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Research

The Stability of Magnetite and its Significance as a Passivating Film in the Repository Environment

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SKI perspective

Background

The integrity of the canister is an important factor for the long-term safety of the repository for spent nuclear fuel. The outer copper shell gives corrosion protection, while the cast iron insert gives mechanical integrity. In case there would be a hole through the copper, the iron will get in contact with water from the repository environment and start to corrode. Earlier studies have indicated that a passivating film of magnetite (Fe_3O_4) is formed on the iron. If this is valid also in high chloride and sulphide concentrations is though not shown.

Purpose of the project

The purpose of this project was to investigate, by a literature study, if magnetite could be formed as a passivating film on iron in the expected repository conditions. The possibility to form other types of passivating films was also to be regarded, e.g. other iron oxides, mixed oxides of iron and copper and also sulphides.

Results

The first conclusion from the project is that magnetite could certainly be formed on iron in an environment with repository potential (E_h) and pH conditions.

Further it can be concluded that due to the presence of copper, sulphides and chloride in the repository environment mixed phases like $CuFeO_2$ or $CuFeS_2$ could easily be formed, and these might outnumber magnetite. The passivating properties of the alternative films are most probably less effective compared to those of magnetite.

Effects on SKI work

The study will be one basis for coming SKI reviews of SKB’s programme for disposal of spent nuclear fuel, especially the review of the performance assessment SR-Can, that will be included in SKB’s application to localise and build the encapsulation plant. This application is planned to be submitted in 2006.

In the performance assessment SKB need to evaluate the internal evolution of a damaged canister, for which the corrosion of iron is an important process.

Project information

Responsible for the project at SKI has been Christina Lilja.
SKI reference: 14.9-011033/02138

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Contents

Summary

A literature review was made in order to highlight if magnetite could be formed as a passivating film on iron in the expected repository environment. The possibility to form other types of passivating films has also been regarded, e.g. other iron oxides or mixed oxides of iron and copper and also sulfides. The conditions for the formation of different types of films have been discussed as well as their compositions and properties.

It is concluded that magnetite could certainly be formed on iron at repository combinations of E_h and pH in the absence of sulphide and chloride. However, magnetite could easily be outnumbered by other solid phases that could be formed at the simultaneous presence of copper. $CuFeO_2$ is such a phase that could appear in a simple Fe-Cu-O-H system. As soon as sulphide and chloride are present other phases like $CuFeS_2$ could also be responsible for the passivation of iron. The probability that magnetite is the passivating film on cast iron at the actual conditions is therefore not very large. It is more likely that the passivating film instead consists of $CuFeO_2$ and/or $CuFeS_2$, the latter depending on the concentration of sulphur in the system. The protective ability of the alternate compounds as passivating films could be discussed. A suggested ranking order of the protective ability is given in the discussion part. If magnetite is not stable, the integrity of the cast iron insert could therefore in such cases be dependent on the protection by less effective passivating substances.

The hypothesis of the formation and nature of alternative passivating films should be tested at relevant conditions in laboratory experiments.

Sammanfattning

En litteraturstudie har genomförts för att belysa om magnetit kan bildas och ge upphov till en passiverande film på kapselns järninsats i den förväntade slutförvarsmiljön. Möjligheten till bildning av alternativa filmer vid närvaro av koppar, t.ex. andra järnoxider eller blandoxider av järn-koppar, ävensom sulfider, har också studerats. Förutsättningarna för bildningen av olika typer av filmer har diskuterats, liksom filmernas sammansättning och egenskaper.

En slutsats är att magnetit bildad på järn i de potential/pH områden som är aktuella i förvaret kan vara stabil så länge sulfid och klorid ej finns i större koncentrationer. Dock kan magnetit lätt bli utkonkurrerad av andra fasta faser som kan bildas i systemet. $CuFeO_2$ är en sådan fas som kan uppträda i det enkla Fe-Cu-O-H systemet. Så snart som sulfid och klorid är närvarande kommer också andra faser som $CuFeS_2$ möjligen att ansvara för järnets passivering. Sannolikheten att magnetit utgör passivfilmen på gjutjärn i den aktuella miljön är därför inte särskilt stor. Det är mer sannolikt att passivfilmen istället består av $CuFeO_2$ och/eller $CuFeS_2$, den senare beroende på svavelkoncentrationen i systemet. Passiveringsförmågan hos de alternativa oxiderna-sulfiderna kan diskuteras. En rankningsordning avseende denna förmåga föreslås i rapportens diskussionsdel. Om magnetit inte är stabilt kommer således gjutjärnets integritet i sådana fall att bero av det skydd som mindre effektiva passiverande substanserna kan tänkas erbjuda.

Hypotesen om bildning av och naturen hos alternativa passivfilmer bör testas i laboratorieexperiment i relevant miljö.

Introduction

The Swedish Nuclear Power Inspectorate, SKI, has studied different aspects of canister and copper corrosion as part of the general improvement of the knowledge base within the area. General and local corrosion has earlier been treated by experiments as well as by thermodynamic calculations. For completeness also galvanic and stress corrosion were treated in a literature review [1] in which also areas needing further focus were indicated. The identification of a couple of such areas is the background to performing the present and related works. The literature referenced in [1] are also accounted here [2-62] for the sake of completeness.

One of the identified areas of further focus according to previous work [1] was to highlight if magnetite could be formed as a passivating film on iron in the expected repository environment. The possibility to form other types of passivating films was also to be regarded, e.g. other iron oxides, mixed oxides of iron and copper as well as sulfides. The conditions for the formation of different films have therefore been studied as well as some information on their compositions and properties.

The foundation for the present work is a literature review focused on the magnetite stability issue. The information found is discussed in relation to a standard repository (KBS-3-type) environment with a low potential and a slightly elevated pH. It is also supposed that the canister consists of an outer cylinder of copper containing a cast iron insert. Another prerequisit is that there is a breach in the copper cylinder and that a part of the cast iron insert is exposed to the outside repository environment.

Literature search

A general literature search was performed on magnetite formation and stability in the repository using the INIS database for the period 1975 – 2002/12. Furthermore, internal databases were searched and found documents added. Relevant documents appearing in the search performed for [1] are also accounted here [2-62] for the sake of completeness. In the following, the results are accounted and discussed briefly under a set of subheadings in accordance with the main objectives of this work.

A specific study was also made in INIS and CA ranging from 1968 to 2002, focused on experimental determinations of magnetite solubilities as this is closely related to stability and formation. Some theoretical works related to magnetite solubility are also accounted.

The search logics contained the following words, sentences and combinations aiming at finding information on whether a magnetite layer is formed and acting as a passivating film on iron in the repository environment and also answering the question if alternate passivating films are formed.

Examples of words and expressions used at data base searches:

Magnetite
Thermodynamic stability
Pourbaix diagram
Repository environment
Iron oxide
Iron-copper oxide
Malachite
Copper-chloride-compound
Oxidant
Polysulphide
Solubility

In addition to the library search in data-bases, an internal search was performed amongst the proprietary documents of Studsvik Nuclear. Some of those, that are publicly available, are also accounted here.

The results of the searches are combined with the authors own calculations and evaluations regarding parts of the system Fe-Cu-S-Cl-C-O-H.

Formation of magnetite

As stated in the introduction, at a breach the cast iron insert is supposed to be exposed to the repository environment just outside the canister and to copper species. It is then questioned if magnetite and other iron oxides could form a passivating film under such conditions or more relevant under the local conditions within the breach. The following literature findings are in some way or another aiming at the answer to this question.

The first step to take would be a description of iron oxides and hydroxides and their basic properties and especially how magnetite relate to those oxides and could eventually form a passive film. Part of such a description can be found in Table 1 from Ref. [63].

Magnetite is a crystalline compound with an inversed spinel structure. The colour is black and the shape of well formed crystals are often octahedral. At all temperatures of interest for the repository, the termodynamical stability of magnetite in the simple aqueous system, Fe-O-H requires a low potential and an alkaline pH.

Table 1
Major phases in the system Fe-O-H [63].

Mineral name	Formula	Mineral name	Formula	
Goethite	α - FeOOH	Hematite	α - Fe_2O_3	
Akaganeite	β - FeOOH	Maghemite	γ - Fe_2O_3	
Lepidocrocite	γ - FeOOH	Magnetite	Fe_3O_4	
Feroxyhyte	δ' - FeOOH	Ferrihydrite	Fe_5HO_8 $4H_2O$	

In Figure 1 a schematic presentation is given of a common formation route for magnetite. Detailed information on formation and transformation routes of iron oxides and hydroxides found in Table 1 together with the approximate formation conditions, can be found in Ref. [63].

It can be seen in Figure 1 that magnetite can be formed from metallic iron via a series of steps involving oxidation, hydration and deprotonation in an alkaline environment.

$$\mathrm{Fe} \underset{A}{\Rightarrow} \mathrm{Fe(II)} \underset{B}{\Rightarrow} \mathrm{Fe(II)(H_2O)_n} \underset{C}{\Rightarrow} \mathrm{Fe_3O_4}$$

A = Oxidation, **B** = Hydration, **C** = Partial oxidation and deprotonation, alkaline pH_t.

Figure 1
A formation route for magnetite.

If the iron insert comes into contact with anoxic geological water, corrosion leading to the generation of hydrogen can also occur. This effect was studied in [64] for carbon steel and cast iron in artificial Swedish granitic groundwaters. The corrosion rate was high initially but was found to be anodically limited by the slow formation of a duplex magnetite film.

Results of experimental investigations of the process of iron oxide scale formation are also presented in [65]. Methods for decreasing and practically preventing scale formations are also proposed in that work.

The thermodynamical stability of magnetite has been calculated by several workers such as Beverskog [66]. An example of a Pourbaix diagram of relevance for the present purpose (slightly elevated temperature) is shown in Figure 2. It can be seen in the diagram that magnetite is stable at low potentials around the hydrogen line and at elevated pH-values above pH_{100} = 7.5. As a comparison it should be mentioned that neutral pH_{100} is about 6.1.

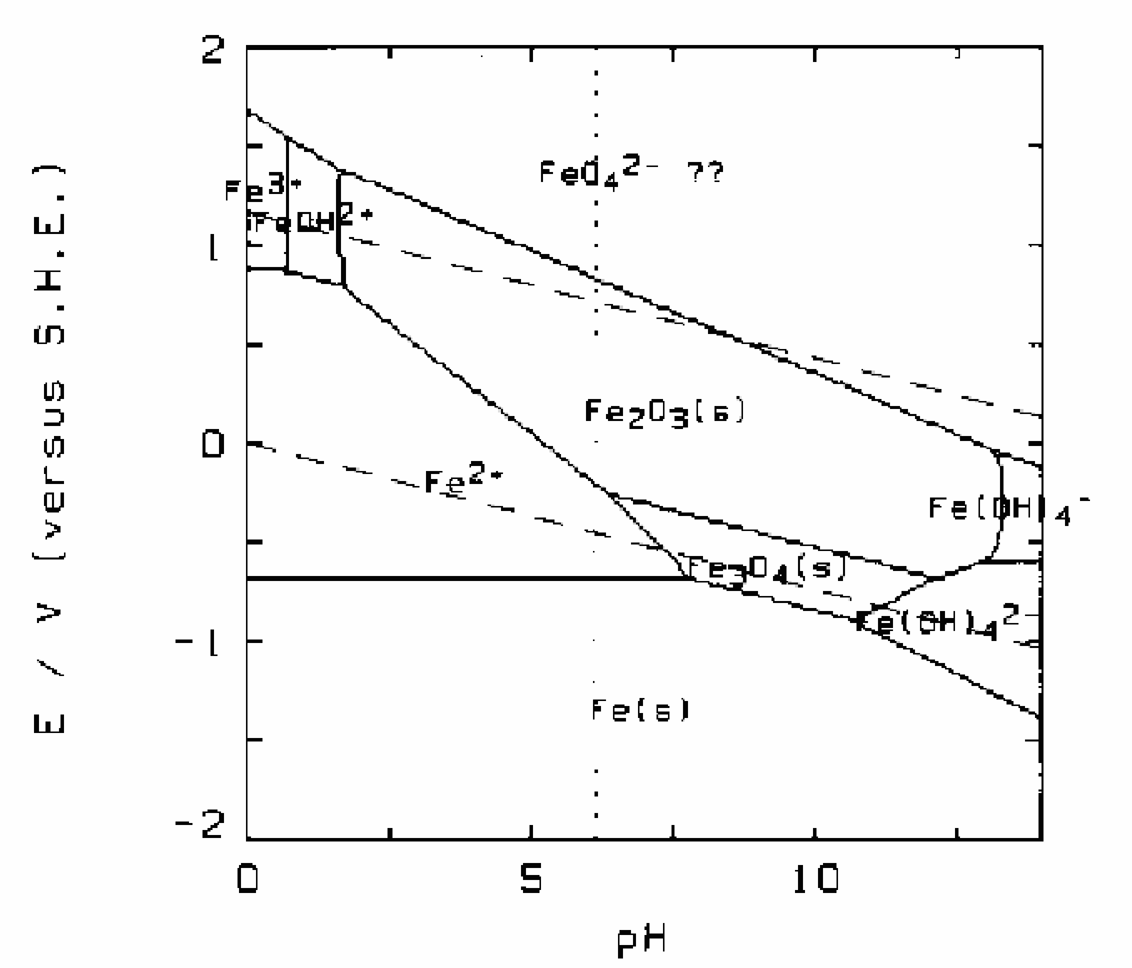


Figure 2
Pourbaix diagram for the system Fe-H_2O at 100 ºC and activity of dissolved species = 10^{-6}.

