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**Anaerobic oxidation of carbon steel in
granitic groundwaters: A review of the
relevant literature**

N Platts, D J Blackwood, C C Naish
AEA Technology, UK

February 1994

SVENSK KÄRNBRÄNSLEHANTERING AB

SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 40 STOCKHOLM

TEL. 08-665 28 00 TELEX 13108 SKB S

TELEFAX 08-661 57 19

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GROUNDWATERS: A REVIEW OF THE RELEVANT LITERATURE

N Platts, D J Blackwood, C C Naish

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

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**Anaerobic Oxidation of Carbon
Steel in Granitic Groundwaters:
A Review of the Relevant
Literature**

N. Platts, D.J.Blackwood and C.C. Naish

Abstract

This report reviews the published literature on the anaerobic oxidation of iron in aqueous solutions which are of particular relevance to Swedish granitic groundwaters. The thermodynamics of iron corrosion in water are briefly considered. Following this the experimental data found in the literature are presented and discussed. Results were found for corrosion of iron in both pure water and solutions containing mineral salts. The literature work on the nature of the films formed on iron surfaces under anaerobic conditions is reviewed and the possible mechanisms of film formation are discussed. Conclusions are drawn on the factors most likely to influence and control film growth.

Abstract (Swedish)

Denna rapport ger en översikt av publicerad litteratur om anaerob korrosion av stål i vattenlösningar, som är relevanta för svenskt granitiskt grundvatten. Termodynamiken för järnkorrosion i vatten beskrivs kortfattat. Därefter presenteras och diskuteras experimentella data från litteraturen. Resultat hittades för såväl rent vatten, som för lösningar som innehöll mineralsalter. En översikt görs över litteraturarbeten på beskaffenheten på de ytskikt, som bildas på järnytor under anaeroba förhållanden och de möjliga mekanismerna för bildningen av ytskikt diskuteras. Slutsatser dras om de faktorer som mest sannolikt påverkar och styr tillväxten av ytskikt.

Executive Summary

The planned disposal route for spent nuclear fuel proposed by the Swedish Nuclear Fuel and Waste Management Co. (SKB) is for interim storage and encapsulation of the spent fuel assemblies, followed by disposal in a repository constructed within a deep granitic rock formation. One component of the multiple engineered barriers that will retard the release of radioactivity to the repository far field will be a metal canister fabricated from copper with an internal carbon steel container as the load bearing component.

It is therefore important in assessing the lifetime over which the barriers will be effective to have an understanding of the corrosion processes occurring on the carbon steel component. These can be split into two time defined areas.

Immediately after repository closure oxygen will be present and therefore, should there be an initial breach in the copper outer canister, aerobic (localised and general) corrosion will occur on the inner carbon steel container. After a period of time, somewhere between a few tens and hundreds of years, the oxygen will be consumed the potential will fall, localised corrosion processes will cease and general anaerobic corrosion of steel will become possible. If the aerobic period is short, or if there is delayed failure in the copper canister, it is likely that anaerobic corrosion will be the life limiting factor for the inner carbon steel container.

The anaerobic corrosion reaction for carbon steel also produces hydrogen gas, although this is not the case for copper which is unreactive on thermodynamic grounds. The hydrogen gas will need to permeate out of the repository, if gas pocket formation and local pressurisation are to be avoided.

It is therefore important for both the above reasons to understand the corrosion mechanism for carbon steel, its likely rate and the factors controlling it.

The aim of this review is to investigate the relevant literature on the anaerobic corrosion process for carbon steel. The thermodynamics of iron corrosion are considered and the relevant experimental studies found in the literature are discussed. The mechanisms of film formation are then examined in more detail. Finally the present status is summarised and conclusions drawn as to the likely rate controlling processes.

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1. Introduction

The disposal route for spent nuclear fuel proposed by the Swedish Nuclear Fuel and Waste Management Co. (SKB) is for interim storage and encapsulation of the spent fuel assemblies followed by disposal in a repository constructed within a deep granitic rock formation. The repository design employs multiple engineered barriers. These barriers consist of encapsulating the waste in a corrosion resistant canister made of copper, with an internal steel container as the load bearing component.

The canister assembly is then embedded with compacted bentonite clay in boreholes drilled in the floor of access tunnels excavated at a depth of approximately 500 m in a hard rock formation. As the repository is filled the access tunnels would themselves be backfilled with a mixture of bentonite clay and sand.

The bentonite clay, which constitutes one of the engineered barriers, has a number of properties that will be beneficial in retaining the radioactive waste within the repository. These are

1. When the repository eventually floods the clay will have a buffering effect on the pH of the solution in contact with the waste canisters (pH= 7.7-10.5).
2. The clay will restrict waterflows within the repository so restricting mass transport in the vicinity of the canisters/waste form to diffusion control.
3. If the canisters are eventually breached the clay will absorb fission products released from the waste form thereby further delaying their release from the repository.

The maximum temperature of the repository will be limited to 80°C so as to prevent possible irreversible chemical changes in the bentonite clay that may reduce its ion exchange capacity. As part of this overall multibarrier design it is assumed that the carbon steel container will isolate the fuel for the first few hundred years, should there be an initial breach of the outer copper canister.

In the situation where there is a breach of the copper canister at early times air trapped in the repository immediately after sealing will result in an initial period of aerobic corrosion of the carbon steel canisters, however this oxygen source will be rapidly exhausted by the corrosion process. Therefore, in view of the anaerobic nature of the prevailing granitic ground waters at these depths, anaerobic corrosion conditions should apply during the majority of the proposed canister lifetime. Under these conditions corrosion of the carbon steel will be supported by water reduction, as the cathodic reaction, resulting in the production of hydrogen.

