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level waste disposal.
Corrosion aspects**

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The corrosion analysis of the copper canister for spent fuel disposal has shown that there is no rapid mechanism that may lead to canister failure. Consequently, the service life of the canister will be several million years. This factor will ensure the safety of the concept. Therefore, future work should be concentrated in identifying and evaluating possible mechanisms other than corrosion that may endanger the integrity of the canister. However, this general aim and direction of the research and development work should not completely exclude specific studies of copper corrosion. As has been stated previously, stress corrosion cracking of copper and pitting corrosion under mildly oxidizing conditions may require further attention.

COPPER CANISTERS FOR NUCLEAR HIGH LEVEL WASTE
DISPOSAL. CORROSION ASPECTS

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ABSTRACT

A corrosion analysis of a thick-walled copper canister for spent fuel disposal is discussed. The analysis has shown that there are no rapid mechanisms that may lead to canister failure, indicating an anticipated corrosion service life of several million years. If further analysis of the copper canister is considered, it should be concentrated on identifying and evaluating processes other than corrosion, which may have a potential for leading to canister failure.

1 INTRODUCTION

Common to all programmes for nuclear waste management is the concept of deep geological disposal. After encapsulating the waste in a suitable canister, it is to be buried at a depth of several hundred to a thousand meters in a geological formation. As host medium, granite, salt, clay, tuff etc. have been proposed. The choice is dictated by, among other things, the availability of suitable rock formations within the different countries planning for waste disposal.

The purpose of the waste canister is to provide safety during handling and emplacement of the waste in the repository and also to ensure complete isolation of the waste for a desired period of time. For this time period, 500 to 1000 years is generally considered as the minimum. During this time, most of the important fission products, such as ^{137}Cs and ^{90}Sr , will have decayed. This is also the time period during which the heat generation of the waste is most important. After some thousand years, the temperature of the repository is approaching that of the undisturbed rock.

In order to fulfil these requirements, several materials have been considered; corrosion resistant materials, such as titanium and titanium alloys, corrosion allowance materials, such as carbon steel and partially thermodynamically stable materials, such as copper. Due to its stability in pure water, copper was presented as reference canister material for the Swedish programme already in 1978 /1/ and was further elaborated in the Swedish KBS-3 study in 1983 /2/.

2 REPOSITORY ENVIRONMENT

The spent fuel canisters are to be deposited in a repository at a depth of about 500 m in granitic rock. The actual layout of the repository as well as the emplacement mode is still to be decided upon, but one alternative was discussed in detail in the KBS-3 study /2/. An outline of a possible layout is shown in Figure 1.

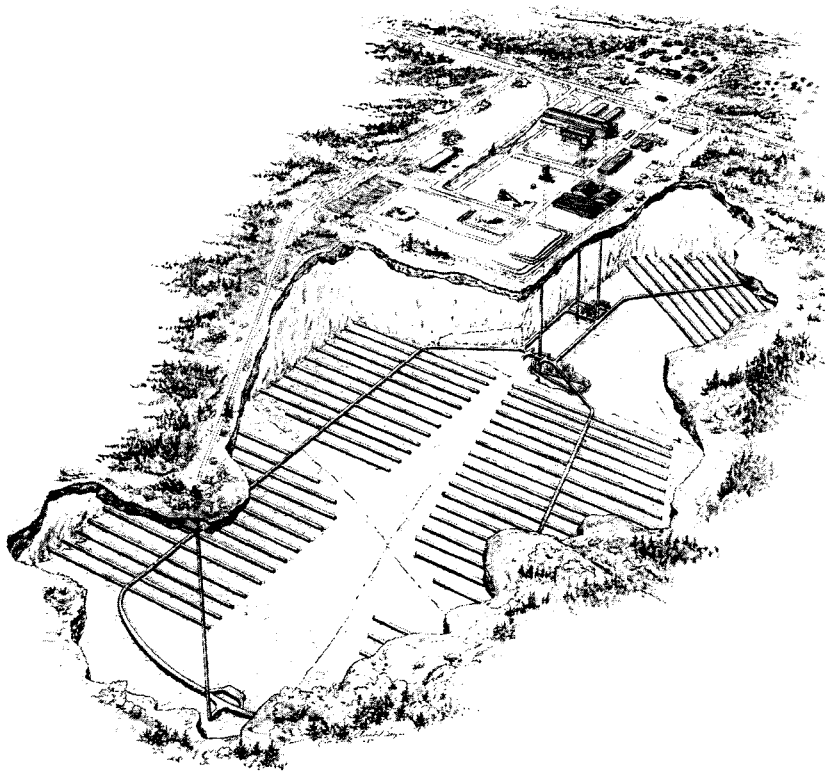


Figure 1 Perspective drawing of final repository.