Keeping in mind the conditions for the Pourbaix diagram shown in Figure 2, it is indicated there that magnetite is thermodynamically stable roughly within $7 < pH_{100} < 12$ and within a narrow band of about +/- 0.2 V(SHE), almost symmetrically surrounding the hydrogen line. The formation could either be a result of oxidation and deprotonation of Fe(II) water complexes in solution as indicated in Figure 1 or as a result of a hydrogen forming reaction route at low potentials on and below the hydrogen line. The first mechanism could result in the formation of a precipitate of the formed magnetite that could deposit onto the metal surface. The other mechanism is prevailing as an iron surface corrodes under hydrogen evolution, giving a magnetite protective layer formed in situ on the surface. Both mechanisms could be active simultaneously on a micro-level in different parts of the chemical system.

Solubility of magnetite

As the solubility in an aqueous environment is a direct measure of the stability, such documents were also searched. They were found to be more abundant than documents dealing solely with thermodynamical stability. Most documents in this chapter are therefore describing magnetite solubility and conditions.

Kelen [67] made a literature survey on the solubility of iron-containing corrosion products. The search confirms that there are very few experimental determinations made before 1972. The number of studies increased as the number of nuclear power plants increased.

Lambert et.al. [68] studied phase relations and solubilities of magnetite and nickel and cobalt ferrites in PWR environment.

Balakrishnan [69] used a radiochemical technique to determine the solubility of magnetite. The method was developed to make it possible to determine solubilities for the oxides of iron, cobalt and nickel in high temperature water. The technique could determine solubilities of the order of 0.01 µmolal, which is about 0.5 µg Fe/kg in the case of iron oxides. The technique could also be used to measure kinetic factors as dissolution rates.

Solubilities were determined for a range of temperatures at pH 10 - 11. The potential was controlled by surging the water with nitrogen. A mean value found for the magnetite solubility was 10^{-7} m (molal, mol/kg).

Jin et.al., [70] studied the solubility of magnetite and stoichiometric nickel ferrite. The effects of temperature, lithium and boron concentrations as well as of pH and hydrogen concentration were monitored. Experimentally determined solubilities were compared with thermodynamical calculations.

The experiments were carried out in a similar manner as described in [68]. Typical results of magnetite solubility are demonstrated in Figure 3.

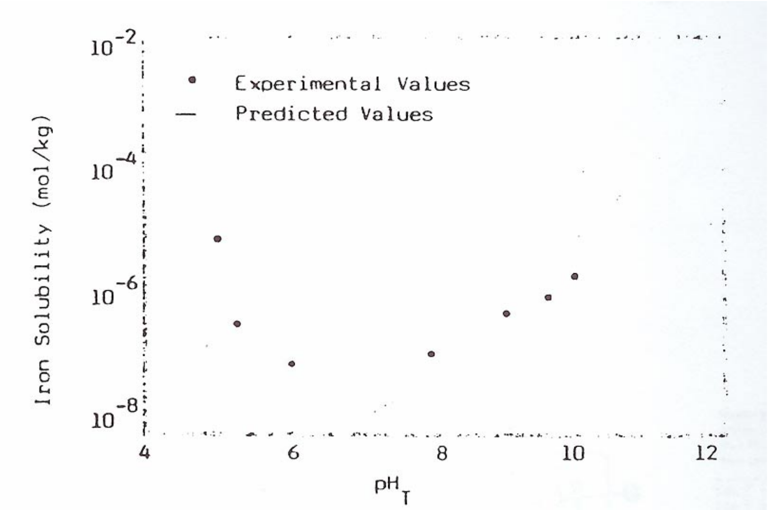


Figure 3
Magnetite solubility as a function of pH_{300} at 15 cm^3 H_2/kg.

It can be seen in Figure 3 that the solubility has a minimum of about 10^{-7} mol/kg in the range $6 < pH_{300} < 8$.

Hermansson and Lewis [71] calculated the solubility of magnetite at reactor operation conditions using extrapolated thermodynamical data. The calculated results coincide very well with other calculations and determinations giving a mean value of [Fe] about 10^{-7} M (molar, mol/l) at operating temperature for BWR (285 °C).

Dinov et.al. [72] measured magnetite solubility at 150 °C in a fully teflon covered autoclave system and sampled through a high temperature, teflon-based filter. Solubility data for magnetite found in this investigation are accounted in Figure 4.

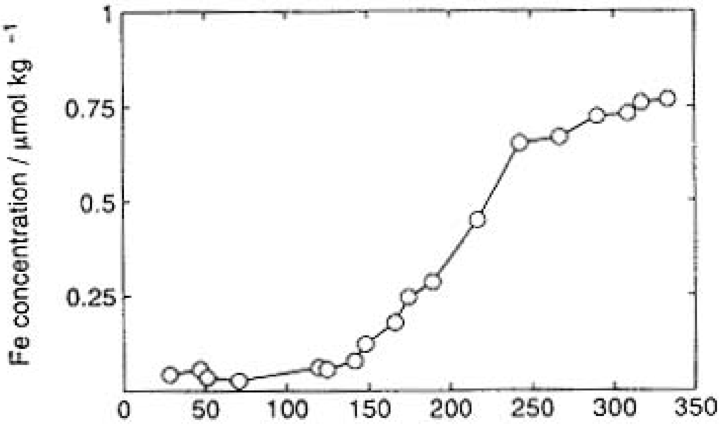


Figure 4
Time dependent solubility of Fe_3O_4 in pure water at 150 °C [72]. Exposure time in hours.

Dissolved iron was measured spectrophotometrically using phenantroline after reduction with L-ascorbic acid. A fairly good agreement was achieved between measured and calculated values assuming the model of magnetite dissolution combined with hematite precipitation.

The asymptotic value of the solubility at 150 °C is thus about 0.8 µmol/kg at neutral pH_{150}. It should also be noted that it takes a couple of weeks to reach this value.

Charles et al [73] also studied the kinetics of magnetite dissolution in the presence of complexing and reducing agents. Typical results in EDTA solutions are shown in Figure 5.

It can be seen that magnetite seems to withstands the dissolving power of EDTA at lower temperatures. At temperatures above 100 ºC the dissolution rate increases strongly with temperature.

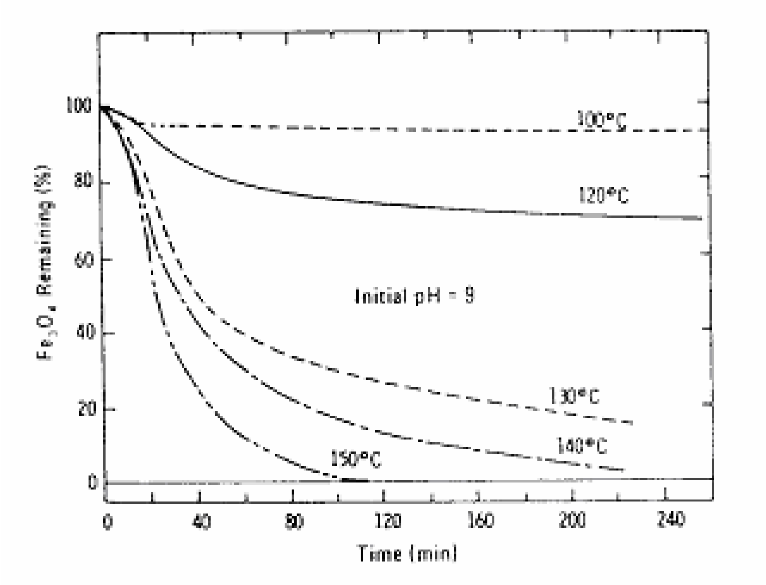


Figure 5
Dissolution kinetics of magnetite in EDA at initial pH=9 [73].

In Figure 6, the dissolution kinetics for magnetite are shown at 93 ºC for EDTA solutions with additives of different reducing agents. It is obvious that an addition of a reducing agent of the types used always increases the dissolution kinetics compared with pure EDTA solutions. It also turns out that ascorbic acid seems to be the best addition in this case to increase the dissolution rate.

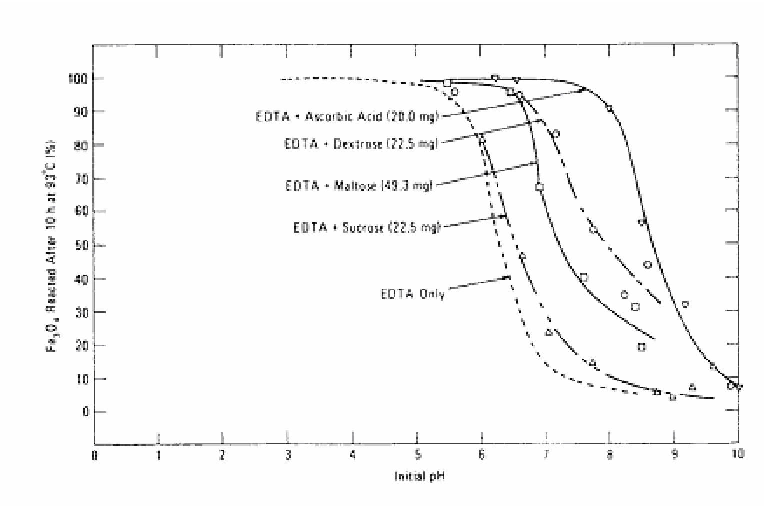


Figure 6
Magnetite dissolution in EDTA as a function of type of reducing additive.

Kanert et. al. [74] determined the solubility of magnetite in LiOH solutions saturated with hydrogen at 25 ºC. Solubilities were determined at a specific flow rate from 150 ºC to 300 ºC. The results are shown in Table 2.

Table 2
Results from solubility determinations on magnetite [74].

Run No.	[LiOH] mol/dm^3/25°	T °C	Flow Rate cm^3/h	Time of Run h	Solubility µmol Fe/kg
A-1	0.0941	200	30	24.0	1.38
A-2	0.0941	200	30	26.0	1.06
A-3	0.0941	200	34	25.8	1.31
A-4	0.0941	200	39	24.0	1.36
A-5	0.0941	200	37	24.8	1.60
A-6	0.0941	250	41	4.5	3.00
A-7	0.0941	250	58	12.0	2.68
A-8	0.0941	300	28	12.5	5.86
A-9	0.0941	300	31	8.3	5. 92
B-1	0.00817	150	40	24.0	0.189
B-2	0.00817	150	43	24.5	0.162
B-3	0.00817	150	55	23.5	0.124
B-4	0.00817	200	23	23.0	0.118
B-5	0.00817	200	18	24.2	0.126
B-6	0.00817	200	28	24.0	0.136
B-7	0.00817	250	45	24.0	0.631
B-8	0.00817	250	53	20.0	0.606
B-9	0.00817	250	41	24.0	0.688
B-10	0.00817	300	31.6	24.5	0.604
B-11	0.00817	300	41.9	24.0	0.718
B-12	0.00817	300	27.8	23.0	0.639

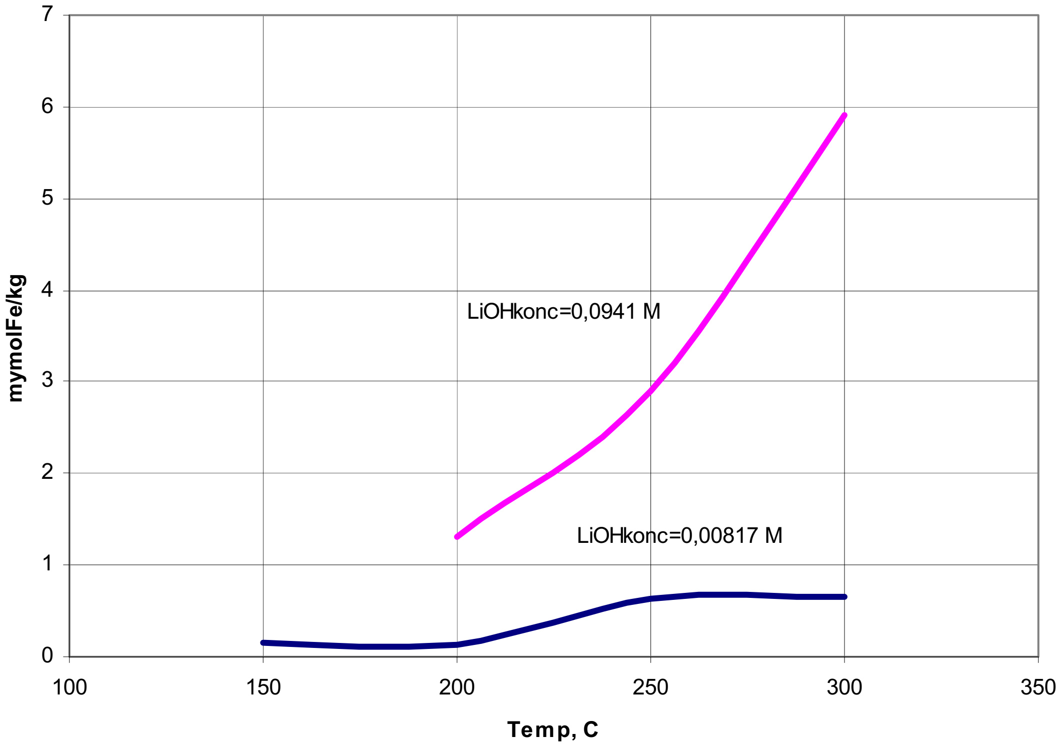


Figure 7
Schematic plot of some data from Table 2.