Even pessimistic calculations of the corrosion rate, based on bare surface reaction kinetics, suggests that the proposed 50 mm thickness of carbon steel will ensure a lifetime in excess of a thousand years. The repository is designed to impose very slow, diffusion controlled mass transport. In such a design it is possible that, even for corrosion rates that would not threaten the integrity of the canister within the required

lifetime, the hydrogen produced as a result of the corrosion process may accumulate and produce gas pockets. The formation of hydrogen pockets could give rise to problems within the repository by, for instance, disrupting the near-field mass transport and generating enhanced transport pathways to the biosphere. Either of these phenomena could compromise aspects of the safety case for the repository.

Fortunately, corrosion products formed on the iron as part of the corrosion process are likely to result in lower corrosion rates and hence reduced hydrogen production rates as time progresses. In order to predict the extent of this retardation of corrosion rates over the design life of a carbon steel canister it will be necessary to understand the mechanism by which the corrosion products modify the corrosion process (and hence hydrogen production rates) under anaerobic conditions. For anaerobic conditions in the temperature range 25 to 100°C whether corrosion product films form on iron surfaces, or the nature and degree of protection offered by such a film, has not been extensively reported in the open literature. The purpose of this review is to assess the information that is available on the mechanism(s) underlying the processes of iron corrosion and hydrogen production for the above conditions. Specifically the review examines the nature of any corrosion product films formed and their influence on the corrosion process.

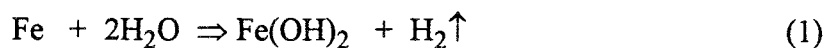
The problems the review attempts to find answers to include:

1. What is the chemical composition of the corrosion films: oxides, hydroxides or incorporated salts (e.g. FeCO_3)?
2. How do the films form :- deposition, 'solid phase' growth or both?
3. Are the corrosion films uniform or are there inner and outer layers?
4. How do the films retard the corrosion process?

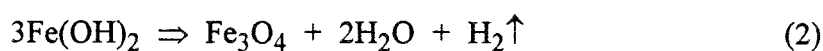
Before considering these mechanistic questions it is useful to look at the limited experimental information available on corrosion rates along with the thermodynamic considerations involved.

2. Thermodynamics of iron corrosion

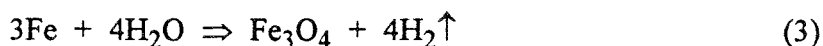
Under anaerobic conditions iron corrodes in water by the reactions below:



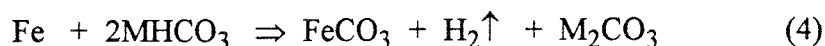
Reaction (1) produces ferrous hydroxide which may then transform to the thermodynamically more stable product magnetite via the 'Schickor' reaction:



giving an overall reaction:



In the event that other ionic species, e.g. carbonate, are present in the ground waters other insoluble corrosion products are also possible, the most likely being iron (II) carbonate



where M is a balancing cation e.g. Na^+ .

A build up of hydrogen within the repository could inhibit these corrosion reactions. From the free energy changes for the reaction it is possible to calculate whether sufficient pressure of hydrogen can arise to suppress further reaction. In order to suppress the production of ferrous hydroxide it is necessary to build up a pressure of approximately 140 bar of hydrogen¹. If the corrosion product is magnetite it would require an overpressure of greater than 800 bar. The presence in the ground waters of chemical species which can give other iron corrosion products less soluble than ferrous hydroxide, for example carbonate or silicate, will require even higher hydrogen overpressures to suppress the corrosion reaction (for example, 10^8 bar for ferrous carbonate). Therefore, in view of the limited hydrostatic head available in the repository (approximately 50 bar), it is not possible to make the argument that the hydrogen overpressure will suppress the corrosion reaction prior to gas formation.

Ferrous hydroxide is reported by many workers to be stable at room temperature. This is a kinetic rather than a thermodynamic stability and the presence of certain impurities, for example Ni, Cu, Co, either from the steel or from solution can catalyse the Schickor reaction². However even with large concentrations of these catalysts present conversion of ferrous hydroxide to magnetite is only about 10 - 20% complete² at ambient temperatures. Increasing temperature increases the rate of the Schickor reaction resulting in an increasing tendency for magnetite formation as indicated by the observations of Linnenbom³ that iron corroded in pure deaerated water to produce a ferrous hydroxide corrosion product film at 25°C but that magnetite formed from corroding iron at 60°C. As well as the factors promoting the Schickor reaction other factors will tend to suppress it. Several workers^(2,4) have shown that excess alkalinity inhibits the Schickor reaction. Similarly it is apparent from equation (2) that dissolved hydrogen may also tend to suppress the Schickor reaction, but only at pressures in excess of those present in the repository.

3. Experimental measurements of anaerobic corrosion rates

Only three direct measurements of hydrogen production were found to be available in the literature under conditions similar to those of interest in this study. However, corrosion weight loss measurements can be cited as supporting evidence assuming that the corrosion reaction is given by equations (1) and (2) above and allowing for reaction (2) (the Schickor reaction) probably being incomplete at temperatures below 150°C for the reasons outlined earlier.

It is convenient at this point to split the results into those obtained in demineralised water and those obtained in solutions containing the dissolved salts occurring in

granitic ground waters. This enables the effects of solute species on the corrosion behaviour to be identified.

