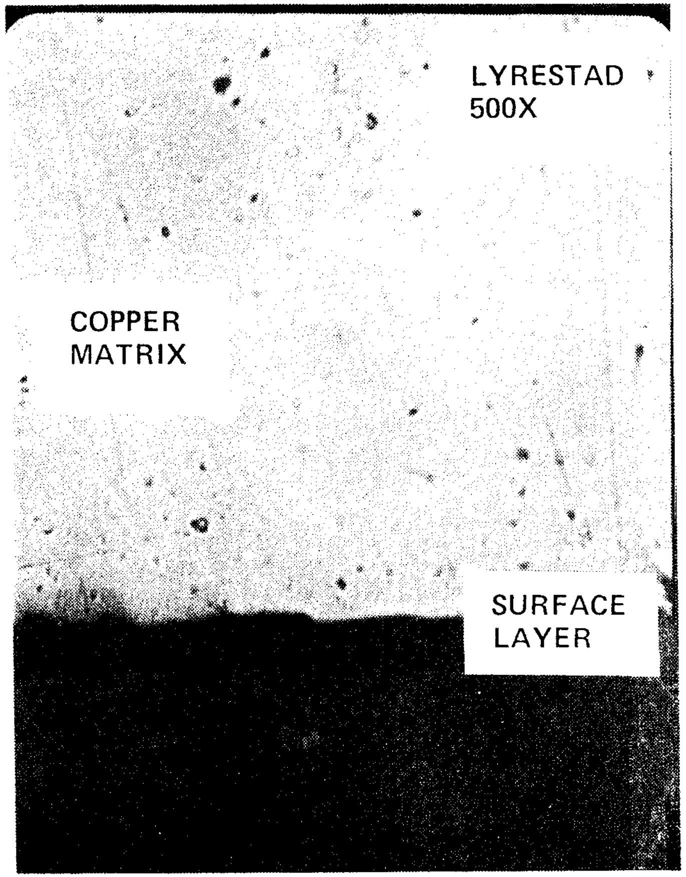


Fig. 1

Light microscopy: ZEISS







Appendix 7
(51 571)

Investigation report

Swedish Corrosion Institute

Assignment: Investigation of corrosion damage on lightning conductor plates

Client:
KBS
Att: Lars Werme
Box 5864
102 48 STOCKHOLM

Persons in charge: Göran Sund & Bo Rendahl

1. BACKGROUND

Three lightning conductor plates were submitted to the Corrosion Institute for investigation. Lightning conductor plate No. 1 was recovered from a horizontal position at a burial depth of about 120 cm in the district around Gyttorp. The soil type was mo (glacial till) with a pH of 6.8-6.9 and a redox potential relative to the normal hydrogen electrode of Eh +50 mV - -100 mV. Lightning conductor plate No. 2 was found in Trollhättan. The burial depth was about 150 cm. The soil type was stiff clay with a pH of 4.7-5.2 and an Eh of +300 mV - +150 mV. Lightning conductor plate No. 3 was buried at a depth of 330 cm in Lyrestad. The soil type was clay with a pH of 7.4-7.6 and an Eh of +250 mV - +150 mV.

2. INVESTIGATION

2.1 Examination

The lightning conductor plates were covered with soil when they were submitted. Lightning conductor plate No. 2 had a soil layer several mm thick while the other two plates had a soil layer about 1 mm thick. The plates were cleaned with a scrubbing brush and water. A rectangular piece measuring about 10 x 10 cm was sawn out of each plate. The pieces were pickled in 10% H_2SO_4 for about 2 min.

After pickling, the pieces were examined for pitting. No clear corrosion pits were detected.

2.2 Microscopic examination

Test pieces were taken from the rectangular pieces for microscopic examination. Three sections were ground and polished. The sections were then examined under a microscope with the following results:

Lightning conductor plate	Thickness	Maximum pit depth	Uniform corrosion
1	1.8 mm	25 µm	30 µm
2	1.4 mm	~0	10 µm
3	1.7 mm	10 µm	15 µm

Extensive corrosion attacks typical of uniform corrosion were found on both sides of the plates. The uniform corrosion has been estimated on the undersides of the plates. The estimates are based on measurements of the level difference to apparently unattacked areas.