The values in Table 2 could be schematically plotted as in Figure 7. It can be seen in this figure that the solubility of magnetite increases both with temperature and LiOH concentration (pH) in this case. The temperature dependence is stronger at the higher LiOH (pH) concentration.

Other high temperature data on magnetite solubility can be found for example in [75]. In Figure 8 such data are accounted for the temperature range 250 – 350 ºC. Note that solubilities are given in µg Fe/kg and should be divided by 56 to give the molal solubility. These investigations were performed at a set of different hydrogen concentrations.

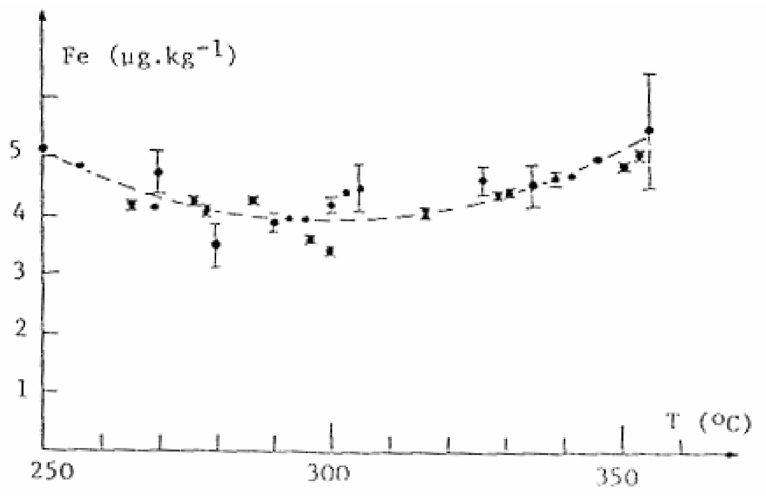


Figure 8
Solubility of magnetite as a function of temperature in PWR.

The molal solubility of magnetite in PWR primary conditions shown in Figure 8 is thus found to vary between $7x10^{-8}$ – $9x10^{-8}$, perhaps passing a shallow minimum within the temperature range 250 – 350 ºC.

In [76] the same authors have used the solubility determinations of the type shown in Figure 8 to calculate log K_o values for magnetite and plot those as a function of inversed temperature at a couple of different PWR chemistries. Log K_o values are given in Figure 9 without concern of the steps of hydrolysis.

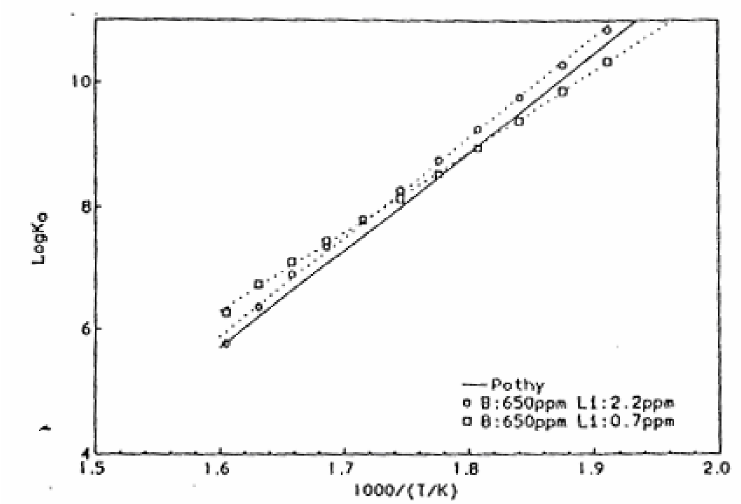


Figure 9
Log K_o values for magnetite as a function of inverse temperature at a couple of PWR chemistries [76].

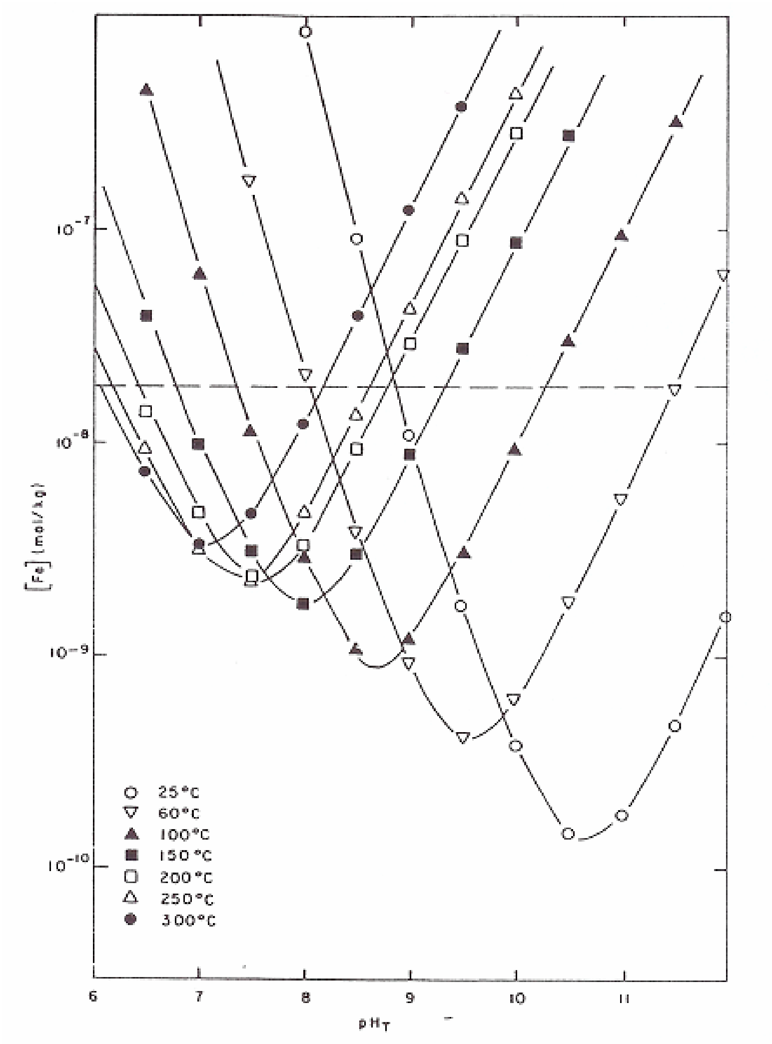


Figure 10
Calculated solubilities of magnetite as a function of pH over the temperature range 25 °C – 300 °C. $p\{H_2\} = 1$ atm.

Macdonald et. al. [77] calculated free energies of formation for iron, iron oxides and ionic species in solution over the range 25 ºC - 300 ºC. The data were used to derive potential pH relationships for the iron water system and to calculate solubilities for magnetite and hematite as a function of pH and temperature. A set of calculated solubilities are accounted in Figure 10.

It can be seen in Figure 10 that the calculated solubility is very strongly dependent on both pH_t and temperature. For 100 ºC there is a minimum in solubility (about 10^{-9} M) found at about pH_{100} =8.8. However, the solubility increses one order of magnitude with the change of one unit of pH_{100} in both directions.

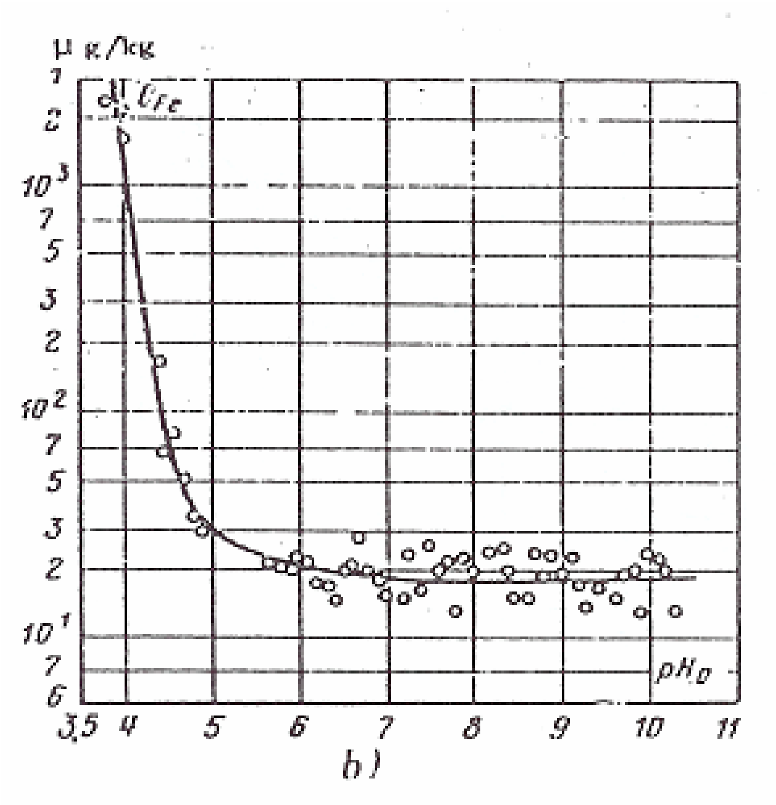


Figure 11
Solubilities of magnetite in boiling reducing water.

Styrikovich [78, 79] determined the solubility of magnetite in boiling water and in a reducing medium. In Figure 11 solubilities of magnetite in boiling water is given as a function of pH.

Also here solubilities are given in μg/kg and should be recalculated to molal values for comparison. The results shown in Figure 11 demonstrate a strong drop of magnetite solubility as a function of pH_{100}. The value at $pH_{100} > 6$ stabilizes at about $3.5x10^{-8}$ mol/kg which holds at least up to $pH_{100} = 10.5$.

Other solubility results in a reducing medium by Styrikovich are given in Figure 12 as a function of pH_{300} and in Figure 13 as a function of temperature in the range 200<t(ºC)<325.

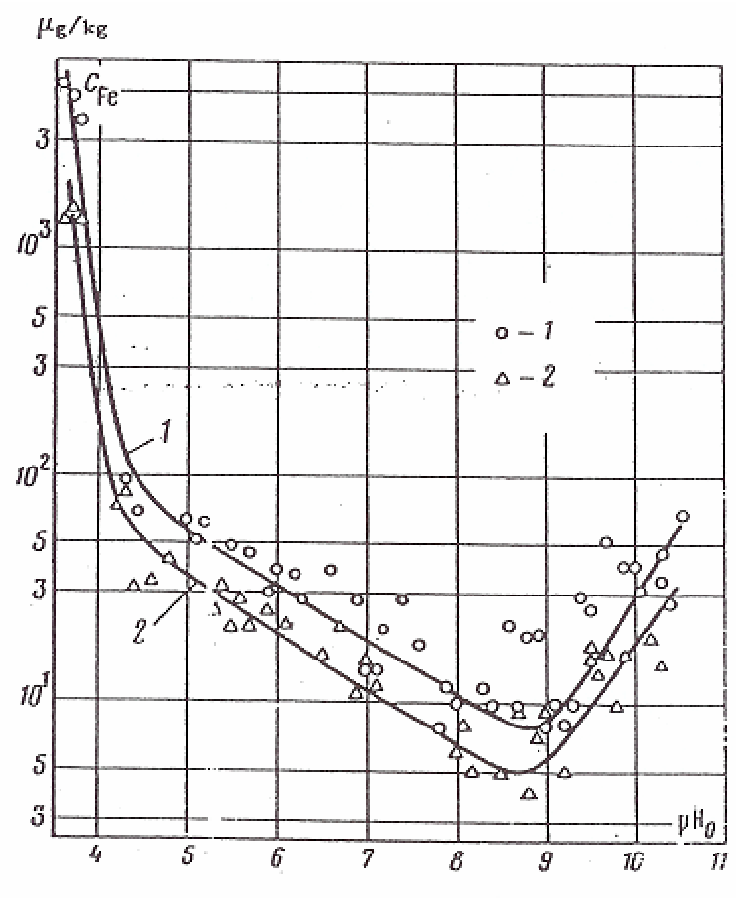


Figure 12
Solubilities of magnetite in a reducing medium as a function of pH at 300 °C.