3.1 Corrosion in pure water

Jelinek and Neufeld⁵ measured hydrogen production from steel coupons exposed to deaerated aqueous environments in the temperature range 60-90°C. Carbon steel coupons were exposed in sealed cells to initially demineralised water which had been deaerated by purging with high purity nitrogen (<0.5 vpm O₂ obtained by passing the nitrogen through a commercial "Nilox" scrubber [based on Cr(II) solution]). The corrosion rates as indicated by weight loss and hydrogen production rates were initially high but fell to a lower steady value over a period of 2-7 days. The eventual hydrogen production rates are presented in Table 1.

Jelinek and Neufeld⁵ compared these hydrogen production rates with those calculated from the weight loss data of Gould and Evans⁶ at 100°C which were calculated as being equivalent to 17 ml/m²/day of hydrogen. This figure was calculated from the weight loss over a 76 day exposure period, assuming reaction (2) goes to completion and ignoring the high initial corrosion rates which might have been expected to be present by analogy to the work of Jelinek and Neufeld⁵. Therefore the value of 17 ml/m²/day is almost certainly an overestimate at 100°C and the actual level of agreement is good, especially in view of the inaccuracies inherent in measuring such small weight losses.

Jelenik and Neufeld⁵ also quote weight loss data at high temperatures measured by Douglas and Zyzyes⁷. The measured weight losses were equivalent to hydrogen production rates of 14 ml/m²/day at 240°C (where reaction (2) should go essentially to completion). This data suggests that the hydrogen production rate is relatively independent of temperature. However this may be purely fortuitous since the structure and composition of the oxide films in these two temperature ranges is probably different.

In the cases of both Jelinek and Neufeld⁵ and Gould and Evans⁶ the measurements were performed by exposing bright metal coupons to either deaerated demineralised water or solutions. In both cases initial corrosion rates, and therefore hydrogen production rates, were higher than the longer term values. Corrosion product films were observed on the specimens after a few days exposure; this would correspond (in the case of the more reproducible Jelinek and Neufeld⁵ data) to the timescale of the shift to lower corrosion rates.

Seo et al.⁸ determined the hydrogen production rate from a steel specimen sealed into a glass tube filled with initially demineralised water by monitoring the potential of a palladium foil. The potential of the palladium can be related to the amount of hydrogen absorbed and hence to the concentration in the sealed cell for a given pH. The hydrogen concentration was calculated from the potential using a prior calibration and the pH of the solution at the end of the test. In this work the specimens were exposed to initially aerated water and hydrogen production was only observed once the trapped oxygen had been exhausted. Calculation reveals that corrosion occurring during the initial aerobic phase of the experiment would have been sufficient to

saturate the solution with ferrous hydroxide and hence the pH should have remained constant throughout the anaerobic period of interest.

The hydrogen production rate in this work was approximately 8 ml/m²/day at 25°C and is therefore in reasonably good agreement with the Jelinek and Neufeld⁵ results. This further confirms that the rate of hydrogen production may well be temperature independent in the region of interest (Ambient to 100°C). Since these specimens all formed a corrosion product film under the initially aerobic conditions, the good agreement between this data and that of Jelinek and Neufeld⁵ suggests that the stable corrosion product film is not highly dependent (at least in demineralised water) on the initial film formed.

Table 1: Summary of literature corrosion rates for iron in pure water

Reference No.	Test duration (days)	Temperature (°C)	Hydrogen evolution rate (ml/m ² /day)	Equivalent metal loss (µm/year)
5	40	60	11.1	1.1
5	40	80	12	1.2
5	40	90	9.4	0.9
6	76	100	17	-
8	30	25	7	-
7	-	240	14	-

It must be emphasised that these are only short term experiments (Jelinek and Neufeld⁵ 40 days; Gould and Evans⁶ 76 days; Seo et al.⁸ 30 days) and hence it is not possible to say whether the hydrogen production rates will remain constant over a prolonged time period or whether they will decrease further.

All of the data discussed above was determined in "capsule" tests under nominally static conditions and it may therefore be seen as being of direct relevance to a sealed and backfilled repository where water movements should be very low.

The importance of flow conditions on the nature and degree of protection afforded by the corrosion film can be inferred from the work on carbon steels under flowing deaerated water conditions^{9,10,11} (relevant to items of power plant such as feed heaters and economisers). Resch⁹ showed that in the temperature range 35 - 100°C at flow rates of 1.6 m/s far higher corrosion rates were found than under static conditions and that these corrosion rates were temperature dependent.

Table 2: Summary of literature values for hydrogen gas production rates in flowing systems

Reference No.	Test Duration (days)	Temperature (°C)	Hydrogen evolution rate (ml/m ² /day)	Rate of metal loss (µm/year)
9	30	35	240	24
9	30	95	2400	240
11	-	30	140	14

Resche's⁹ weight loss corrosion rates were linear with time from 7 - 10 days up to 30 days. Brush and Pearl¹⁰ also found similar behaviour in this temperature range.

Similarly Berry et al.¹¹ found corrosion rates equivalent to 0.7 g Fe/m²/day in deaerated water (< 20 ppb O₂) at a temperature of 30°C and flow rate of approximately 1.8 m.s⁻¹ in reasonable agreement with the work of Resch⁹. The work of Berry et al.¹¹ also indicated that the corrosion rate increased with flow rate, possibly indicating that the reaction rate was under mass transport control. There may be the possibility that the imposed flow regime is bringing oxygen to the surface at an enhanced rate and resulting in a higher corrosion rate. Without further experimental details this would be difficult to ascertain.