In the KBS-3 concept, the canisters are emplaced in bore holes at the bottom of a drift and surrounded by compacted bentonite clay. After canister emplacement, the drift is sealed with a bentonite/clay mixture as is indicated in Figure 2. After water saturation of the repository the external pressure will reach a value of 15 MPa resulting from a hydrostatic pressure of 5 MPa and a bentonite swelling pressure of a maximum of 10 MPa.

The dimensions and waste load of each canister have been chosen such that the temperature on the outer surface of the canister never exceeds 100° C. The canister wall thickness is dictated by corrosion allowance and radiation shielding; the radiation level at the canister surface should be low enough for radiolysis effects to be negligible.

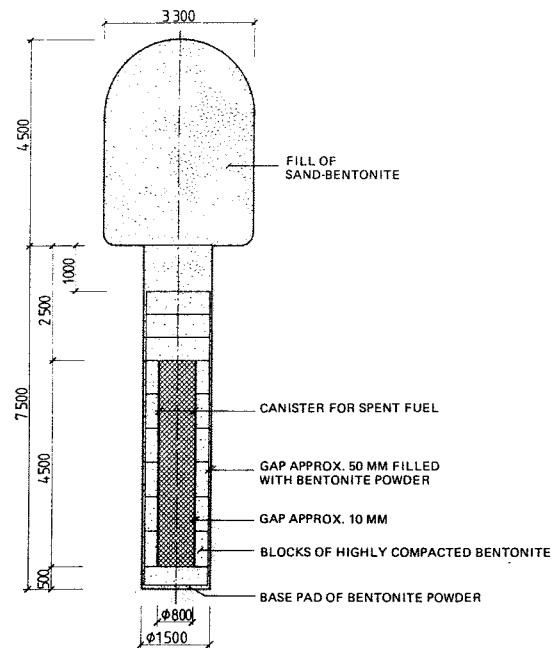


Figure 2 Deposition hole with canister, buffer material and backfill.

Since copper is thermodynamically stable in pure water, the extent of corrosion of the canister will be controlled by the supply of corrodents from the environment. These are in the initial stage oxygen trapped in the tunnels and deposition holes and oxygen (hydrogen peroxide) produced by radiolysis of water. In the longer time perspective, oxygen may be transported to the canister through the groundwater. This is, however, more unlikely since the deep groundwaters are reducing, in which case the main corrodents will be sulphides. These sulphides may be supplied by the buffer mass in the deposition holes and the tunnel filling materials. The supply of sulphides from these sources is limited, but there may be a continuous supply from the groundwater, which may contain sulphides at the level of about $0.5 \text{ mg} \cdot \text{dm}^{-3}$. A corrosion evaluation has been presented by the Swedish Corrosion Institute /5/ for the KBS-3 study. There have been no developments that indicate that this evaluation should be revised at this stage except in details and the results will, therefore, be reviewed here as a basis for the subsequent discussion.

The water flow in granitic rock is, of course, very unevenly distributed, since it is controlled by the fracture pattern in the rock. The inward transfer of corrosive species at the steady state is determined mainly by diffusion in, and by advection of water outside the buffer. The transfer rate can be expressed as:

$$R = Q_{eq} \cdot C_{amb} \quad (Eq. 1)$$

where C_{amb} is the ambient concentration and Q_{eq} is the rate constant. The latter is assumed to be 1 dm³ per canister and year in the following analysis, corresponding to a 0.3 dm³ · m² · a⁻¹ flow rate of the groundwater, which is a typical value for Swedish crystalline rock at about 500 m depth. The composition of granitic groundwater varies within rather wide limits, is shown in Table I.

Table I. Typical composition of the groundwater in the near-field. Estimates are made on the basis of extensive field investigations and the bentonite/water interaction tests.

pH		6.5...9.0
Eh{V}		-0.5...0
HCO ₃ ⁻	mg/dm ³	40..500
SO ₄ ²⁻	"	40...60
HS ⁻	"	0.1...1
HPO ₄ ²⁻	"	0.1...0.2
PO ₄ ³⁻	"	0.01..1
NO ₃ ⁻	"	0.01..0.6
NO ₂ ⁻	"	0.01..0.1
Cl ⁻	"	1..17000
F ⁻	"	0.2..10
Ca ²⁺	"	5...3200
Mg ²⁺	"	1...50
Fe ²⁺	"	0.1...3
Fe ³⁺	"	< 10 ⁻¹
Mn ²⁺	"	0.2...0.5
K ⁺	"	1...25
Na ⁺	"	10...4000
Al ³⁺	"	0.01...0.2
SiO ₂	"	2...20
TOC	"	1...8

In addition to the variability in groundwater composition, the interaction with the bentonite clay must also be considered. As can be seen in Table I, deep granitic groundwaters are reducing, neutral to basic in pH and has low ionic strength, although relatively high chloride concentration can be found. Apart from chloride, the more important anions in concentration are bicarbonate, and to some extent sulphate.