If the results shown in Figure 12 is compared with those accounted in Figure 11 for boiling water (100 ºC and stripped from oxygen and thus also slightly reducing), it can be seen that the solubility at the higher temperature of Figure 12 is lower. There seems also to be a minimum in solubility as a function of pH at the higher temperature that cannot be seen in the boiling system at 100 ºC.

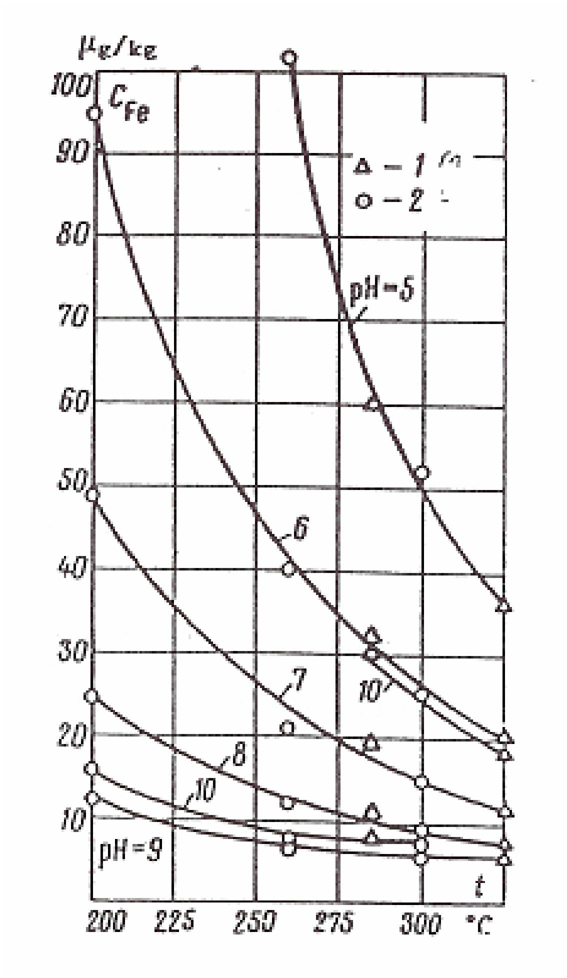


Figure 13
Solubilities of magnetite in a reducing medium as a function of temperature and pH.

In Figure 13 there is a comparison by Styrikovich of magnetite solubilities as a function of temperature and pH. Both the temperature and the pH dependencies are strong.

Sweeton and Baes [80, 81] determined the solubility of magnetite in dilute acid and basic solutions at 300 °C and from room temperature up to 300 °C.

The iron concentrations were analyzed spectrophotometrically using phenantroline on samples recieved on ion exchange columns after acidifying, cooling and filtering the solution.

As an example of results the solubility of magnetite as a function of temperature and acidity is accounted in Figure 14.

A strong dependency of acidity is demonstrated in Figure 14. The solubility drops as the acidity decreases (pH increases) at all temperatures and pH values except at some combinations of high temperature and pH. At latter conditions a minimum is found as a funktion of pH. At a slightly elevated pH at about 100 ºC, the solubility seems to be about 10^{-6} molal in a reducing environment.

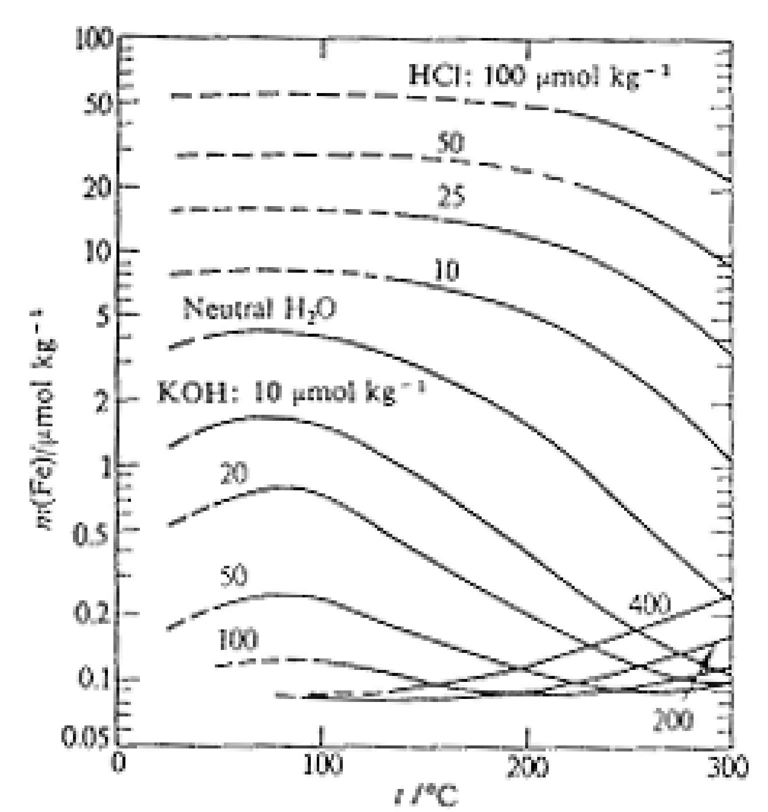


Figure 14
Solubility of magnetite in water saturated with 1 atm of H_2 at 25 °C as a function of temperature and acidity.

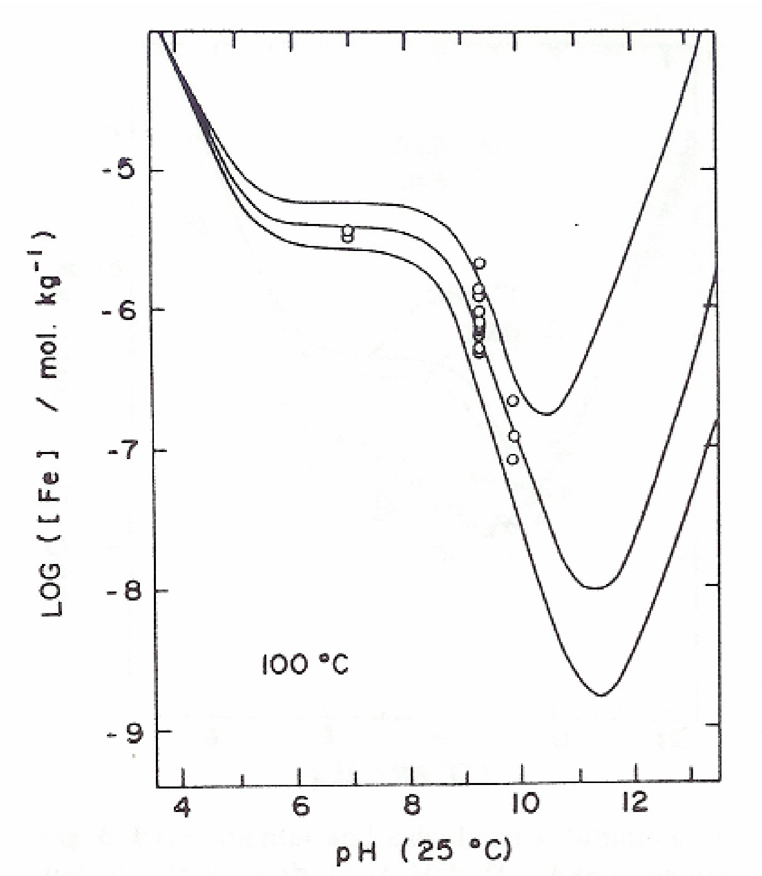


Figure 15
The solubility of magnetite in H_2O at 100 °C.

Tremain [82] reviewed Gibbs energy and entropy data for aqueous Fe^{2+}, $FeOH^{+}$, $HFeO_2^{-}$ and FeO^{+}. The most reliable values were used in a Criss-Cobble extrapolation to calculate Gibbs energies to 300 °C and, hence, the solubility of Fe_3O_4 in H_2O and D_2O as a function of pH or pD. An example of calculated magnetite solubility is shown in Figure 15.

Aaltonen [83] summarized the published results relevant to the corrosion of iron base materials in repository conditions. The general corrosion behavior as well as the localized corrosion, stress corrosion cracking and the influence of hydrogen on the behavior of iron base materials is discussed.

Bohnsack [84] discussed chemical aspects of magnetite solubility in water. Magnetite is considered to be complex since it is a compound formed from the hydroxides of ferric and ferrous iron. Beside this, in its crystalline form it is either not hydrated at all or only slightly so on its surface. The chemical nature and the structure or the surface of the metal oxides play major roles in the interaction with water and the establishment of the solution equilibrium.

Field [85] discussed the growth, structure and breakdown of magnetite films on mild steel. He examined by optical and electron microscopy magnetite films grown in alkaline solutions in laboratory pressure vessels and in operational boilers. There is formation of a protective inner layer oxide and an outer layer oxide. The inner, protective layer material occupies the same volume as the steel from which it is formed. Measurements of the countercurrents of the oxygen and iron atoms show that the magnetite is laid down in a porous condition and direct density measurements indicate a porosity in the range 10-15 percent. Electron micrographs of the inner layer magnetite show a grain-size in the range 250-5000 nm and are consistent with a porous structure in this case.

The breakdown of magnetite films grown in the laboratory and in operational boilers is compared. Strains on the magnetite due to thermal cycling and to high heat fluxes in boilers have been shown to be significantly close to the critical strains for fractures determined in simple laboratory experiments.

Park [86] accounts impedance studies of the growth of porous magnetite films on carbon steel in high temperature chloride solutions. At both 200 and 250 °C the reciprocal of the polarization resistance, which is proportional to the corrosion rate, at first increases with time, but eventually tends to a constant value. Accordingly, the early stages of corrosion are considered to be auto catalytic, but at longer times a linear rate law is observed. The early auto catalytic stage is attributed to the gradual development of a highly aggressive solution within the porous film due to cation hydrolysis and transport of chloride ions from the bulk solution into the pores.

Furthermore imposition of an anodic overpotential causes the rate of corrosion to increase; however, the effect of the applied overpotential decreases as the exposure time becomes longer. This indicates that an increasingly larger fraction of the applied overpotential is lost as IR potential drop across the porous film as the film thickens.

The impedance characteristics of corroding carbon steel over a wide range of frequency ($10^{-3} - 10^{4}$ Hz) are successfully accounted for by a one-dimensional finite transmission line electrical model. The success of this model indicates that the electrochemical and corrosion properties of the carbon steel/solution interface are determined by distributed impedance elements of the type expected for porous corrosion product films, in which current flow occurs across both the pore wall/solution and pore base/solution interface simultaneously.

As a summary of all those investigations could be said that the solubility of magnetite in an aqueous environment is a direct measure of the stability. Before 1972 very little data on this topic is available. This is certainly in accordance with the fact that at that time magnetite as a passivating/protecting film is of fast growing importance in large power plants such as nuclear plants. Beside solubility determinations for pure magnetite, solubilities for related compounds such as nickel-spinel and others are found from that period and on. Therefore many investigations are also found from nuclear power plant environments, containing LiOH and boric acid and performed at elevated temperatures. However, there are also solubility determinations from other environments like those containing complexing agents.

Many investigations are confirming each other, but others give deviating information. However, there seems to be a common agreement that the solubility of magnetite depends on many parameters, like temperature, pH and the presence of complexing agents. At the actual conditions of the repository, the solubility for magnetite is very low if the water is pure. Very roughly it is in the range 10^{-6} - 10^{-7} moles/kg over actual temperatures. If potential and pH are not kept within the stable area of magnetite it will in the pure water case either dissolve to form Fe^{2+} at low pH and lower potentials or transform to hematite, Fe_2O_3 at higher potentials and pH. The solubility of hematite, Fe_2O_3 is very low, roughly 10^{-12} moles/kg. The solubility in the system Fe-O-H will therefore vary with many orders of magnitude depending on the value of potential and pH and the values of other environmental parameters. It is therefore of cardinal importance to state all parameters when giving a solubility value for the system Fe-O-H and especially magnetite. Even if hematite has a higher stability than magnetite it is probably not protecting the metal as good as magnetite do.

The appearance of complexing agents as organic ligands and chloride ions, require very specific treatment of the solubility in those cases. The formation of magnetite could be inhibited and other compounds at best take the role of acting as a passivating film.