3.2 Corrosion in solutions containing mineral salts

Simpson et al.^{12,13} performed both weight loss and hydrogen evolution rate experiments in geologic waters typical of Swiss granitic formations. Weight loss measurements were conducted for up to 6,000 hours though the timescale of the hydrogen evolution rate experiments were of only 180 hours duration (shorter than the above work). Simpson's findings were in reasonable agreement with those of Jelinek and Neufeld⁵ and Seo et al.⁸; the initial hydrogen evolution rate was high but fell after about 2 - 3 days to an apparently constant level of between 8 and 50 ml/m²/day in the temperature range 25 - 80°C.

Simpson's work¹² indicated that the corrosion rate goes through a maximum at around 50°C, Simpson attributed the maximum in corrosion rate to a tendency for the Schikkor reaction to occur at temperatures above 50°C giving more tenacious and protective corrosion product films.

Simpson et al.'s weight loss data¹² was presented in the form of total weight losses and hence include the initial period of high corrosion, as indicated by the hydrogen evolution experiments. Therefore the values from the weight loss data are substantially higher than the final "steady state" corrosion rates measured in the hydrogen evolution experiments. However Simpson states that no increase in depth of attack was observed in the weight loss tests between approximately 4,000 hours and 6,000 hours. This appears to indicate that the apparently constant hydrogen evolution rates found in

the hydrogen evolution experiments are a consequence of the short term nature of the experiments.

More recently Kreiss¹⁴ has measured hydrogen gas production rates in a range of environments relevant both to cementitious and granitic groundwater anaerobic environments. He measured gas generation rates for neutral water with chloride additions and a simulated groundwater ('Bottstein water'). Both produced gas generation rates that fell from initial values of 100 mmol/m²/year to longer term values (> 4,000 hours) of the order of 10 mmol/m²/year. These are equivalent to 2,200 to 220 ml/m²/year and can be seen to be in good agreement with the data already presented. He noted that in both the neutral media tested (chloride water and Bottstein) that the pH increased during the experiment. He suggests that this change along with oxide film growth may influence the reduction in gas production and corrosion rate.

Kreiss¹⁴ also examined hydrogen production under anaerobic conditions from iron immersed in a range of cement pore waters. He found differences in the initial rates of hydrogen production for sodium, potassium and calcium hydroxides, with calcium hydroxide showing the lowest rate. He attributes this to the divalent calcium ion participating in the film growth on the corroding iron surface, resulting in a more protective film.

The reasonable agreement between the results of Simpson et al.^{12,13}, and those of the other workers for initially demineralised deaerated water indicate that the concentrations of dissolved salts present in granitic ground waters (predominantly HCO₃⁻/CO₃²⁻, Cl⁻, and SO₄²⁻ along with Na⁺, Mg²⁺ and Ca²⁺ as the balancing anions) do not significantly effect the corrosion rate of carbon steels under deaerated conditions. Further information on the effect of these solute species can be assessed from Jelenik and Neufeld⁽¹⁾ who showed that for 0.1N HCO₃⁻ the hydrogen production rates are similar or even somewhat lower than for demineralised water. The work of Kreiss¹⁴ indicates however that pH changes and the cation species present do have an influence on the corrosion rates under more alkaline conditions (pH 12 to 14).

Table 3: Summary of literature values for hydrogen production rates in aqueous salt systems

Reference	Temperature (°C)	Hydrogen evolution rate (ml/m ² /day)	Rate of metal loss (µm/year)
5	60	8.5	0.83
5	90	4.3	0.42
14	25	6 to 0.6 as time increases	-

Similarly Gould and Evans⁶ found no effect of the aggressive anions Cl⁻ and SO₄²⁻ at concentrations of 0.01 M on the corrosion of iron under deaerated conditions. This suggests that the use of data from initially demineralised water should not provide an underestimate of the hydrogen production rates.

Under flowing conditions (1.8 m/s) Berry et al.¹¹ investigated the effect of both chloride (3 ppm) and carbon dioxide (= 2 µS/cm) contamination under deaerated conditions and found that they both significantly increased the corrosion rate (by a factor of approximately 6). The specimens exposed to the carbon dioxide-bearing solutions showed significant surface roughening but no signs of pitting. Berry et al.¹¹ suggested the possible involvement of Fe(HCO₃)₂ to explain this enhanced corrosion.

Videm and Dugstad¹⁵ investigated the corrosion films formed in flowing deaerated brine solutions saturated with carbon dioxide. In the temperature range 25°C - 90°C, when the brines were low in dissolved iron the steel remained "bright" with high sustained corrosion rates, as one might have predicted from the work of Berry et al.¹¹. However, at lower temperatures (10 - 20°C) they found that while the steel remained bright for prolonged exposures, the corrosion rate decreased with time in accordance with approximately t^{-1/2} kinetics over the 10 - 15 day period of the experiments. They attributed this to the formation of a passive ferrous hydroxide film (the Fe:O ratio in the film was 1:2).

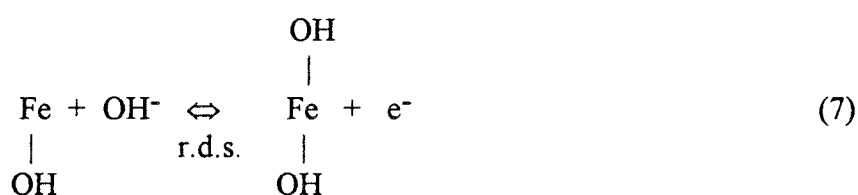
Videm and Dugstad¹⁵ also observed that when the solution was saturated with ferrous ions a corrosion film (predominantly ferrous carbonate) built up on the steel which also tended to inhibit the corrosion process. In the temperature range 25 - 50°C this film was only loosely adherent and was easily wiped away whilst in the temperature range 50 - 90°C the film became increasingly adherent. This is similar in many ways to the growth of ferrous hydroxide and magnetite films. These are found to be non-adherent at low temperatures but become increasingly adherent at higher temperatures, especially above 150°C.