3 AEROBIC CORROSION

Corrosion by oxygen

The oxygen available for corrosion is the oxygen initially present in the deposition holes and in the tunnels. In KBS-3, the oxygen in the deposition holes was assumed, somewhat arbitrarily, to be consumed entirely by copper corrosion during the initial 1000 years. Of the oxygen in the tunnels, only a small fraction (1 %) will reach the canister during a time period of less than 10,000 years, while most of the oxygen will be consumed by oxidation processes in the near field, such as oxidation of Fe(II) in the surrounding rock. From a mass balance calculation, the total amount of corroded copper per canister could be calculated, see Table II.

Table II. Quantity of oxygen supplied to the canister surface, expressed in equivalent quantities of Cu(I) in kg (from ref. /5/).

Reactant	Exposure time, years			
	10^3	10^4	10^5	10^6
Initially in deposition hole	4.8	4.8	4.8	4.8
From tunnel	0.30	0.38	0.38	0.38

As can be seen from the table, these are very small quantities, corresponding to a uniform corrosion of less than 50 μm copper.

Form of attack

The uniform corrosion caused by the entrapped oxygen in the repository poses no threat to the integrity of the canister. However, if the corrosion had a highly localized character, the situation could conceivably be different. The oxygen in the near field would be sufficient to cause penetration through several pits. Thus, pitting corrosion may be of concern during the aerobic phase of the repository service life. This is supported by ongoing modelling studies of pitting corrosion under mildly oxidizing conditions. Current results are presented in ref. /13/. These indicate that at elevated temperatures (100°C) for prolonged periods of time corrosion pits may develop to some depth, while at room temperature it poses no threat to the canister integrity. However, the modelling has so far only been applied to a limited range of repository conditions and the study will be extended in the future.

The aerobic phase of the repository is a limited period, the length of which is determined by factors such as the amount of residual oxygen in the buffer mass, deposition holes and tunnels, the diffusivity of oxygen in the buffer and the rate at and extent to which this residual oxygen can be consumed through reactions with Fe(II) minerals present in the buffer mass. An analysis performed by MBT Tecnología Ambiental (see Appendix) has shown that the aerobic phase is relatively short. In less than 200 years 99.95 % of all the residual oxygen has been consumed by reaction with pyrite present in the bentonite buffer. For the remaining 0.05 % of oxygen to cause penetration, the corresponding pit will have to be in the order of 0.2 mm in diameter. Such a corrosion pit is highly unlikely to develop on copper. This is also supported by observations on Bronze Age archaeological objects, on which pitting corrosion was evaluated in the KBS-3 study /14/. Albeit these bronzes were exposed to temperatures lower than expected during the first centuries of the service life of the repository the observations

on the specimens indicated a pitting factor of 5 as an upper limit and 2 as a probable realistic value.

An interesting approach to the evaluation of the pitting data presented in ref. /14/ has been used by King and LeNeveu /15/. By applying extreme value statistical analysis, they concluded that even after 10^6 years, there is a vanishingly small probability that the maximum pit depth on a canister will exceed 4 mm.

On the basis of these data and observations, canister penetration from pitting corrosion can be excluded during the aerobic phase of the repository service.

Corrosion by radiolysis products

The analysis of the radiolysis from spent fuel disposed of in copper canisters presented in ref. /7/ is still valid. Although refinements can be made, they do not seem to be justified in view of the relative unimportance of radiolysis for the corrosion of copper canisters with a wall thickness of 5 cm or more.

At the radiation levels expected outside the canister, a maximum of 4.1 kg of copper can be corroded over 10^6 years /5/.

4 ANAEROBIC CORROSION

Thermodynamic considerations

Copper is the most noble of the ordinary construction materials and has consequently a fairly broad range of stability in the Eh - pH field - a range where copper is immune to corrosion in water. This is illustrated in the Pourbaix diagram in Figure 3.

The size of the stability field depends strongly on the chemical composition of the system and a necessary task to perform is to identify the components in the ground

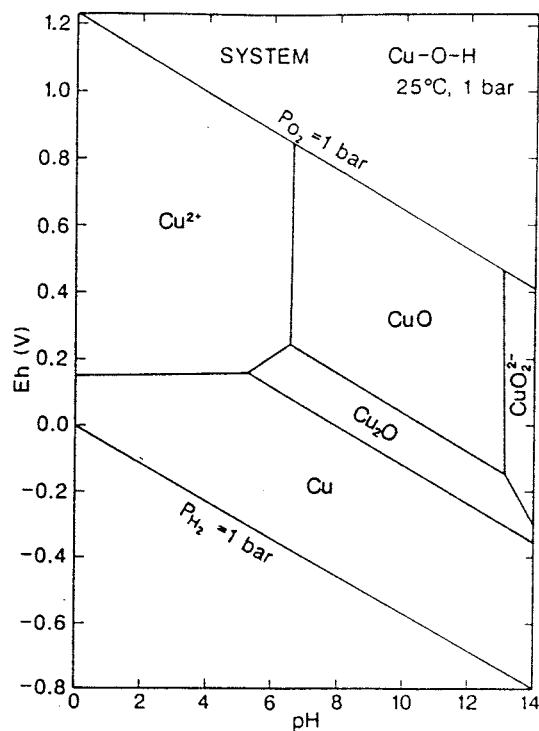


Figure 3 Potential - pH diagram for the copper/water system (after ref. /3/).