The kinetics of the diverse processes involved in the dissolution of magnetite has been partly treated by some authors. Those results are of course very strictly tied to the selected conditions of study, and are not generally applicable in the same way as equilibrium data. The kinetic time frames in presented data seems to be of the order of hours-weeks-months, and should be applied to repository conditions with great care.

Alternative passivating films

When conditions for the formation of magnetite are disadvantegous, alternative passivating films could be formed or the metal could be left naked, without any such film. The latter situation could be the case for copper contacting a high chloride concentration solution. When discussing alternative passivating films in the actual case, focus should be on low potential, slightly elevated pH and temperature as well as the possible presence of, beside iron and copper, also chloride and sulfide. The literature was searched with these starting criteria, but the results were rather small.

Cubicciotti [87] investigated flow assisted corrosion, FAC of steel and the influence of Cr and Cu additions. FAC of steel feed water lines occurs by dissolution of the surface oxide layer on the steel. The solubility of iron in water under FAC conditions is discussed through the use of potential-pH diagrams. Alloying additions of chromium and copper both decrease FAC. An assessment is presented that Cr additions decrease FAC by forming a mixed oxide with iron instead of a pure iron oxide. The solubility of iron from the mixed oxide is smaller than for pure iron oxide and leads to a smaller FAC rate. The stable form of copper under FAC conditions is not, however, the mixed iron-copper oxide but metallic copper, which may act in the underlying steel surface to slow down FAC. A Pourbaix diagram from [87] is shown in Figure 16.

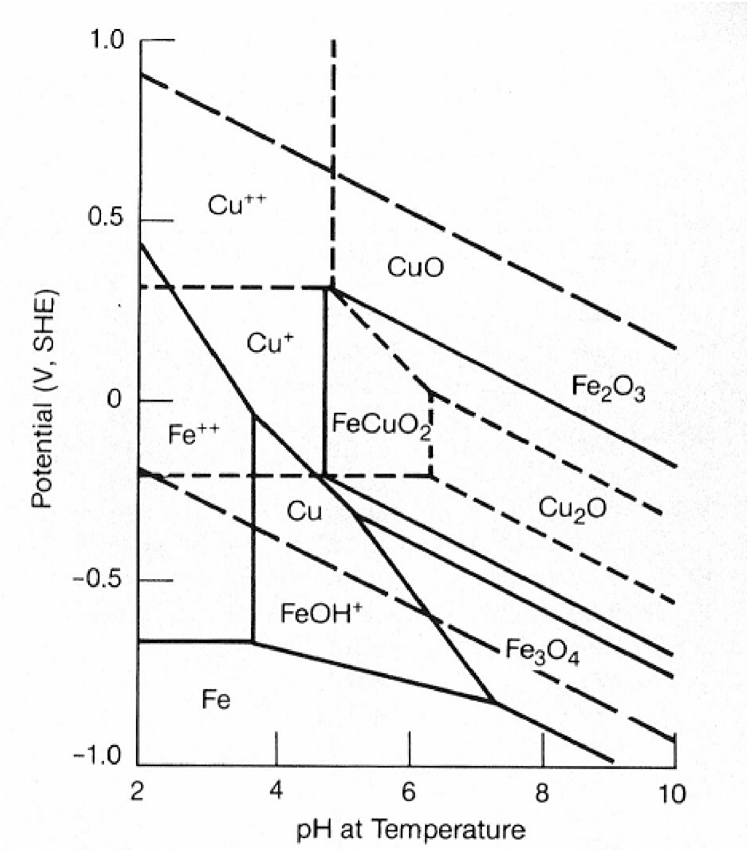
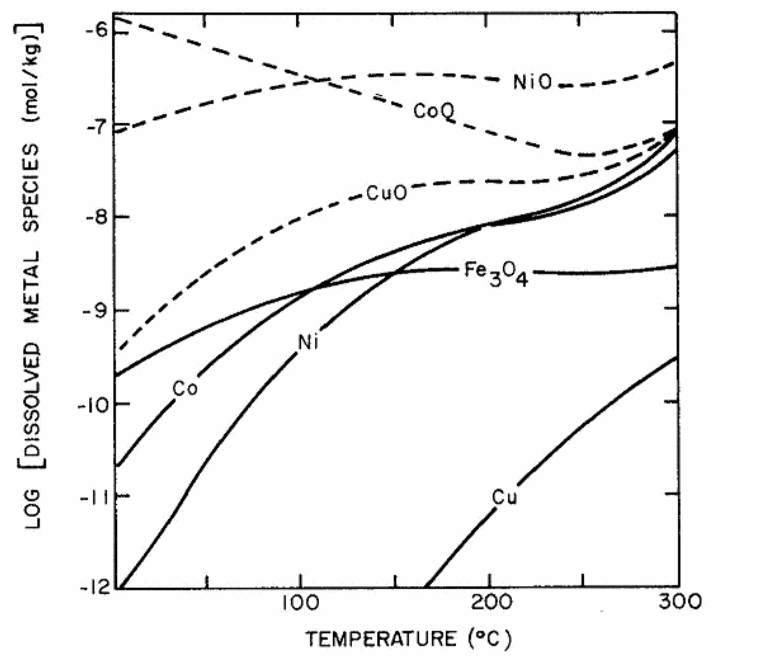


Figure 16
Potential-pH diagram for the system Fe-Cu-H_2O at 200 °C.

The factors which affect FAC of steel in water can be grouped as follows: (1) flow rate (hydrodynamics), (2) material (alloying components), (3) environment (water chemistry). In FAC, iron reacts with water to form a surface oxide layer. This oxide dissolves in the water, and the rate of iron removal (i.e. the rate of FAC) is controlled by the rate of diffusion of dissolved iron species through the boundary layer of water near the surface into the bulk water. This diffusion (or mass transport of iron away from the surface) depends directly on the concentration of soluble iron species at the oxide surface and inversely on the thickness of the boundary layer. Thus, a decrease of the boundary layer thickness because of increased water flow rate or because of local turbulence causes an increase of corrosion rate in this case.

Macdonald [88] investigated the stability and solubility of metal oxides in high temperature water. Some compilations of elementary thermodynamic properties of metal-water systems and derived quantities which are needed for optimum design and operation of nuclear steam generation equipment are summarized. Free energies of iron, cobalt, nickel, copper and aluminum metal, oxides and ions in dilute aqueous solution at temperatures up to 300 °C are tabulated in this work and derived data on potential-pH relations extracted.

Examples of calculated solubilities of some important metals and oxides are plotted in Figure 17 as a function of temperature. It is seen in Figure 17 that magnetite is less soluble than CuO at all investigated temperatures. However, the conditions are different.



t. Solubility of metals and oxides in 10^{-4} mol/kg OH^- solution at elevated temperatures.

▬ Hydrogenated solution (0.1 MPa H_2)

·- Oxygenated solution (10^{-10} Pa O_2)

Figure 17
Solubilities at conditions indicated in the figure.

Tahara [89] accounts an estimation of complex oxide formation with iron by use of aqueous chemical potential diagrams. The study is concerned with the construction of aqueous chemical potential diagrams of multiple metallic elements systems and the interpretation of the equilibrium diagrams to the effect of alloying elements on the stabilization of rust of weathering steels. Among chemical potential diagrams, the focus is on E_h-pH diagrams of bimetallic systems. In the corrosion process of weathering of steels it is recognized that stabilization of rust proceeds accompanying the co-precipitation or sorption of minor elements to ferric hydroxide. Since the data are scarce for the stability of aqueous reactions the tendency for the co-precipitation and sorption were estimated on the analogy of complex oxide formation based on the high temperature thermodynamical data. The derivation of E-pH diagrams of bimetallic systems led to a conclusion that elements beneficial for weathering steels are those forming insoluble complex oxides with iron at relatively low pH. A clear correlation exists between tendencies of complex oxide formation and of co-precipitation and sorption.

For the purpose of improving chemical stability evaluation for multiple metal species in aqueous solution system, potential-pH diagrams were calculated, see Figure 18 for an example.

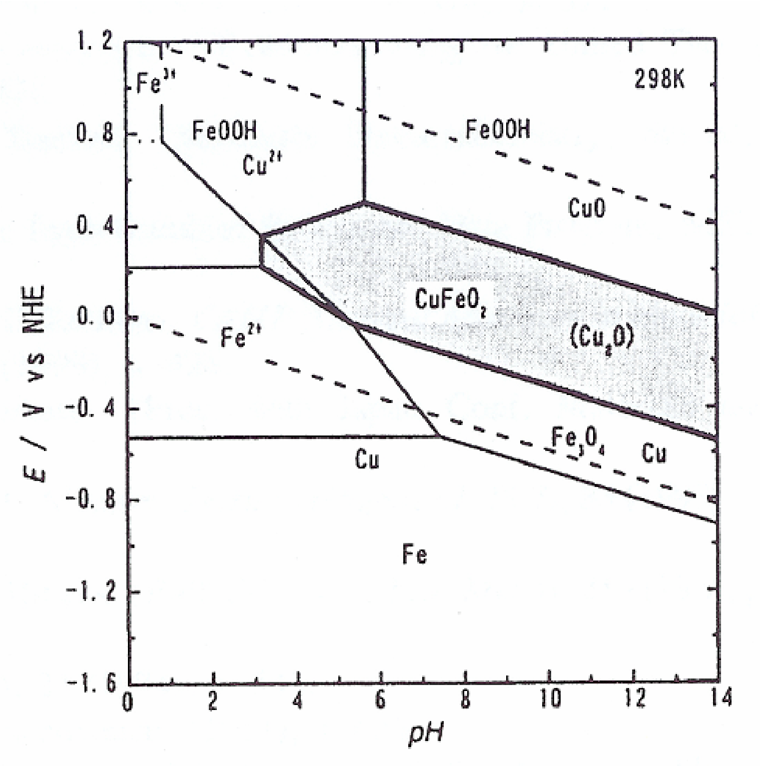


Figure 18

E-pH diagram for the Fe-Cu-H_2O system. [Fe] = [Cu] = 10^{-4} Mol/kg.

In Figures 19-22 a couple of calculated Pourbaix diagrams from Ref. [2] are shown for parts of the system Cu-Fe-Cl-S-C-O-H, which has relevance for the repository system.

It is seen in Figure 19 that high concentrations of Cl^- results in a copper surface without a passivating film in the simple system.

If the system is more complicated and Cl^- concentrations moderate, as it would be in the repository also containing sulphur, there could be a surface film on copper, either of copper sulfide at very low potentials or mixed copper iron oxides as $CuFeO_2$ and $CuFe_2O_4$ at higher potentials, see Figure 20.

At higher concentrations of carbonate and chloride in the system there could also be basic copper carbonate and chloride forming on copper, see Figures 19 and 21.

In Figure 22 a diagram is shown for the full system Cu-Fe-Cl-S-C-H-O showing the presence of phases like copper sulfides and carbonates and CuFeS2, $CuFeO_2$, $CuFe_2O_4$ all depending on conditions.

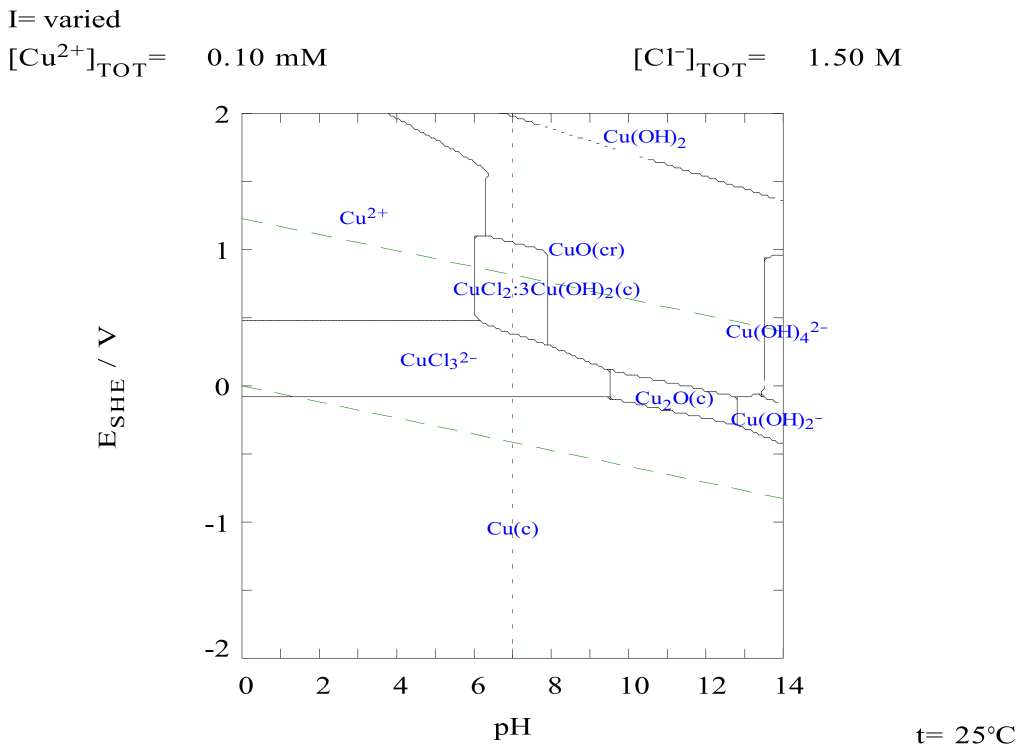


Figure 19
Pourbaix diagram for the simple system Cu-Cl-H-O at indicated conditions