3.3 Nature of the films formed on iron under deaerated conditions

The corrosion rates found in the above studies suggest that some form of mass transport control could be important in determining the corrosion rates. The observation of a dependence of the corrosion rate on the flow rate in the work of Berry et al.¹¹ lends further support to the importance of mass transport processes. The observation of visible film formation in the work of Jelenik and Neufeld⁵ on the same timescale as that observed for the decrease in corrosion rate to its steady state value indicates the probable importance of the nature of the corrosion product formed.

Most studies of the films formed on iron are concerned with the passive films formed under anodic polarisation. Two reasonable reviews are by Kruger¹⁶ and Cohen¹⁷.

There is only limited work available on iron corrosion films formed at the active potentials typical of deaerated conditions. Bockris et al.¹⁸ suggest, on the basis of ellipsometry, that at a pH of 8 (experiments in borate buffer solutions) the film formed at active potentials is not consistent with an adsorbed ion film. They instead suggest that it is a two dimensional phase oxide. They propose that the mechanism for the formation involves a place exchange step, the OH going below the original metal surface, with the second electron exchange being rate determining:



They propose that the oxide is approximately 1 - 2 monolayers thick and that the degree of surface coverage is dependent on the electrode potential; the coverage increasing to completion at the active peak present in the potentiostatic polarisation scan, see Figure 1(a). In this mechanism the dissolution process is proposed to occur from areas of the surface not covered by the film. They discount the possibility that the film is formed by dissolution precipitation on the basis that iron borate complexes would be soluble at pH 8.

Burstein and Davies¹⁹ have shown the existence of $\text{Fe}(\text{OH})^+$ using scratching electrode techniques in bicarbonate solutions. This can be seen as supporting evidence for the first stage of this mechanism. Davies and Burstein²⁰ looked at the active peaks in carbonate solutions, where 2 anodic peaks rather than one occur in the polarisation

scan, (see Figure 1(b)) and suggested that the first active peak, marked A on the figure, corresponds to the formation of a ferrous hydroxide film by a mechanism similar to that of Bockris et al¹⁸. However they argue that surface coverage by the film is complete under steady state conditions and that dissolution occurs through it. Under these conditions they envisage the cathodic reaction occurring at the oxide to solution interface.

Similarly Valentini et al.²¹ regard the film as a hydroxide with the corrosion process occurring through the film. They also state that the surface process leading to the formation of this prepassive film is effectively temperature independent.

Though only a thin film was observed in these experiments¹⁷⁻²⁰ in long-term exposure under static or closed systems, it seems probable that a thicker ferrous hydroxide film may still form, probably by deposition from the solution phase once the solubility product of $\text{Fe}(\text{OH})_2$ is exceeded in the diffusion layer. Where a deposited ferrous hydroxide film is formed it will have a significant effect on the corrosion process. Mass transport (probably of soluble corrosion products) through the porous deposited oxide is a likely rate controlling step. Hence it is important to understand the factors effecting the long-term stability and behaviour of such a layer.

As discussed in an earlier section ferrous hydroxide is kinetically stable with respect to magnetite at 20 - 25°C with even large concentrations of catalytic species resulting in only 10 - 20% conversion of ferrous hydroxide to magnetite². Murata²² and Linnenbom³ found that iron corroded in pure water to produce a ferrous hydroxide corrosion product film at 25°C, but Linnenbom³ found that magnetite does form from corroding iron at 60°C in deaerated water. This appears to correlate well with the corrosion rate work, discussed in the previous section, which indicated a change in the protective properties of the film at around this temperature.

However other workers, for example Thompson²³, state that magnetite is produced by corroding iron at 25°C. The apparent contradiction may be due to impurities in the iron catalysing Schickor or incomplete exclusion of air since as pointed out by many workers (e.g. reference 3) any oxygen ingress will lead to hydroxide converting to magnetite and, given enough oxygen, hematite.

From these observations it is reasonable to predict that at the higher temperatures of interest in this study (approximately 90°C) the film will contain some magnetite and a possible indication of its structure may be inferred from the structure of higher temperature oxides. At higher temperatures, greater than 150°C - 200°C, hydrogen evolution occurring at the metal film interface inhibits deposition of magnetite within the pores of the oxide film.

In such circumstances ferrous ions diffuse out through the porous oxide and deposit as magnetite on the outer surface where the hydrogen over-pressure or concentration is lower. This deposited film grows into a columnar magnetite outer layer overlying a less highly crystalline inner magnetite layer²⁴. Fujii et al.²⁵ suggest that diffusion of $\text{Fe}(\text{OH})^+$ out through the porous oxide is in fact the rate determining step in the temperature range 200 - 275°C. Though such a mechanism is feasible at 90°C it seems likely that ferrous hydroxide still exists in the inner layer.

The incomplete conversion to magnetite at 90°C is demonstrated by Jelinek and Neufeld's⁵ observation that though the corrosion products formed in demineralised water were magnetic (consistent with Fe₃O₄) the hydrogen evolution and weight losses found indicated only approximately 20-30% magnetite in the films. Therefore, although the major soluble iron species at ambient temperatures is seen as being Fe(OH)⁺²⁶, it is difficult to see how Fe(OH)⁺ diffusion can be rate determining when ferrous hydroxide is present in the film at the metal film interface.