water that might affect the thermodynamic stability of copper. It is well known that the presence of sulphur markedly reduces the stability field of copper. This is illustrated in Figure 4 for the Cu/S/C/H₂O system.

As can be seen, the presence of sulphur reduces the stability field of copper to a rather narrow strip at a limited potential range, above which Cu₂O is stable and below which Cu₂S is the stable solid phase. The results of thermodynamic calculations can also be expressed graphically as plots of the activity of various copper species as a function of Eh in a system of given chemical composition. An example of such a diagram is given in Figure 5. (Note that instead of the Eh - pH plots for constant concentration given in a Pourbaix diagram, the presented diagram shows concentration vs Eh for a given pH and given concentrations for the most important ligands present in groundwater.)

Figure 5 shows that under reducing conditions, metallic copper is stable and also that in a normal granitic groundwater the dominant dissolved species are chloride complexes. The concentrations of the chloride complexes depend on the chloride concentration in

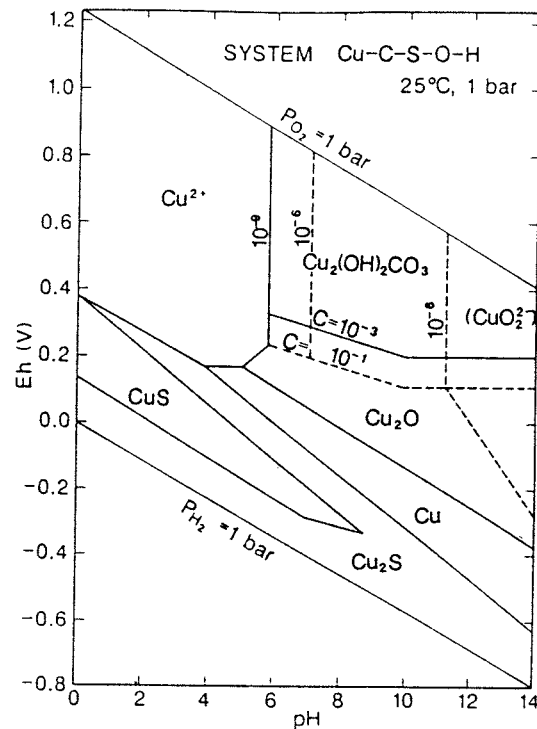
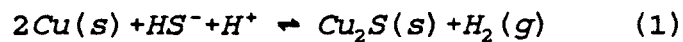


Figure 4 Potential - pH diagram for the Cu/S/C/H₂O system (after ref. /3/).

the groundwater; 1 molar of Cl⁻ in the water would correspond to an increase in the concentration of chloride complexes of about 4 orders of magnitude.

The following conclusions can be drawn from the thermodynamic analysis:

- copper can be oxidized by water in the presence of chemical substances which stabilize Cu(I) and Cu(II). As can be seen in Figure 4, one such substance is sulphide following the reaction:



- copper may also be oxidized by water in the presence of high concentrations of chloride at low pH. (The diagrams in Figure 5 refer to a chloride concentration of about 500 mg/l).

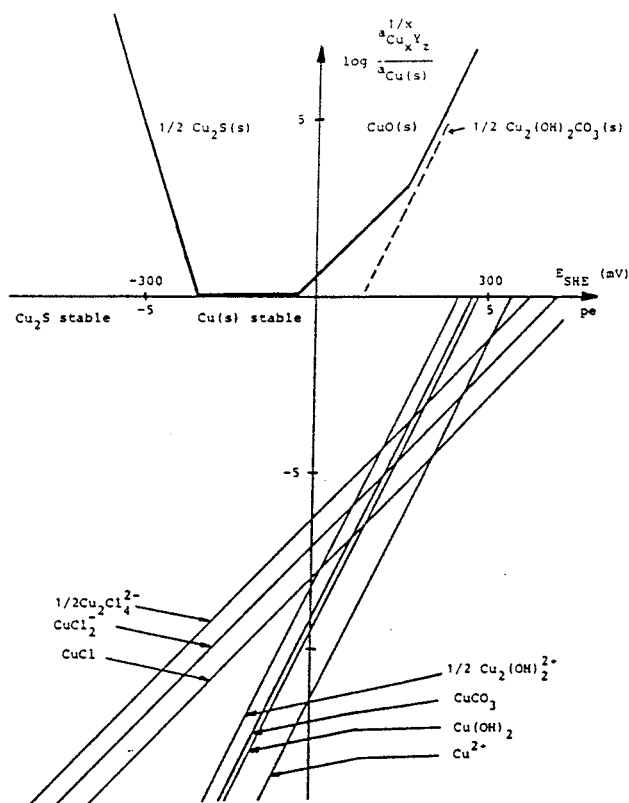
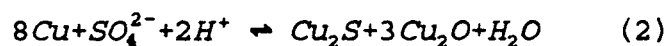
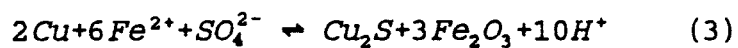