3. CONCLUSIONS

- No real pitting was observed. There were some pits, however, since a corrosion attack is never completely uniform. The maximum pit depth in these pits was measured at 25 µm in plate No. 1.

- Uniform corrosion was found on relatively extensive areas. The depth of penetration was estimated at 30 m for plate No. 1, 10 µm for plate No. 2 and 15 µm for plate No. 3.

Appendix 8

MICROSCOPIC INVESTIGATION OF THE STRUCTURE OF COPPER SPECIMENS

Sten Modin and Helfrid Modin
Metallografikonsult HB, Skattungsvägen 14, 121 70 Johanneshov

Introduction

This is a summary report of three separate reports on the structure of electron-beam welded copper and hot isostatically pressed copper. The investigation concerns:

1. The structure and predicted corrosion resistance of electron-beam-welded copper.
2. The structure and predicted corrosion resistance of copper welded by means of a hot isostatic pressing technique (HIP).
3. The structure and corrosion resistance of copper produced from copper powder by means of hot isostatic pressing (HIP).

For the copper material produced from copper powder, three different powder grades have been used.

Specimens with HIP joints

According to the manufacturer, the surfaces to be joined have been cleaned carefully, the last step being a surface treatment with a rotary copper brush. The pieces are then joined together by means of hot isostatic pressing.

In the etched specimens, the joint can be seen with the naked eye, due to the considerably smaller grain sizes in the joint area as compared to the surrounding material, see Fig. 1. In the polished specimens, the joint is not discernible to the naked eye or under a microscope, see Fig. 2. As is apparent in this figure, there is a crack in the joint. According to the manufacturer, this is most probably due to test bending of the specimen before it was submitted for metallographic investigation.

A closer study of the joints reveals that the zone of finer grain sizes varies in thickness. The manufacturer attributes this to the process of cleaning the surface with a copper brush. This treatment may not have been uniform over the whole surface area.

Electron-beam welded specimens

In the electron-beam-welded specimens, the grain sizes at the centre of the welded zone are somewhat smaller than in the surrounding material, see Fig. 3. Only a few pores can be found in the welded zone. In the outer, somewhat coarse parts of the welded zone, faint striations are evident after etching. These striations run through the depth of the weld, i.e. along the direction of the electron beam. Only a few pores were found. The surrounding, unfused, material is characterized by grains with twins.

An attempt has also been made to determine the corrosion resistance of the welded zone. The specimen was etched in depth using an aqueous solution with 20% ammonium persulphate with ammonia added. The etching was carried out at about 40°C. The welded zone did not etch stronger than the surrounding material, see Fig. 4. However, the striations mentioned above appeared more clearly in relief.

Based on this study, the corrosion resistance of the welded zone should not be lower than that of surrounding material. The weld should, however, be investigated for the presence of pores by means of either X-ray or ultrasonic technique.

Specimens prepared by hot isostatic compaction of powder

Three different specimens, prepared from copper powder of increasing purity, were investigated (see Figs. 5, 6 and 7 in order of increasing purity). The less pure specimens exhibited Cu_2O inclusions of various sizes. Porosities were also found to some extent. However, the sample with the highest purity, i.e. lowest oxygen content, had no Cu_2O inclusions, although a small number of pores and/or slag were seen.

Judging from the microscopic examination of the specimen with the lowest oxygen content, the low frequency of pores and/or slag inclusions should not appreciably affect mechanical strength or corrosion resistance.