In the presence of potentially complexing anions other soluble complex species (besides Fe(OH)⁺) are possible and these may effect the mechanism of the corrosion process and the structure and composition of the resulting film. The involvement of other soluble species, and their subsequent incorporation into the corrosion films, has been indicated in a number of environments involving 'passivating' anions. Working with borate buffer solutions Seo et al.²⁷ suggest the involvement of the complex ferrous borate ions e.g. FeB(OH)₄⁺. Using Auger spectroscopy they found boron both in the outer passive oxide layers formed under anodic polarisation and in the 'oxide' films formed at active potentials. They attributed these observations to the formation of deposited ferrous hydroxyborates such as FeOH(B(OH)₄). This observation further supports the hypothesis that a deposited film forms under static conditions but on a timescale longer than that studied in the electrochemical and ellipsometric investigations of Bockris et al.¹⁸.

Of greater relevance to this review are those studies in bicarbonate solutions, where Davies and Burstein²⁰ postulated the involvement of the complex anionic species Fe(CO₃)₂⁻ in the mass transport controlled reactions associated with the second active peak found in the potentiostatic polarisation scans for iron in these solutions. However it should be born in mind that since their work was primarily concerned with the behaviour at the second active peak in the potentiostatic polarisation scan (figure 1(b)), it is associated with electrochemical potentials more positive than those present in the anaerobic granitic groundwater system.

The incorporation of carbonates into the prepassive films formed on iron in the more positive electrochemical potential region has been shown by both Davies and Burstein²⁰ and by Valentini et al.²¹ They do however differ in the structure they propose for the film formed in the region of the second active peak.

Vilche postulates that this occurs by a solution precipitation reaction, with a film of ferrous carbonate being formed on top of the initial ferrous hydroxide layer so that effectively a duplex film is formed. Corrosion occurs through the inner hydroxide layer and a porous ferrous carbonate is deposited in the outer layer of the corrosion film. This outer layer will be continuously dissolving in a solution which is not saturated with ferrous iron.

It is unclear whether Valentini et al.²¹ consider mass transport of HCO₃⁻ to the surface and its dissolution of the outer film to be the rate controlling step, or diffusion of ions through the FeCO₃ layer.

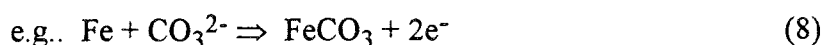
Davies and Burstein²⁰ envisaged two surface reactions forming ferrous hydroxide and ferrous carbonate in competition for surface coverage of the electrode, with attack of

the ferrous hydroxide film by bicarbonate ions in solution leading to its breakdown and replacement by ferrous carbonate. They proposed that the ferrous carbonate film was effectively non-protective and dissolution of it occurred via the complex anion $\text{Fe}(\text{CO}_3)_2^-$. The prepassive film is therefore a mixture of ferrous carbonate and ferrous hydroxide; the proportion of ferrous carbonate increasing until total coverage is achieved at the second anodic peak in the polarisation scan.

They propose that the rate controlling step is diffusion of HCO_3^- to the surface. Sykes²⁸ performing transient measurements on this system using a rotating ring disc electrode demonstrated that, in the region of the second anodic polarisation scan peak, steel initially passivated with $t^{-0.5} - t^{-1.2}$ kinetics and with the production of little soluble iron. However this film broke down after approximately 0.2 - 0.5 s resulting in a rapid increase in the amount of soluble iron being produced, and then a period of slow decline. This breakdown was associated with the production of soluble iron species which Sykes attributed to the ferrous carbonate complex proposed by Davies and Burstein²⁰. Only about a third of the iron which should have been produced during this period was collected on the ring (after allowing for the ring's collection efficiency), indicating that a solid corrosion product layer was growing on the electrode.

The apparent observation of film breakdown seems to support Davies and Burstein's mechanism and structure for the prepassive film in this potential region²⁰ involving attack of the initial ferrous hydroxide film by bicarbonate ions. Valentini et al.²¹ observed that if the potential is held in the region of the second anodic peak a thicker but still non-passive mixed hydroxide and carbonate film is formed. These two observations appear to be mutually supportive but do not indicate what the structure of the film might be at longer times.

Although it is generally assumed that the ferrous carbonate is formed by a deposition process, Valand et al.²⁹ point out (though with no experimental evidence) that it is thermodynamically feasible for FeCO_3 to form by direct reaction of CO_3^{2-} with the steel under repository conditions.



This supports part of Davies and Burstein's mechanism of competitive surface coverage by ferrous hydroxides and carbonates²⁰. It also supports the suggestion that carbonate rather than magnetite and hydroxide based films may be produced.

The presence of high levels of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in solution appears to inhibit magnetite formation on iron, promoting an iron carbonate film instead. The films formed in Videm and Dugstad's¹⁵ experiments in iron saturated solutions were analysed as being predominantly ferrous carbonate throughout the temperature range from 30 - 90°C. Greenberg and Tomson³⁰ state that the dissolution and precipitation rates for ferrous carbonate increase with increasing temperature. Hence it seems likely that there will be a greater rate of recrystallisation of the porous deposited films with increasing temperature. This may explain the tendency in the work of Videm and Dugstad for denser, more compact ferrous carbonate films to form in the temperature range 50 - 90°C.

4. Mechanism of film formation

In proposing a mechanism for the anaerobic corrosion process on carbon steel it is necessary to reconcile and correlate the observations on the composition and structure of the corrosion product films formed with the corrosion rates observed under both static and flowing conditions.