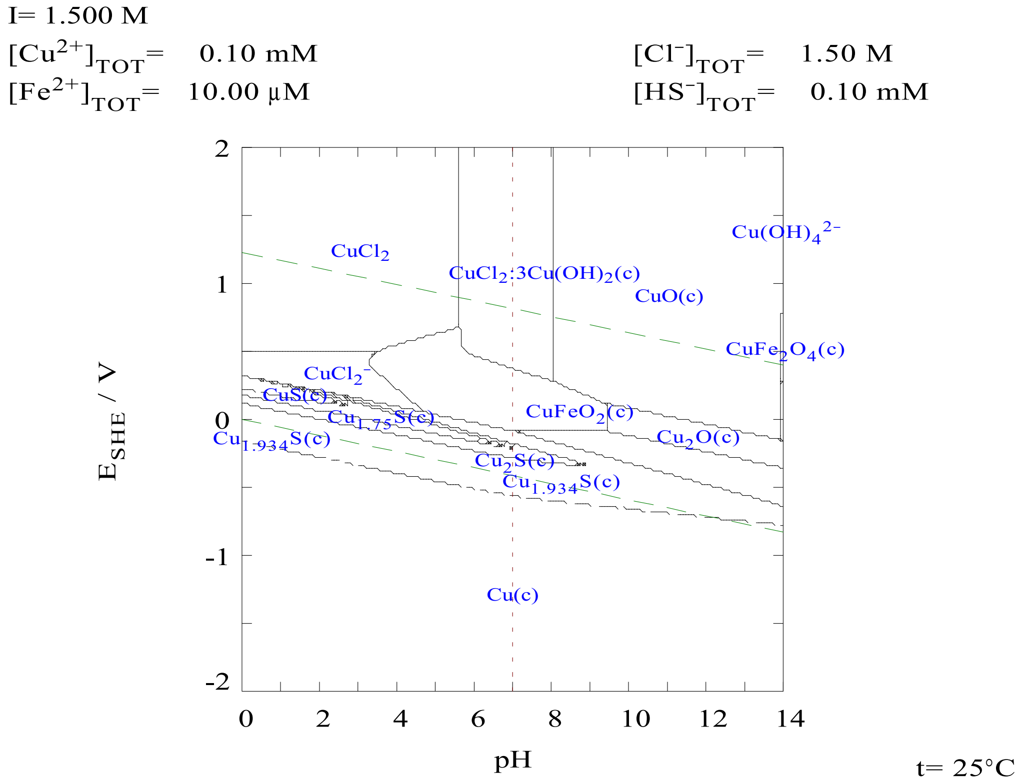


Figure 20
Pourbaix diagram for the system Cu-Fe-Cl-S-H-O at indicated conditions

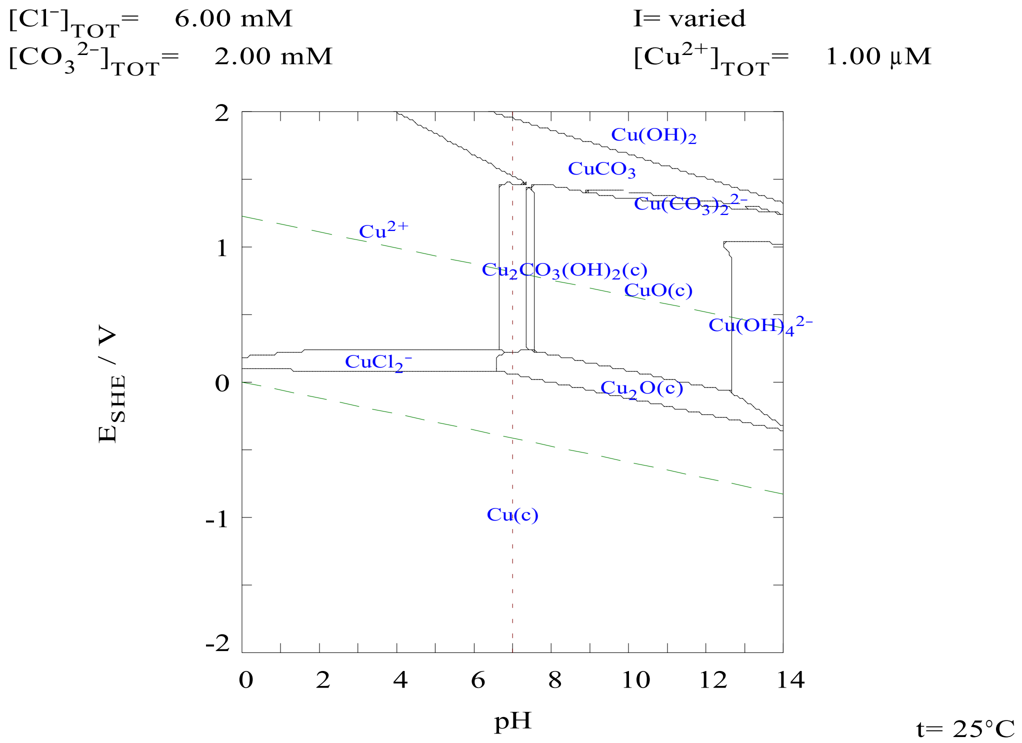


Figure 21
Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions

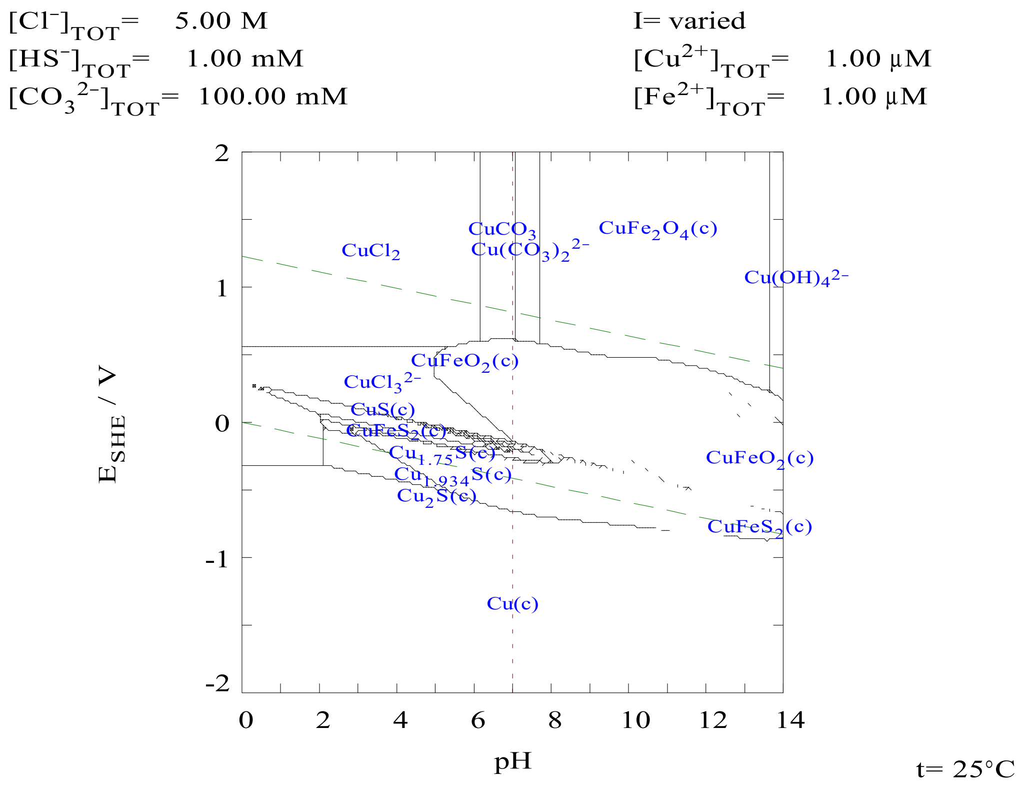


Figure 22

Pourbaix diagram for the system Cu-Fe-Cl-S-C-H-O at indicated conditions.

The information found in Figures 19-22 indicates that magnetite could be stable on an iron surface, but the presence of copper could also cause mixed oxides like $CuFeO_2$ and $CuFe_2O_4$ to be present at least at slightly elevated potentials. In a complicated system of course sulfides like $CuFeS_2$, chlorides, carbonates and mixtures of those are also possible, depending on conditions.

Under hydrothermal conditions, magnetite and hematite have been shown to undergo interconversion reactions, the extent of which is controlled in part by the presence of copper oxides [90]. In oxygenated water, the degree to which magnetite was oxidized to hematite was found to be dependent on the presence of CuO or Cu_2O. When these species were absent, the oxidation of magnetite was limited by the dissolved oxygen in the aqueous system. Participation of the copper oxides in the oxidation process was confirmed by a more complete conversion of magnetite to hematite when these oxides were present. The reduction of hematite to magnetite was also influenced by the presence of the copper oxides. In addition to driving the reduction to completion, the presence of the copper oxides also exerted a strong influence over the morphology of the magnetite that formed.

Thermodynamic information for copper compounds and aqueous species, including estimated values at elevated temperatures, is analyzed in [91]. Potential-pH diagrams for the Cu-H_2O, Fe-H_2O and Fe-Cu-H_2O systems are presented and the solubilities of copper and iron oxides (including mixed copper-iron oxide) are evaluated. These results are used to interpret the observed precipitation of oxides on BWR fuel and to estimate the effect of hydrogen water chemistry on their behavior.

Copper mineral formation in the Swedish "repository site environment" is discussed in [92]. Special attention is given to ore mineral textures (= the spatial relation among minerals), with examples given from nature. It is concluded by analogy with observations from natural occurrences, that an initial coating of Cu-oxide on the canister surface (because of entrapped air during construction) will probably not hinder a later sulphidation process. Early formation of Cu-sulphides on the canister surface may be accompanied by formation of CuFe-sulphides. The latter phase(s) may form through replacement of the Cu-sulphides or, alternatively, by means of reaction between dissolved copper and fine-grained iron sulphide (pyrite) in the surrounding bentonite. Should for some reason the bentonite barrier fail and the conditions become strongly oxidizing, growths of Cu(II)-phases, like malachite ($Cu_2(OH)_2CO_3$) can be expected. A presence of Fe in the clay minerals making up the bentonite might prove to have an adverse effect on the canister stability, since, in this case, the bentonite might be expected to act as a sink for dissolved copper. The mode of mineral growth along the copper - bentonite interface remains an open question.

The multi-sweep cyclic-voltammograms of Cr-, Cu-, Ni-, N-, Ar- and Zn- implanted iron electrode/acetate buffer solution systems were measured in [93]. Information about the electrochemical behavior, such as anodic dissolution and passivation, of the ion-implanted iron electrodes was obtained from the voltammograms. The anodic peak current density on the voltammograms, IP, was plotted against the number of potential-sweep cycles, nc. The IP-nc curves were classified into four types of electrochemical properties, from "inert" to "active". It was found that the IP-nc characteristics are useful to evaluate the reactivity or the durability of the ion-implanted surface layer. The concentration profiles of Cr and Cu implanted in iron were measured by secondary ion mass spectroscopy, and the effect of electrochemical dissolution on the composition of the surface layer is discussed.

In [94], the effect of the concentration of dissolved sulfide on the corrosion of Cu-Ni alloys in standard seawater was investigated. It is seen that the corrosion rates of Cu-Ni alloys generally increase with increasing sulfide concentrations. The result of the investigation was compared to the data reported in the literature and excellent agreement was obtained in some cases. A possible mechanism for the acceleration of corrosion is proposed. It is concluded that sulfide acts as a catalyst for both the anodic and cathodic reactions. It is shown that CuS precipitates first and is converted to Cu_2S during the corrosion process.

The behavior of copper in sea water containing sulphides has been examined in the pH range 5-8 [95]. The weight loss values show that sulphides increase the corrosion of copper at pH values > 7. In aerated solutions with pH values < 7 the sulphides cause some inhibition of corrosion due to the formation of a layer of copper sulphides less permeable than the oxychlorides formed when sulphides are absent. The main copper-sulphur compounds formed are Cu_2S, $Cu_{1.8}S$, Cu_7S_4. $CuS:Cu_2O:CuO$ and $Cu_3(OH)_2(CO_3)_2$ have also been observed, the last at pH 6-8 only.