Helfrid and Sten Modin
METALLOGRAFIKONSULT HB

Sten Modin

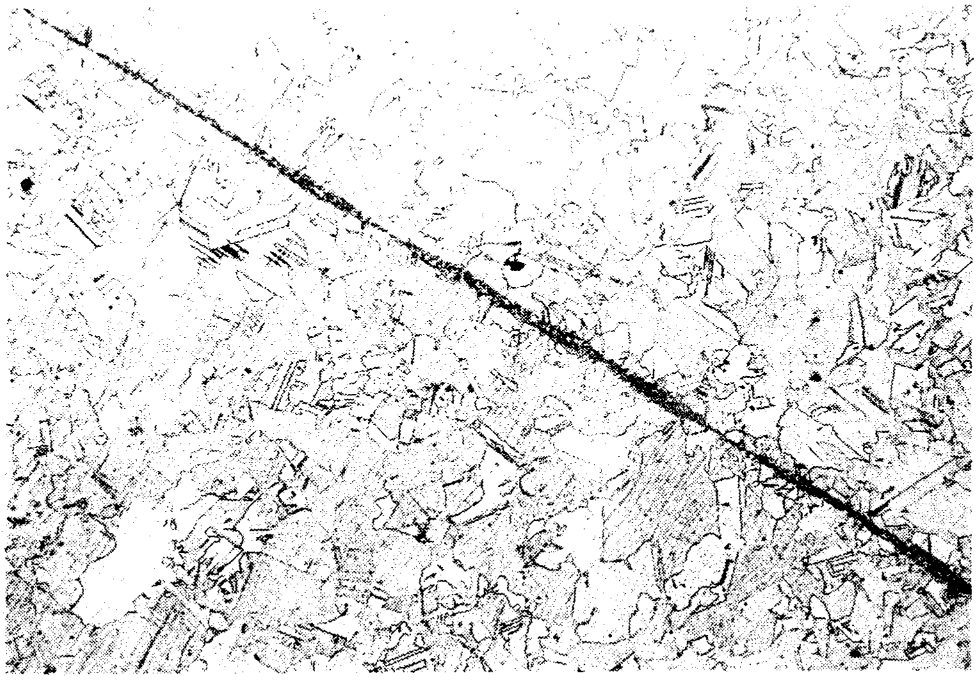


Figure 1. HIP joint. Etched in ammonium persulphate. 50X.

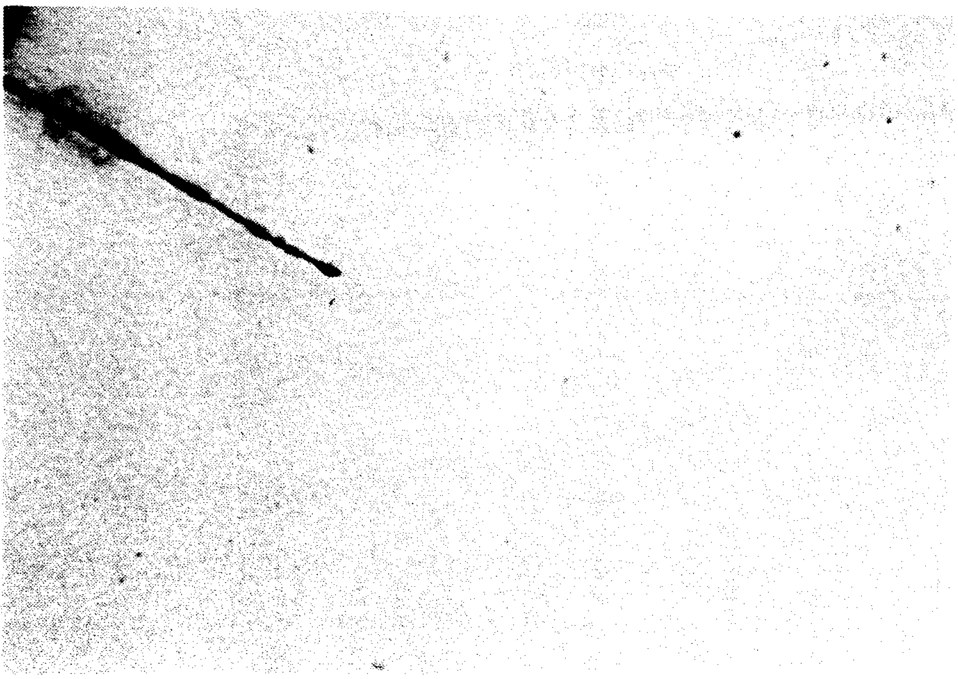


Figure 2. HIP joint. Unetched. 25X.