It seems to be reasonable, and generally accepted, that the initial stage of the corrosion process will be iron dissolution via the intermediate Fe(OH) phase oxide film, in accordance with Bockris's mechanism above. Such a film may only partially cover the surface under the anaerobic potentials of interest here so that the dissolution process occurs predominantly from the uncovered areas, as suggested by Bockris¹⁸. The cathodic reaction occurs on the oxide at the metal to oxide interface. However it may spread to cover the whole surface as suggested by Davies and Burstein²⁰, so that dissolution occurs through the film and the cathodic reaction occurs on the outside of this oxide layer.

It seems likely that the protective nature of this film is generally low. Though the results of Videm and Dugstad¹⁵ below 20°C suggest that it might be possible, under certain environmental conditions, for the film to thicken as a passive layer. The observed $t^{-1/2}$ kinetics are consistent with a migration mechanism of growth. This infers that the passive layer is probably porous, and hence may have been formed by deposition of Fe(OH) from the boundary layer.

In bicarbonate solutions at slightly higher potentials than those of interest here the work of Sykes²⁸ suggests that the film is not stable and undergoes attack by HCO_3^- . Certainly the high corrosion rates found in the temperature range 30-90°C in the flowing systems of pure water¹¹ and CO_2 saturated brines^{11,15} suggest that this initial prepassive film is thin and only poorly (or non) protective.

Similarly the observation of flow rate dependence of the corrosion process¹¹ in pure water under deaerated conditions appears to support a mass transport, rather than film or activation controlled, dissolution process. This is in apparent disagreement with Davies and Burstein²⁰ and Valentini et al.²¹ who both state that the process in carbonate solutions in the region of the first peak in the polarisation scans (i.e. where a Fe(OH)_2 film is present) is not mass transport controlled. However if the mass transport control was on the cathodic reaction this would not be revealed in potentiostatic experiments, where the cathodic reaction is occurring on a remote counter electrode.

Under static or low flow conditions it is possible for the concentration of soluble species to build up in the solution and eventually exceed the solubility product of an iron oxide/salt (e.g.. ferrous hydroxide or carbonate). At this point a deposited film will form on top of the initial ferrous hydroxide film. It is important in understanding the corrosion process to know whether at the bicarbonate/carbonate concentrations (10 to 100 times lower than in most of the work referenced above) and pHs (8-10) found in granitic ground waters the deposited film will be a ferrous hydroxide or ferrous carbonate film.

As magnetite is less soluble than ferrous carbonate it seems reasonable that environmental conditions where ferrous carbonate will precipitate in preference to ferrous hydroxide may inhibit magnetite formation and hence possibly result in less protective films. Consideration of the relative solubilities in 0.01 M HCO_3^- at pH 9, Appendix 1, indicates that on the above logic the film is most likely to be a ferrous carbonate film. However the difference is sufficiently small (ferrous hydroxide is preferred at pH 10) that a mixed hydroxide-carbonate film may be the most likely deposited film under expected repository ground water conditions.

The long-term nature of this deposited film and its effect on the corrosion process will depend on a number of factors: the temperature, the flow rate (boundary layer thickness) and the presence of film-forming solute species in the environment (e.g. HCO_3^-). There appears to be a change in the composition and structure of this film with temperature. The kinetically favoured but poorly protective ferrous hydroxide films are formed at lower temperatures, whilst the thermodynamically favoured magnetite is the major constituent of high temperature films.

The point at which the nature of the corrosion product films changes between these two regimes depends on the temperature at which the transformation of ferrous hydroxide to magnetite via the Schikkor reaction becomes significant relative to the corrosion and dissolution reaction. Therefore factors which may favour the Schikkor reaction, such as catalytic impurities in the steel or solution, or conditions which inhibit the corrosion process, such as low flow rates and consequently lower mass transport and thicker corrosion product films, will favour magnetite formation at lower temperatures.

The work of Simpson and Schenk¹² indicates that the transition from essentially ferrous hydroxide/carbonate corrosion product films to ones increasingly dominated by magnetite formation occurs at around 50°C. This is backed up by Linnenbom's³ observation that magnetite was formed in pure water tests at 60°C, but only ferrous hydroxide at 25°C. Therefore, in considering the long-term nature of the film formed, it is convenient to split the problem into two temperature ranges, above and below 50°C and then to consider in turn the likely structure of the films formed in pure water and the effects of film forming solutes such as carbonate on the films and corrosion mechanisms proposed.

4.1 Temperatures below 50°C

In pure water the film deposited on top of the inner prepassive layer under near static conditions should be ferrous hydroxide. Such a deposited film will almost certainly be porous and hence its action in inhibiting the corrosion process will be by mass transport limitation of aqueous diffusion within the pores (i.e. by increasing the effective diffusion path). Since the solution within the pores will be saturated with $\text{Fe}(\text{OH})_2$ any further iron released by the corrosion process will precipitate close to the metal oxide interface. Therefore, once an initial deposited film has formed, further growth will effectively be from the metal oxide interface; the new oxide effectively pushing the existing film ahead of it.

The cathodic reaction is envisaged as being hydrogen evolution occurring at the metal to oxide interface. The alternative action of deposition within the pores would be to produce densification of the oxide. This would ultimately lead to the pores becoming blocked and an effective barrier oxide would result. This latter option appears to be at odds with the experimental observations that the oxides formed in this temperature range are non-adherent and poorly protective and can probably be discounted. The thickness of the porous oxide will be determined by the rate of formation (i.e. the corrosion rate) and the rate of dissolution/erosion from the surface. A limiting thickness for the film will be reached when the rate of $\text{Fe}(\text{OH})_2$ precipitation in the pores equals the rate of film dissolution at the surface.