Cu, Ag and Cr concentrations in natural water may be lowered by mild chemical reduction involving ferric hydroxide-ferrous ion redox processes [96]. V and Mo solubilities may be controlled by precipitation of ferrous vanadate or molybdate. Concentrations as low as 10^{-8} or 10^{-9} M are readily attainable for all these metals in oxygen-depleted systems that are relatively rich in Fe. Deposition of manganese oxides such as Mn_3O_4 can be catalyzed in oxygenated water by coupling to ferrous-ferric redox reactions. Once formed, these oxides may disproportionate. This reaction produces strongly oxidizing conditions at manganese oxide surfaces. The solubility of Ag is significantly influenced by ferric iron only at low pH. Spinel structures such as chromite or ferrites of Cu, Ni and Zn are very stable and if locally developed on ferric hydroxide surfaces could bring about solubilities much below 10^{-9} M for divalent metals near neutral pH.

In order to complement the above accounted literature information on alternative, bimetallic passivating films, some calculations of Pourbaix diagrams were performed by the author using Medusa [97]. The results are accounted in Figures 23 - 28. All calculations are performed at 25 ºC and considering the ionic strength of the system. The results complement the information found in [2].

The system Cu-Fe-O-H is shown in Figures 23 and 24. The Figures represent the same calculation but in Figure 23 copper containing species are shown and in Figure 24 iron containing species. It can be seen in Figure 24 that at actual repository conditions (low potential and slightly elevated pH), magnetite could appear as a passivating film, but could also be replaced by $CuFeO_2$, which is stable over a wide area of the E_h/pH field. It can also be concluded that both E_h and pH has to be slightly elevated to avoid dissolution of iron as no passivating film is formed on iron around the hydrogen line at pH<9.5. As seen in Figure 23 copper is either immune or passivated at all conditions of interest.

The system Cu-Fe-S-O-H is shown in Figures 25 and 26. Other conditions are the same as in Figures 23 and 24. The presence of sulphur could obviously cause the formation of $CuFeS_2$ on iron and this phase seems to outnumber both Fe_3O_4 and $CuFeO_2$ at a sufficiently high sulphur concentration.

The system Cu-Fe-Cl-S-O-H is shown in Figures 27 and 28. Conditions are the same as in Figures 23-26. The presence of chloride at the concentration level of 1 µmolal does not change the situations found in Figures 25 and 26. However, much higher concentrations of chloride will certainly have an influence as was demonstrated in [2].

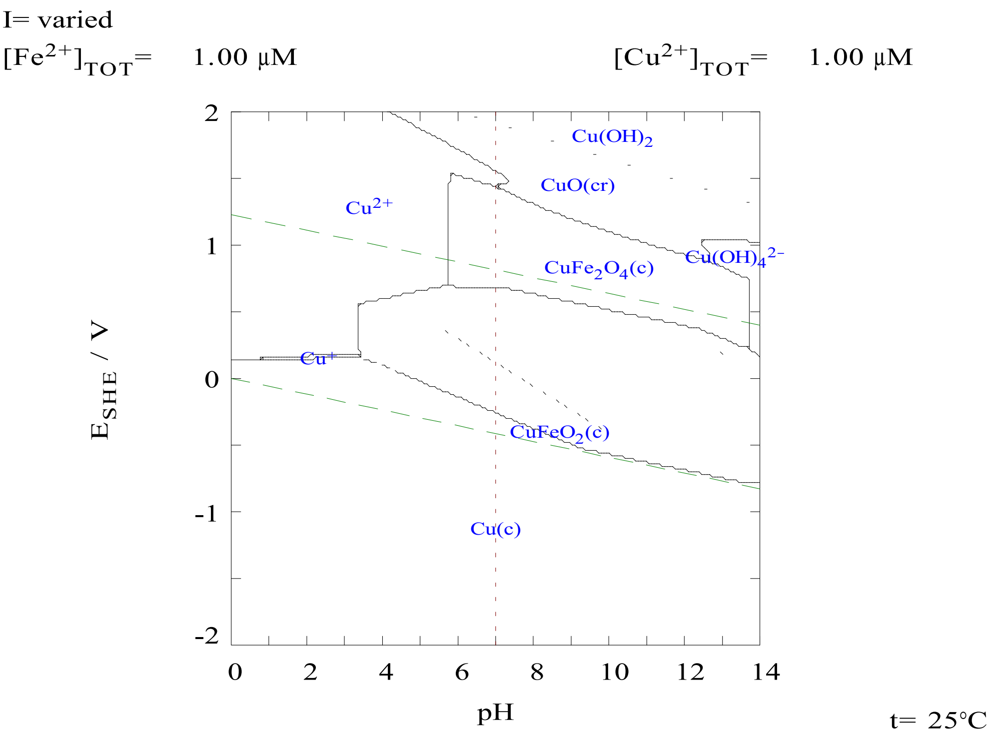


Figure 23
Calculated Pourbaix diagram of the system Cu-Fe-O-H at indicated conditions. Copper containing species are shown.

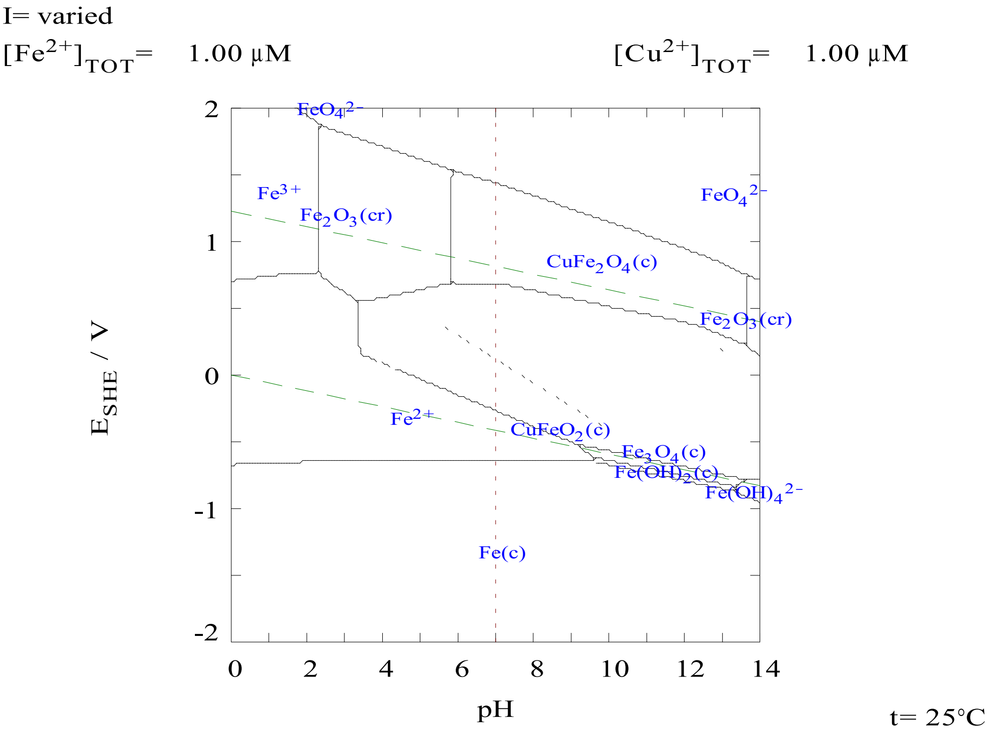


Figure 24
Calculated Pourbaix diagram of the system Cu-Fe-O-H at indicated conditions. Iron containing species are shown.

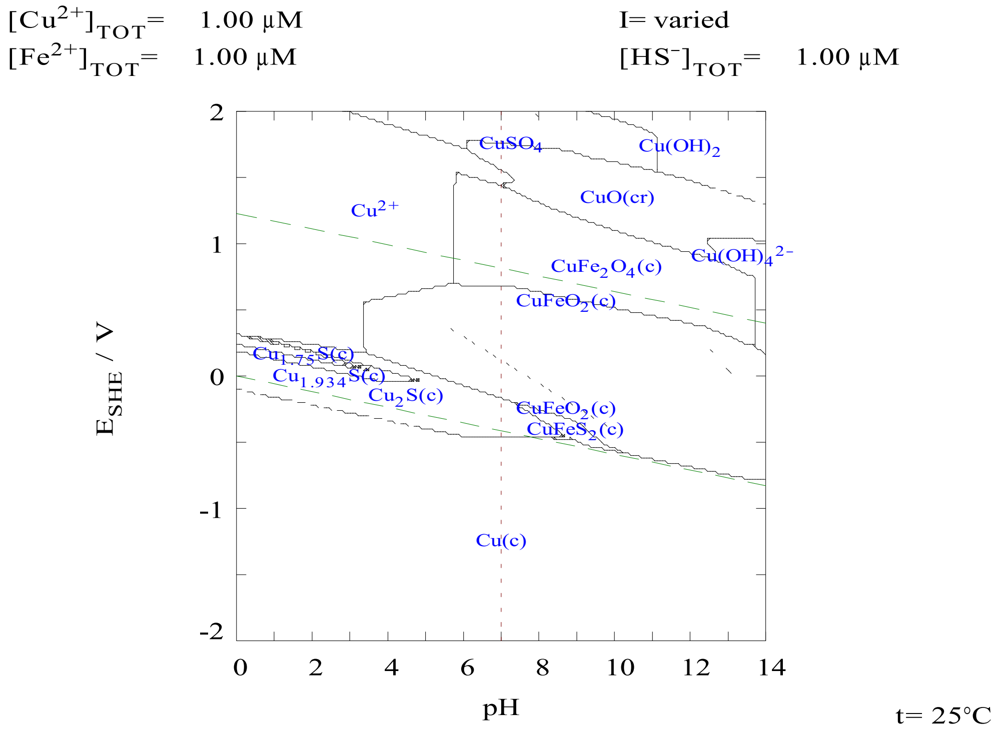


Figure 25
Calculated Pourbaix diagram of the system Cu-Fe-S-O-H at indicated conditions. Copper containing species are shown.

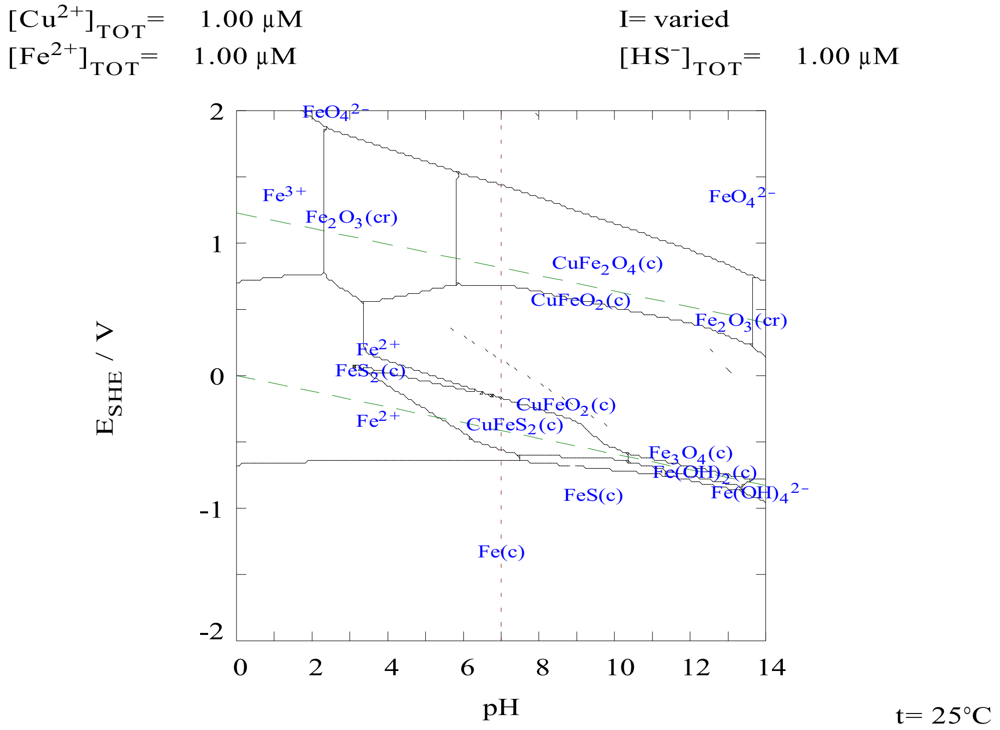


Figure 26
Calculated Pourbaix diagram of the system Cu-Fe-S-O-H at indicated conditions. Iron containing species are shown.