Figure 5 Redox diagram for copper in 'normal groundwater' at 25°C, pH=8.5.

- copper may also be oxidized by sulphate reduction to sulphide. The direct oxidation by sulphate in accordance with



is thermodynamically impossible in the pH range of natural waters. However, in the presence of additional electron-donors, oxidation of copper is in principle possible:



Reaction kinetics

Although the thermodynamic analysis indicate which types of corrosion reactions are possible in the system, it is more complicated to decide the rates of these reactions. There is very little information available in the chemical literature, at least about mechanistic details of these reactions. However, in a repository environment with limited groundwater flow and availability of corrodents, such detailed knowledge will not be necessary for determining the corrosion rates and waste canister lifetimes.

In the case of sulphate oxidation of copper (according to e.g. reaction (3)), it is known that the kinetic inhibition of the reaction is so strong that no examples of inorganic reduction at repository relevant temperatures are known /4/. Bacterially assisted sulphate reduction is, however, possible but will be limited by the availability of organic matter in the repository and the groundwater.

Corrosion by sulphide

As for oxygen, the sulphides can be supplied from the buffer mass/backfill in deposition holes and tunnels as well as from the groundwater. In addition to these sources, it can also be produced from sulphates through microbial activity. The KBS-3 analysis was made under the assumption that the bentonite would be subjected to oxidizing treatment to reduce the contents of sulphides and organic matter. Untreated commercial bentonite may have a total sulphide content of up to 0.2% and a content of organic matter of up to 0.3%. After heat treatment, the residual sulphide and organic matter contents are less than 0.02%.

In the KBS-3 analysis, this bentonite was assumed to be rapidly (within 1,000 years) depleted in sulphides and organic matter. For sulphides produced through microbial activity, it was assumed that 5.6 mg of organic matter will give rise to 1 mg of sulphide and that organic matter in the groundwater would increase the sulphide concentration to $1 \text{ mg} \cdot \text{dm}^{-3}$. As was discussed previously, inorganic reduction of sulphate

to sulphide is an extremely slow process and can, also for the time perspectives for a nuclear waste repository, be disregarded. The resulting corrosion is presented in Table III.

Table III. Quantity of sulphide supplied to the canister surface, expressed in equivalent quantities of Cu(I) in kg (from ref./5/).

Reactant	Exposure time, years			
	10 ³	10 ⁴	10 ⁵	10 ⁶
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

The assumption that the bentonite will be very rapidly depleted in sulphides is very conservative. It is not compatible with the low solubility of the sulphides present in the bentonite and the fact that the sulphide ions will have to be transported by diffusion to the copper surface. Indeed, the importance of the diffusion resistance was pointed out already in the KBS-3 work, but not taken fully into account in the analysis /5/.

If instant equilibrium is assumed, the diffusivity of sulphide in the clay will be limiting the corrosion rate. The rate of corrosion caused by sulphides initially present in the clay can be calculated with a front propagation model /8/. Assuming a homogenous

distribution of sulphide minerals in the clay, the propagation of the mineral front (the distance from the canister wall where the sulphide ions are consumed) can be expressed approximately as:

$$x(t) = \sqrt{2t \cdot D_e \cdot \frac{C_{HS}}{q_{HS}}} \quad (Eq. 2)$$

where $x(t) \leq 0.35$ m (thickness of depleted layer), and:

D_e = diffusivity in bentonite ($1 \cdot 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$)

q_{HS} = concentration of sulphide in bentonite, including sulphide produced by bacteria
($0.16 \text{ mol} \cdot \text{dm}^{-3}$)

C_{HS} = concentration of sulphide in pore water ($5 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$)

The corroded amount of copper as a function of time can be expressed as:

$$M(t) = h \cdot [d_1 + 2x(t)]^2 - d_1^2 \cdot \frac{\pi}{4} \cdot q_{HS} \cdot f \quad (Eq. 3)$$

where:

h = canister height (4.5 m)

d_1 = canister diameter (0.8 m)

f = stoichiometric factor for the Cu_2S production
reaction (2)

The contributions from the bentonite above and under the canister, which will cause corrosion on the canister lid and bottom, can be expressed similarly.