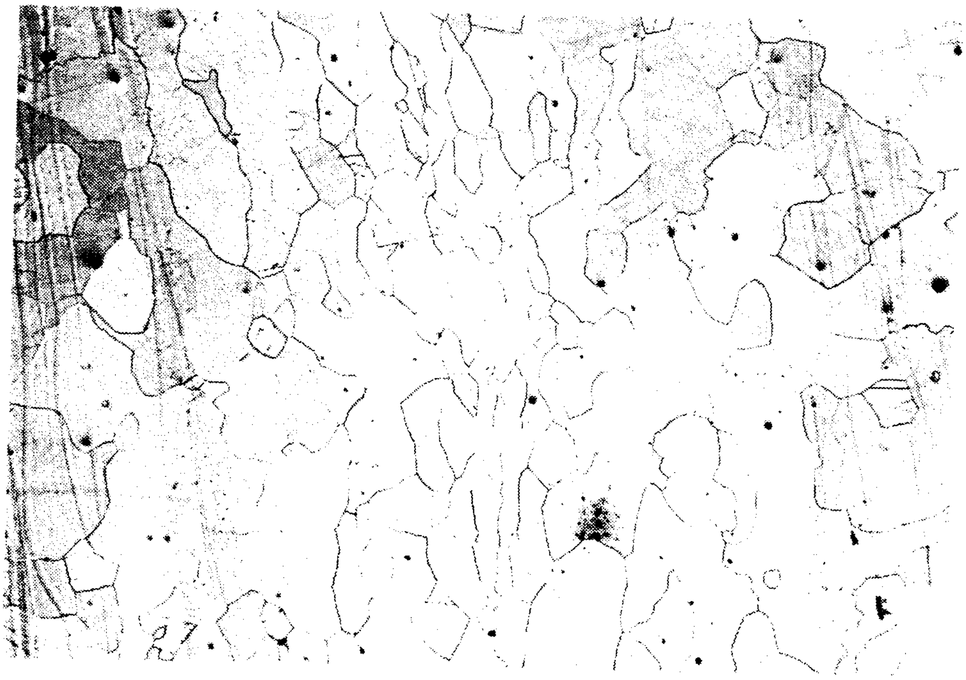


Figure 3. Electron-beam-welded copper. Etched in ammonium persulphate. 25X.