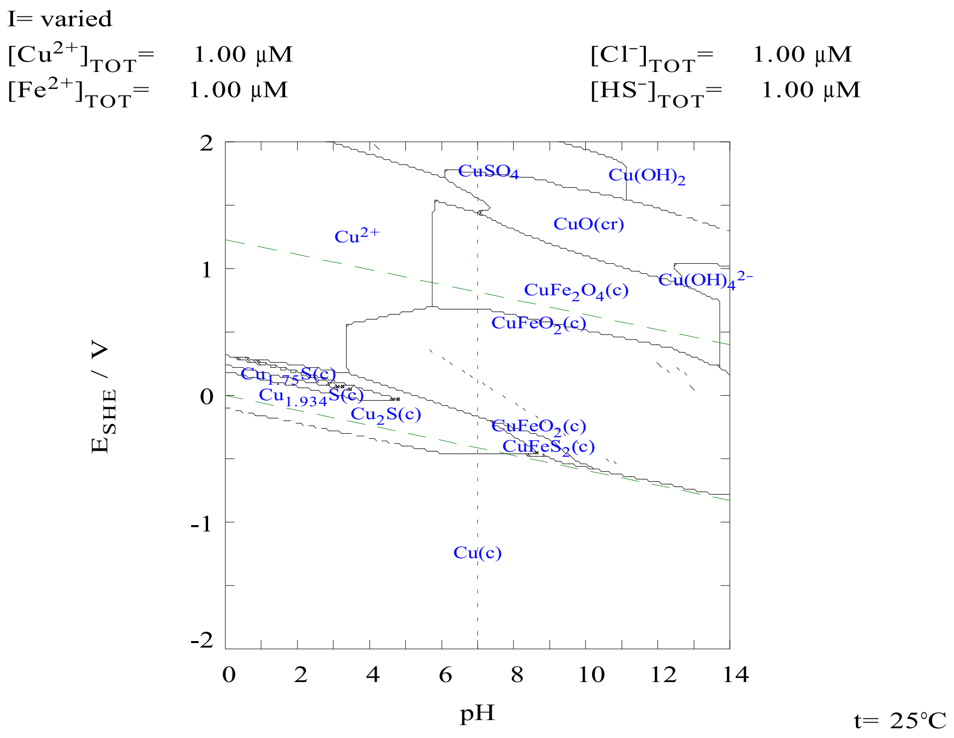


Figure 27
Calculated Pourbaix diagram of the system Cu-Fe-Cl-S-O-H at indicated conditions. Copper containing species are shown.

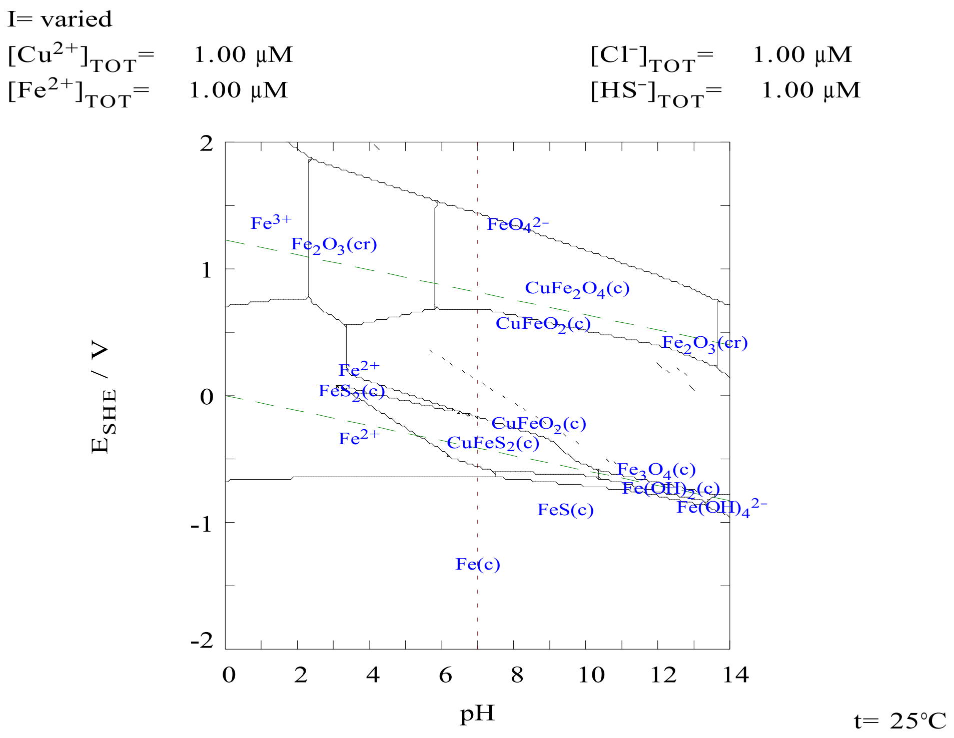


Figure 28
Calculated Pourbaix diagram of the system Cu-Fe-Cl-S-O-H at indicated conditions. Iron containing species are shown.

The information accounted in this chapter indicates that magnetite could certainly be formed on iron at repository E_h and pH at the absence of sulphide and chloride. However, both the investigations found in literature and the calculations made by the author indicate that magnetite is easily outnumbered already by $CuFeO_2$ in a simple system. As soon as sulphide and chloride are present in sufficient concentrations the importance of other phases like $CuFeS_2$ will increase for the passivation of iron. Those compounds, containing both Fe and Cu could also appear on the adjacent copper surfaces but $CuO/Cu_2O/Cu_xS$ are the most likely phases there.

It can therefore be said that it is likely that magnetite is not the passivating film on iron under the actual conditions. It is more likely that this film consists of $CuFeO_2$ or $CuFeS_2$, depending on the concentration of sulphur. If the chloride concentration is high enough [2], copper could appear without any passivating film.

Discussion

In a previous work [1] on copper corrosion, areas needing further focus were indicated. Giving priority to a couple of those areas is the background to performing the present and related works. One of the identified areas was to highlight if magnetite could be formed as a passivating film on cast iron in the expected repository environment. The possibility to form other types of passivating films when copper is present was also to be regarded, e.g. other iron oxides, mixed oxides of iron and copper as well as sulfides. The conditions for the formation of different passivating species have therefore been studied as well as some information on their compositions and properties.

The foundation for the present work is a literature review focused on the magnetite stability issue. The information found is discussed in relation to a standard repository (KBS-3-type) environment with a low potential and a slightly elevated pH. It is also supposed that the canister consists of an outer cylinder of copper containing a cast iron insert. It is supposed that there is a breach in the copper cylinder and that the cast iron insert is exposed to the repository environment surrounding the canister.

It is questioned if magnetite and other iron oxides could form a passivating film on cast iron under the conditions formed in the breach of a canister. The literature findings are selected to try to find an answer to that question.

Most investigations indicate that magnetite is thermodynamically stable roughly within a narrow band in the E_h/pH plane. At 100 ºC the area is defined within $7 < pH_{100} < 12$ of a narrow band of about +/- 0.2 V(SHE), almost symmetrically surrounding the hydrogen line. The definition of the band varies slightly with temperature, and the relevant Pourbaix diagrams should be consulted for more exact information. The formation of the magnetite is either as a result of oxidation and deprotonation of hydrated Fe(II) complexes or as a result of a hydrogen forming reaction route. The first mechanism would result in the formation of a passive film by precipitation of the formed magnetite. The other mechanism is prevailing as an iron surface corrodes at those conditions under hydrogen evolution, giving a magnetite protective layer formed in situ. Both mechanisms could be active simultaneously and result in a duplex type of magnetite layer of different origin that is mentioned by some authors. Probably, the layer formed in situ is of a good passivating quality while the deposited layer could be porous and less protective.

Solubility in an aqueous environment is a measure of the stability. Documents dealing with solubility were found to be more abundant than documents dealing with other stability parameters. Many investigations are found from nuclear power plant environments in pure water, water containing LiOH and boric acid as well as solubility determinations from other environments like those containing complexing agents.

Many investigations are confirming each other, but others give deviating information. However, there seems to be a common agreement that the solubility of magnetite depends on many parameters, like temperature, pH and the presence of complexing agents. At the actual conditions of the repository, the solubility of magnetite is very low if the water is pure. Very roughly it is in the range 10^{-6} - 10^{-7} mole/kg over actual temperatures. If potential and pH are not kept within the stable area of magnetite, solubility will of course increase dramatically and dissolve either to form Fe^{2+} at low pH and lower potentials or transform to hematite, Fe_2O_3 at higher potentials and pH. The solubility of hematite, Fe_2O_3 is very low, roughly 10^{-12} mole/kg. The solubility in the system Fe-O-H will therefore vary with many orders of magnitude depending on the value of potential and pH and the values of other environmental parameters. It is therefore of cardinal importance to state all parameters when giving a solubility value for the system Fe-O-H and especially for magnetite. It should be emphasized that even if hematite has a higher stability (lower solubility) than magnetite it is probably not protecting the metal as good as a magnetite film grown in situ would do.

The appearance of complexing agents as organic ligands and chloride ions, require very specific treatment of the solubility parameter. In such cases the formation of magnetite could be inhibited and other compounds at best take the role of acting as a passivating film. At worst the result could be dissolution of the metal.

The collected information indicates that magnetite could certainly be formed on iron at repository E_h and pH at the absence of copper, sulphur and chlorine. However, both the investigations found in literature and the calculations made by the author indicate that magnetite could also be easily outnumbered by other solid phases that could be formed when the mentioned elements are present. $CuFeO_2$ is such a phase that could appear in the simple Fe-Cu-O-H system. As soon as sulphide is present in sufficient concentrations (~ 1 μM) the importance of other phases like $CuFeS_2$ will also increase for the passivation of iron. Those compounds, containing both Fe and Cu could also appear on the adjacent copper surfaces but $CuO/Cu_2O/Cu_xS$ are there the most likely phases.

The probability that magnetite is the passivating film on cast iron at the actual conditions is therefore not very large. It is more likely that the passivating film instead consists of $CuFeO_2$ and/or $CuFeS_2$, depending on the concentration of sulphur. If the chloride concentration is high enough, copper could be left without any passivating film. Iron on the other hand would be less influenced by chloride within the stability area of magnetite.

The protective ability of the alternate compounds as passivating films could be discussed. This is often a question of kinetics and there is always a rate determining step involved. The nature and value of this parameter for the mentioned candidates is not very well known, and experimentally determined kinetic parameters found in literature are not directly applicable to the repository conditions. On the other hand comparisons of solubilities and other thermodynamical parameters do not either give a relevant answer as the time dependence is lacking in such data. However, generally seen, sulfides often grow faster than comparable oxides, as sulphides tend to form a skeleton of immobile sulphur atoms in which metal atoms can move rather freely and rapidly. At least this is often the case for copper. Therefore copper containing sulphides are probably less protective than comparable oxides. Magnetite is well reputated as a passive film former and is probably the best of those mentioned here.

Having these speculations in mind it could be a nice try to give the following ranking order of the protective ability of the above discussed passivating film forming substances:

$$Cu_xS < CuFeS_2 < Fe_xS < CuFeO_2 < Fe_3O_4$$

This means that if magnetite is not stable, the integrity of the cast iron insert is dependent on the the protection by less effective passivating substances, probably by $CuFeO_2$ in a sulphur free environment and by the even less protective $CuFeS_2$ in a sulphur containing environment. Beside the properties of the passivating film, the integrity of the cast iron insert will of course also depend on combined properties of the galvanic element formed together with copper as well as the concentrations of reactants and the transportation capacities (geometries, temperature, flows and concentration gradients, etc.) in the electrolyte of this element. Those factors will further complicate the corroding system largely, but are not the subject of this study.

The results of this work indicate that magnetite might be outnumbered by other phases in the specifically defined environment. However, no firm evidence could be produced that this is the case. The hypothesis of the formation of alternative passivating films, their rate of formation and their protective ability should therefore be tested at relevant conditions in laboratory experiments. The development of the passivating film could at such experiments be followed by the application of electrochemical methods and the chemical phase conditions checked by Raman spectroscopy.

Summary and conclusions

- The collected information indicates that magnetite could certainly be formed on iron at repository combinations of E_h and pH at the absence of sulphide and chloride.

- Magnetite could easily be outnumbered by other solid phases that could be formed.

- $CuFeO_2$ is such a phase that could appear in a simple Fe-Cu-O-H system.

- As soon as sulphur is present phases like $CuFeS_2$ can also be responsible for the passivation of iron.

- The probability that magnetite is the passivating film on cast iron at the actual conditions is not very large. It is more likely that the passivating film instead consists of $CuFeO_2$ and/or $CuFeS_2$, depending on the concentration of sulphur.

- The protective ability of the alternate compounds as passivating films could be discussed. A suggested ranking order of the protective ability is:

  $Cu_xS < CuFeS_2 < Fe_xS < CuFeO_2 < Fe_3O_4$

- If magnetite is not stable, the integrity of the cast iron insert is dependent on the protection by less effective passivating substances. Probably by $CuFeO_2$ in a sulphide free environment and by the even less protective $CuFeS_2$ in a sulphide containing environment.

- The hypothesis of the formation and nature of alternative passivating films should be tested at relevant conditions in laboratory experiments.

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