Using these expressions, it can be shown that complete depletion of sulphides in the surrounding bentonite would require a time period of 850,000 years. The corresponding amount of copper corroded will be some 120 kg or a corrosion depth of just over 1 mm. During that period, there can be no sulphide contribution from the groundwater or tunnels, since the sulphide concentration in the pore water is equal to or exceeds that

of the surrounding fluids. Once the bentonite has been depleted in sulphide, sulphides in the groundwater will contribute to the corrosion. With a sulphide content in the groundwater, conservatively set to 1 ppm, this corresponds to ca 1.6 g corroded copper per 1000 years.

The bentonite layer over the canister lid is 2.5 m thick. The sulphides in this part of the buffer will cause corrosion of the lid region of, i.e. ca. 10% of the canister surface. The calculations show that the time for total sulphide depletion of this section of the buffer mass will be over 40 million years. The corresponding amount of corroded copper is about 100 kg. If this corrosion is assumed to take place on the canister lid alone, it corresponds to a depth of 20 mm. Not until after this time period will the sulphides in the tunnel backfill contribute to the canister corrosion. Thus, also with bentonite of much higher sulphur content, the canister will have an expected service life of several million years.

Corrosion by chloride

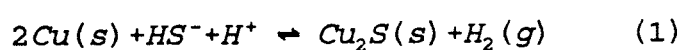
The central scenario for KBS-3 was a low salinity water with a maximum temperature of 80°C. It is possible that the maximum service temperature will be increased to 100°C, by increasing the amount of spent fuel in each canister. However, analysis of the effect, under these conditions, of chloride concentrations up to 35,000 ppm on the stability of copper was performed. It was found that also for this high salinity, the presented analysis was valid. Recently, a study has been performed for a water containing 3.0 M Cl⁻. Also at these very high chloride concentrations, it was found that the effect on the copper corrosion was negligible /6/.

Form of attack

As can be seen in Table III, the corrosion attack that can occur on the copper canister will only be of importance if it has a localized character. The most important form of

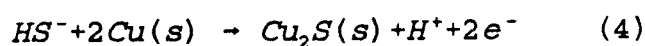
localized corrosion to be concerned with is pitting, but stress corrosion cracking need also to be considered. The pitting attack on copper under the relevant conditions appears to give rise to pits with a relatively low aspect ratio (or pitting factor, P_f). In KBS-3, a pitting factor of 2 to 5 was considered as the most realistic range. In the analysis, a pitting factor of 5 was assumed. With a pitting factor of 5 applied to the analysis presented above, corrosion failure through pitting will occur after ca. 20 million years.

As was mentioned before, copper can corrode under hydrogen evolution in the presence of sulphides:

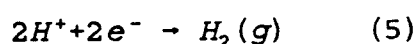


The hydrogen evolution is made possible by the low solubility of copper sulphide. The concentration of Cu^+ at the solubility limit is so low that the redox potential of the $\text{Cu}(s)/\text{Cu}^+$ system attains values such that evolution of gaseous hydrogen is thermodynamically possible. This is not possible when Cu_2O or CuCl are formed, which both have higher solubilities than Cu_2S .

The anodic step in the reaction can take place only at sites where sulphide is present:



while the cathodic step:



is independent of local presence of sulphide and hydrogen evolution can take place at cathodic sites anywhere at the copper surface /12/.

As can be seen, the anodic reaction is limited by the supply of sulphide, which will be limited by diffusion in the bentonite buffer. This fact would strongly favour an even corrosion and make local attacks by sulphide corrosion improbable. In view of this, a pitting factor of 5 can be considered as a very conservative upper limit. However, even under the highly improbable assumption that available sulphides diffuse to and react

only in a corrosion pit, the service life of the canister can be shown to be well within the design goals /12/.

5 STRESS CORROSION CRACKING

Calculations of rates of penetrations on basis of general corrosion with allowance for pitting would have a limited value if there were a likelihood of stress corrosion cracking in the environment surrounding the canisters. In an earlier study /9/, the risk for stress corrosion cracking was deemed to be nil in canisters of oxygen free high conductivity copper. There are, however, laboratory observations of stress corrosion cracking of pure copper /10/, and it was questioned whether the risk could be completely ruled out. For this reason an experimental stress corrosion cracking study was carried out within the KBS-3 analysis /11/. The study showed that stress corrosion cracking is indeed improbable under the conditions at hand in a repository. Only at extremely high nitrite concentrations (ca $1 \cdot 10^{-3}$ mol \cdot dm⁻³), as compared to the highest concentration reported in groundwater, and at high redox potentials will stress corrosion cracking be promoted in oxygen free pure copper and in oxygen free low phosphorus copper. Such conditions are very far from what is expected in the repository. Furthermore, since the corrosion resistant outer copper shell is supported internally, there will be very limited stresses in the material resulting from actions of the external pressure. However, further studies may be required before stress corrosion cracking can be completely ruled out.