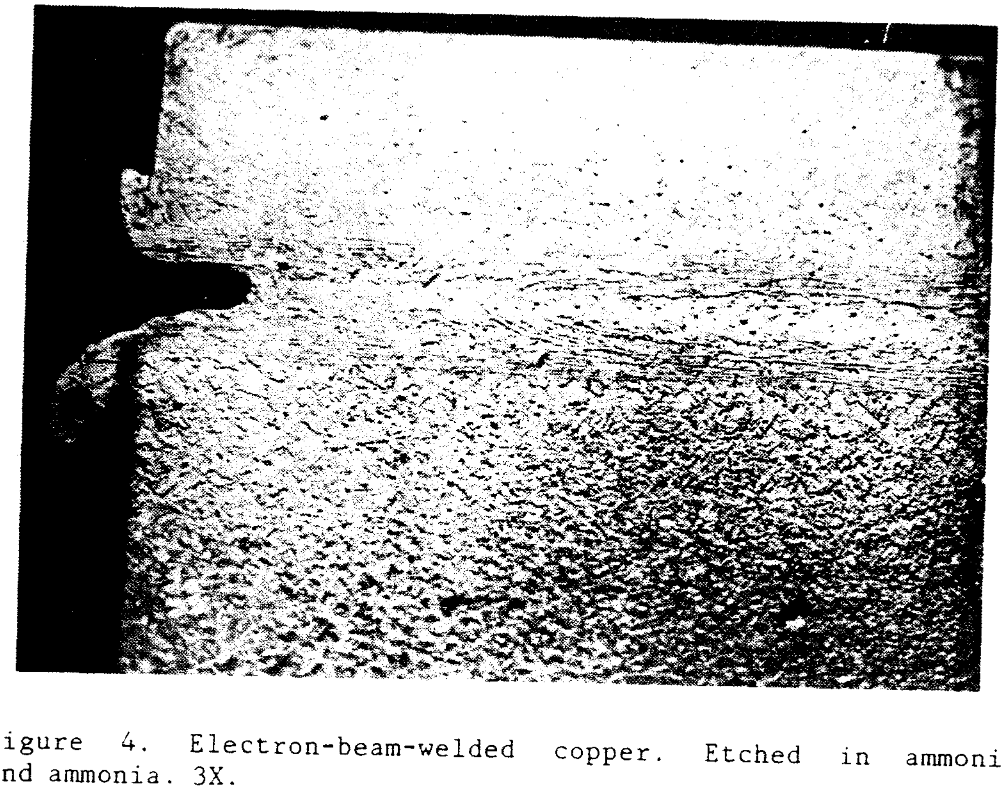
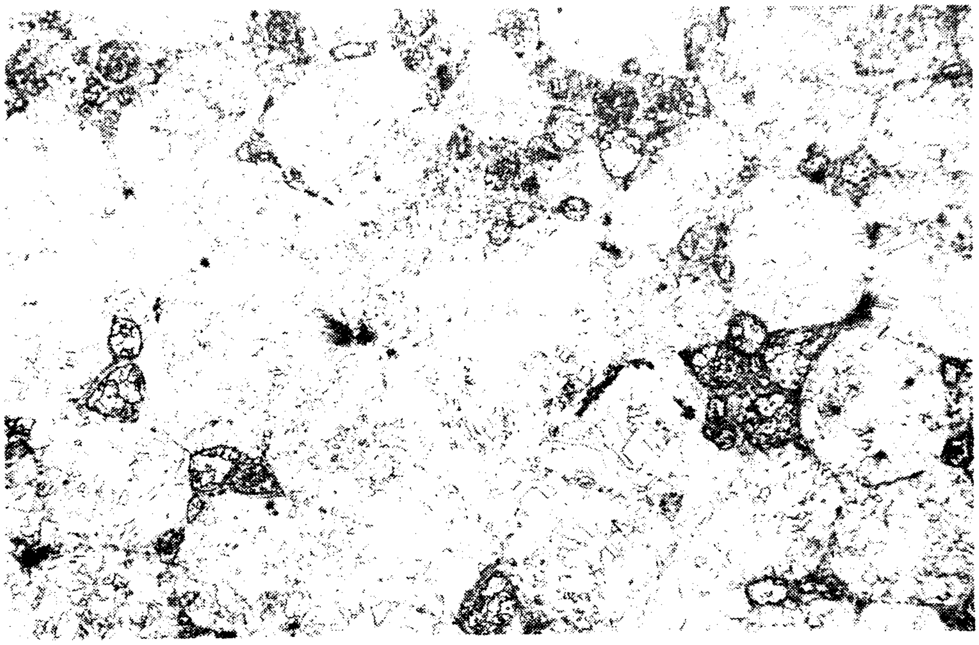
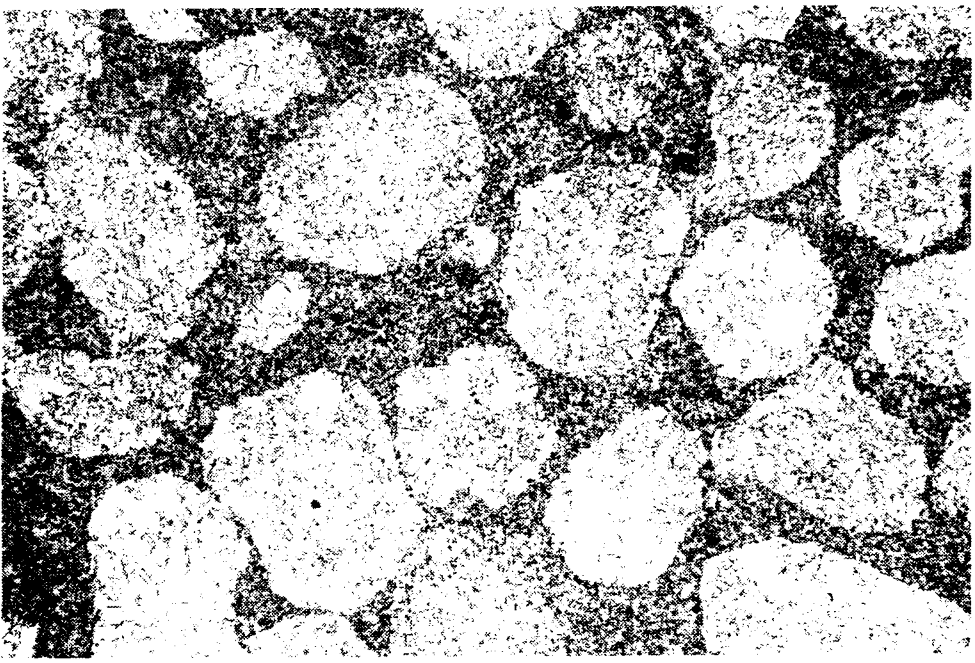


Figure 4. Electron-beam-welded copper. Etched in ammonium persulphate and ammonia. 3X.





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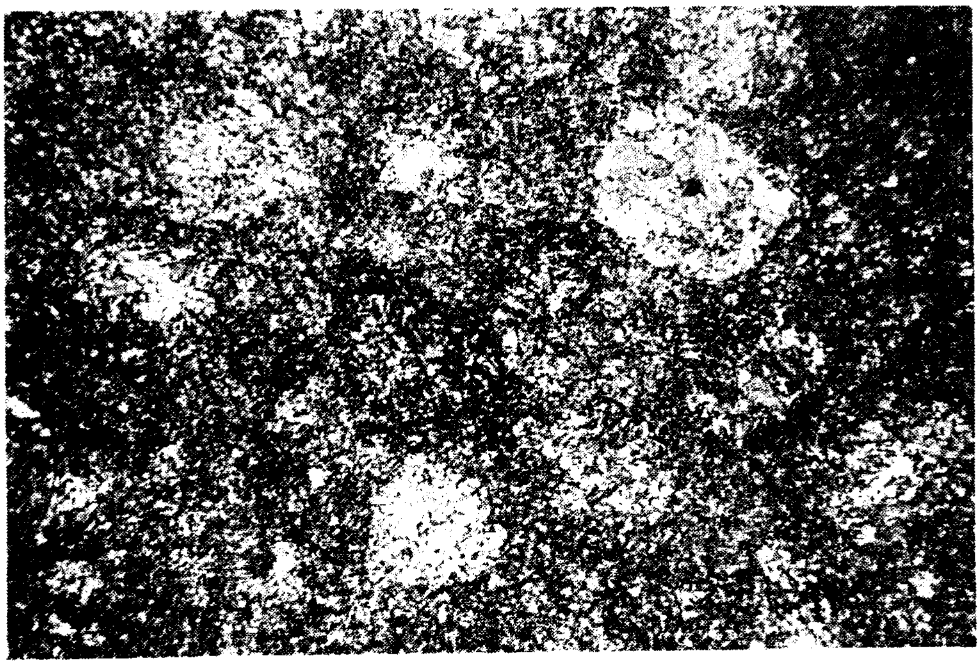

Figures 5, 6 7. HIP copper powder. Purity increases from the top downwards. Etched in ammonium persulphate. 25X.

The corrosion resistance of copper canisters for spent nuclear fuel - follow-up

(Report from the Swedish Corrosion Institute, April 1983)

Supplementary statement
by
Professor Gösta Wranglén

Having found myself able to concur this time - in contrast to what was the case with regard to KBS Technical Report 90, published in 1978 - with the Swedish evaluation of the Corrosion Institute of copper as a canister material intended primarily for spent nuclear fuel according to the above-mentioned report, the main body of which was published in advance in OKG-Aktuellt 83.1, March 1983, I can cite the following three factors as the basis for my decision:

1. The flow of groundwater around the canisters (see section 2.3 in the above report) has been studied and elucidated in far greater detail than was the case in 1978.