6 DISCUSSION AND CONCLUSIONS

As has been shown above, the service life of a copper canister, based on the corrosion evaluation, will be several million years, provided the redox conditions in deep groundwater prevail. At the time of corrosion failure, the radiotoxicity of the spent fuel originating from fission products and actinides will have dropped considerably as can be seen in Figure 6. (In the figure, the relative toxicity of natural uranium has been

illustrated with a band from 1 to 6. This is because approximately six tonnes of natural uranium is required for producing one tonne of fuel.)

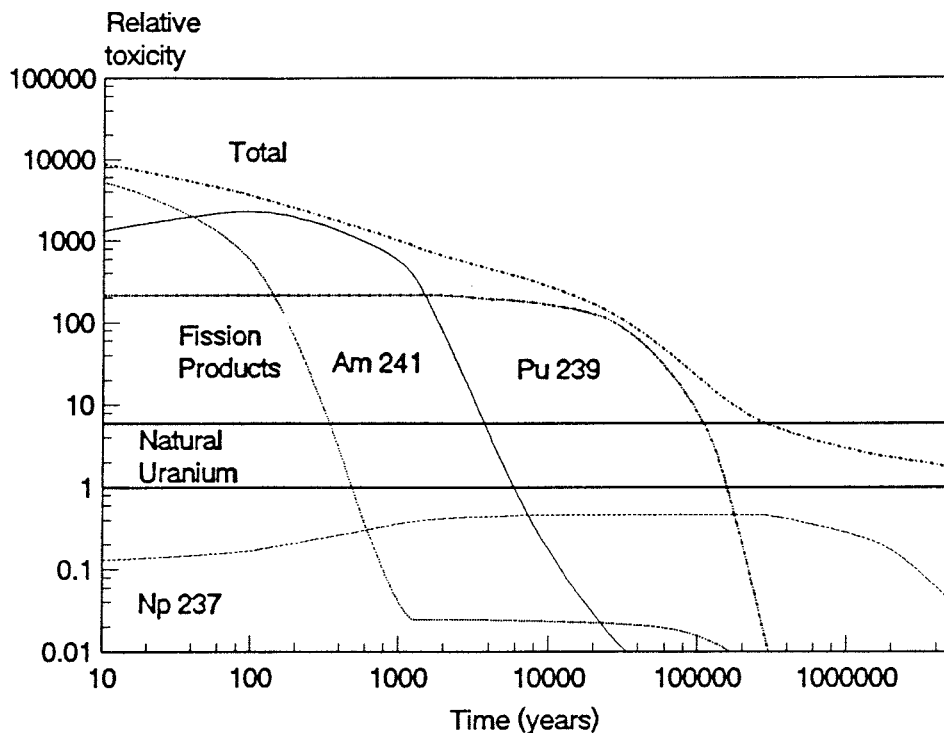


Figure 6 Toxicity comparison, spent fuel versus natural uranium.

As can be seen from Figure 6, only a few nuclides are of importance for the toxicity of the fuel after some thousand years and after the foreseen corrosion service life of the canister, the waste is not very different from a naturally occurring high grade uranium deposit. In view of this, the highest need for analysis as well as for proven safety would be scenarios which could result in release of radionuclides to the biosphere in the period up to some several thousand years. Interest should therefore be focused on failure modes other than corrosion processes, which may lead to early releases of radionuclides. These processes have all a very low probability for occurring and include defects in closure welds on the canisters, materials defects and mechanical failures. Again, it should be emphasized that such scenarios are improbable in the sense that their probability for occurring can to a large extent be controlled by quality

control measures during manufacture of the canisters, during loading and during emplacement in the deposition holes in the repository. Nonetheless, future work should be concentrated in these areas rather than in further refinement of the corrosion analysis.

The corrosion analysis of the copper canister for spent fuel disposal has shown that there is no rapid mechanism that may lead to canister failure. Consequently, the service life of the canister will be several million years. This factor will ensure the safety of the concept. Therefore, future work should be concentrated in identifying and evaluating possible mechanisms other than corrosion that may endanger the integrity of the canister. However, this general aim and direction of the research and development work should completely exclude specific studies of copper corrosion. As has been stated previously, stress corrosion cracking of copper and pitting corrosion under mildly oxidizing conditions may require further attention.