2. I now found reason to accept the geological premises stipulated by KBS, which I previously felt I should question, particularly in view of a report dated 12.3.1979 written on assignment for the Swedish Nuclear Power Inspectorate by the Consultant Group for Geology Matters (A. Wesslén et al). I would, however, like to point out that no refutation of the aforementioned report was submitted to the Corrosion Institute's Reference Group for Canister Material for Nuclear Waste.

3. The Social Democratic Government has announced that the so-called "Stipulation Act" of 1977, with its requirement for an "absolutely safe" disposal of nuclear waste, has been repealed, something which I myself recommended in an article in the Social Democratic press back in the summer of 1977. In its motivation for a forthcoming "Nuclear Activities Act", the Nuclear Legislation Committee, under the chairmanship of Director-General Valfrid Paulsson, states in its report (Legislation in the field of nuclear energy, SOU 1983:12, Liber Förlag, March 1983):

"that with the present state of knowledge, no absolutely safe method of solving this technical problem can be stipulated". By this formulation, the Nuclear Legislation Committee has thus supported my rejection of the various proposals for the final disposal of nuclear waste, based on the Stipulation Act, which I have publicly announced on a number of occasions over the past 6 years.

According to the KBS report "Handling of Spent Nuclear Fuel and Final Storage of Vitrified High Level Reprocessing Waste, part IV, Safety Analysis", Fig. 3-8, page 30, the so-called "hazard index" for spent nuclear fuel, specified with 1 tonne of pure natural uranium as a unit, takes approximately 10 million years to decline to the corresponding hazard index for 30% uranium ore, which is an unusually rich uranium ore with a high content of the mineral pitch blende (U_3O_8). Thus, even after 10 million years, the spent fuel is 100 times more dangerous than normally occurring and feasible uranium ore with 0.3% uranium and 1 000 times more dangerous than the normally unfeasible Ranstad ore, which contains only about 0.03% uranium.

Against this background, it is reasonable to require a canister life of 1 million years. According to the report cited in the heading, table 7, Total attack on the canister, improbable case, a copper canister with a wall thickness of 100 mm could conceivably be perforated after only 10 000 years. According to chapter 4 of said report, Conclusions, this risk is avoided by adopting either of the following measures

- the mouth of the borehole is sealed with a granite lid

- the assumed bentonite grade with 0.81% SO_4^{2-} is exchanged for a sulphate-poor grade with a maximum of 0.03% SO_4^{2-}.

Under either of these conditions, a copper canister with a wall thickness of 100 mm would not have been perforated even after 1 million years, even under otherwise very unfavourable and improbable conditions.

Even in consideration of the new factors mentioned above (improved knowledge of groundwater flow, acceptance of the geological premises stipulated by KBS and repeal of the Stipulation Act), I persist in my rejection of the lead-lined titanium canister (approved by the three-party Government in 1979) specified in KBS I, as well as of the so-called ASEA canister, consisting of aluminium oxide that has been compacted under high pressure and at high temperature. In both of these cases, my position is based on the pronounced risk of cracking, a risk that should be possible to disregard in the case of the copper canister.

In view of what has been said above and present-day knowledge, it also follows that I assume that not only spent nuclear fuel but also vitrified high-level waste from the reprocessing of such fuel will be finally disposed of after encapsulation in copper.

Stockholm in April 1983

Professor Gösta Wranglén

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Roland Pusch
Division Soil Mechanics, University of Luleå
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L A Benjamin
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R N Parkins
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Chalmers University of Technology
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2 Pressed copper canisters (HIPOW)
3 BWR Channels in Concrete
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H Larker, ASEA
L Ageskog, VBB
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R Thunvik
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L Fälth, University of Lund
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The Swedish Corrosion Research Institute and its
reference group
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TR 83-12 Calculation of activity content and related
properties in PWR and BWR fuel using ORIGEN 2
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Studsvik Energiteknik AB
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B Torstenfelt
B Allard
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Chalmers University of Technology
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State University of New York at Buffalo, Buffalo,NY
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Division of Soil Mechanics, University of Luleå
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C-E Klockars
O Persson
E-L Tullborg
S Å Larson
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B Allard
B Torstenfelt
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