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Appendix 1

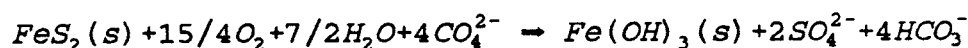
PYRITE OXIDATION IN CARBONATE BUFFERED SOLUTIONS

Kastriot Spahiu and Jordi Bruno

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The oxidation of pyrite and the subsequent production of acidic drainage has been studied in detail. The bacterial catalysis at low pH is responsible for the rapid oxidation rate of surface and subsurface waters associated with oxidizing pyritic environments /1,2/. However, when sufficient carbonate is present to neutralize the hydrogen ions produced from the oxidation of pyrite, the solution remains nearly neutral and the overall oxidation reaction can be represented by:



In these conditions ferric iron, which is an important oxidant at low pH, is almost totally precipitated as iron hydroxide, while the Thiobacillus bacteria that catalyze pyrite oxidation do not thrive above pH values of about 4 /3,4/. Lately the kinetics of oxidation of pyrite in carbonate solutions has been studied /5/. The solutions had sufficient buffer capacity to neutralize the acidity produced by pyrite oxidation and it was established that the rate of oxidation depends on the surface area of pyrite (particle size/, oxygen concentration and temperature, It was found that the formation of a layer of iron hydroxide on the surface of the pyrite particles slows the reaction rate of oxidation. The observed oxidation rates were explained by a shrinking core model, which combines the surface reaction with the accumulation of the product layer.

In the case of pyrite particles contained in bentonite, the groundwaters have sufficient buffer capacity which is also increased by ion exchange with bentonite. The oxygen content was assumed as air saturated waters in the limiting case, then calculations for

lower oxygen contents were performed. The time (in hours) to consume the pyrite particles of different size (the radius was assumed 50 μm) is calculated with the equation /5/:

$$t = [\rho_m R^2 / (6bD_g C)] [1 - 3(1-X)^{2/3} + 2(1-X)] + [\rho_m R / (bk_g C)] [1 - (1-X)^{1/3}]$$

where:

- t - is time in hours to react a mole fraction X of pyrite
- k_g - surface rate constant, determined in /5/ as $3.07 \cdot 10^6$ m/h
- D_g - diffusion coefficient for oxygen through the oxide layer, $1.08 \cdot 10^{-12}$ m²/h
- R - initial radius of pyrite particles (m)
- C - bulk concentration of oxygen in the gas phase (mol/m³)
- ρ_m - molar density of pyrite (mol/m³)
- b - stoichiometric coefficient relating pyrite oxidized to oxygen consumed

In 11 m³ of bentonite there are around 30 moles of oxygen, which then totally consumed will react with 8 moles of pyrite, giving a value for mole fraction of pyrite consumed $X = 0.030$ (calculated with density of bentonite 2000 kg/m³ and 0.2 % pyrite content).

The initial oxygen concentration is 20 %, as in air, but it will be lowered during the process of pyrite oxidation, approaching zero. In the following tables the time to consume 30 moles of oxygen by the corresponding number of moles of pyrite is calculated assuming various constant oxygen percentages in air.

As seen from the tables, even assuming a very low oxygen percentage (0.05 %, which should model the last stages of oxidation) the time required to consume 29.92 moles of oxygen is of the order of 120 years. This is due to the small particle size of pyrite (hence a big surface area) and to the stoichiometric excess of pyrite over oxygen, which means no thick layer of iron hydroxide until total oxygen consumption.

% Oxygen	Time (years)	% Oxygen	Time (years)
20	0.29	1	5.85
19	0.31	0.95	6.16
18	0.33	0.9	6.50
17	0.34	0.85	6.89
16	0.37	0.8	7.32
15	0.39	0.75	7.80
14	0.42	0.7	8.36
13	0.45	0.65	9.01
12	0.49	0.6	9.76
11	0.53	0.55	10.64
10	0.59	0.5	11.71
9	0.65	0.45	13.01
8	0.73	0.4	14.63
7	0.84	0.35	16.72
6	0.98	0.3	19.51
5	1.17	0.25	23.41
4	1.46	0.2	29.27
3	1.95	0.15	39.02
2	2.93	0.1	58.54
1	5.85	0.05	117.07

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Ebbe Eriksson¹, Bertil Johansson², Margareta Gerlach³, Stefan Magnusson², Ann-Chatrin Nilsson⁴, Stefan Sehlstedt³, Tomas Stark¹

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Christer Ljunggren³, Sven Tirén², Clifford Voss⁴

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Kemakta Consultants Co, Stockholm

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Swedish Institute for Metals Research, Stockholm

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Johan Claesson

Department of Building Physics, Lund University,
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J E Geier, C-L Axelsson, L Hässler,

A Benabderrahmane

Golden Geosystem AB, Uppsala, Sweden

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Sven Norman

Starprog AB

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Description of groundwater chemical data in the SKB database GEOTAB prior to 1990

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Sven Norman

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Royal Institute of Technology

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W Dershowitz¹, K Redus¹, P Wallmann¹, P LaPointe¹, C-L Axelsson²

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