In a static system, or one with very low mass transport, this dissolution process is expected to be slow, therefore the porous layer would continue to grow and thereby place an increasing mass transport limitation on the corrosion process. In contrast in a flowing system dissolution from the surface will be rapid, so that the film will remain relatively thin and porous. Under conditions of sufficiently high flow and low bulk ferrous ion concentration the film may be unable to form at all. Therefore this mechanism would predict stable mass transport limited corrosion in a flowing system, such as a model boiler feed system or pipeline, at higher rates than would be expected under static conditions, in keeping with the experimental observations^{9,11}.

Considering the effect of film forming anions such as carbonate on the nature of the corrosion film, the solubility arguments raised earlier suggest that the film may well be a mixed hydroxide/carbonate or hydroxycarbonate rather than a pure carbonate. The proportion of carbonate in the film should increase with increasing bicarbonate concentration and increasing potential, for instance in the CO_2 saturated brines the films were analysed as being predominantly FeCO_3 . Similarly in a system with bicarbonate present dissolution will be to some extent promoted via bicarbonate attack of the film and the intermediation of the $\text{Fe}(\text{CO})_3$ complex ion. The importance of this reaction will not be as great under the low HCO_3^- conditions present in a deep underground repository as it has been suggested to be in the mechanistic and model boiler/pipeline studies quoted above.

Therefore the prediction is essentially the same as for pure water; a porous deposited oxide overlying a very thin inner layer, with the cathodic reaction occurring at the metal oxide interface, and precipitation of ferrous hydroxide/ carbonate within the film pushing the prior loose deposits ahead of it. Though bicarbonate attack of the hydroxide inner layer, with consequent formation of carbonate directly on the steel surface, may occur at the more positive potentials associated with the second anodic peak in potentiostatic polarisation scans in 0.1 M bicarbonate solutions, the importance of this reaction scheme will be significantly reduced in the region of the first peak and below, i.e. the region of interest for anaerobic repository conditions.

The possible rate controlling steps are:

A. If the inner oxide film were to achieve complete coverage of the iron surface two possible rate controlling steps would be:

- (i) The oxide serves as a passive film on the steel surface and corrosion is controlled by solid state diffusion through the film, rather than by the porous outer oxide layer
- (ii) If a complete cover of inner oxide is present, then the hydrogen evolution reaction must occur on the outside of this film rather than the metal surface and would be expected to have a different overpotential. It has been reported that in acidic media the kinetics of hydrogen evolution are slower on magnetite than on bare iron³¹. Therefore the corrosion reaction could be under cathodic control for this reason.

B. However, if as predicted, the inner oxide is not protective, mass transport of either reactants or products to and from the iron / solution interface will be rate controlling.

- (iii) The only reactant which must access the interface is water. It is possible, if the porosity of the oxide is low enough, that the access of water would be rate controlling.
- (iv) Inhibition of the anodic reaction by the concentration of ferrous ions in the interface could occur. Diffusion of ferrous ions through a porous film is thought to be the rate controlling step at higher temperatures.
- (v) Diffusion control by the other reaction product, hydrogen, could lead to inhibition of the cathodic reaction due to a build up of hydrogen at the metal/solution interface.

4.2 Temperature range 50-90°C

Considering the possible mechanism in pure water first, in this temperature range it seems probable that a deposited ferrous hydroxide film will form on top of the initial hydroxide layer suggested by Bockris¹⁸ in a similar manner to that proposed for the lower temperatures. The cathodic reaction (water reduction) is again likely to occur at the metal/oxide interface. As discussed in the thermodynamics section, overpressures of hydrogen will tend to inhibit magnetite formation. Therefore at these temperatures transformation of hydroxide to magnetite may occur preferentially in the outer layers of the oxide, giving an essentially duplex oxide in which an outer oxide layer rich in magnetite overlies an essentially ferrous hydroxide inner one.

Once the solution outside the corrosion film is in equilibrium with magnetite as opposed to with ferrous hydroxide it will become possible to generate a diffusion gradient for the ferrous ions, enabling them to move out through the porous oxide. These ions should not be deposited within the porous oxide as magnetite since hydrogen produced by the corrosion process will tend to suppress this. Therefore the iron should deposit as magnetite on the outer surfaces of the corrosion film.

At higher temperatures, above approximately 150 - 200°C where the inner oxide is also magnetite, there may be a tendency for this deposited magnetite film to grow into a columnar magnetite outer layer, though there is no direct evidence for such an ordered structure to the oxides formed below 100°C.

Where carbonate is present, it is likely that the low temperature film formation route described above will still be followed. Therefore a porous ferrous hydroxide/carbonate film is expected to be deposited which should inhibit the corrosion process by providing a barrier to diffusion. The evidence of film analyses, suggests that the presence of the deposited film of ferrous carbonate may make the transformation to magnetite less favourable. Therefore it is possible that the film may develop in different ways, depending on the proportion of ferrous carbonate. It still seems likely, at the carbonate concentrations of relevance to a repository, that a degree of magnetite formation will occur in the outer layers of the film giving a similar duplex structure to that proposed for pure water based systems. This would result in no significant difference in the corrosion behaviour from the case of pure water. At higher concentrations of carbonate/bicarbonate the film is likely to be predominantly ferrous carbonate just as below 50°C (with no significant magnetite formation). However, at higher temperatures there will be an increased tendency for ferrous carbonate films to recrystallise, becoming more compact and adherent.

The same rate controlling steps in the mechanism of film formation / growth are possible above 50°C as below. Thus it is convenient to consider the two temperature ranges together in deciding which are the most likely rate controlling steps. In any case the distinction made between temperatures above and below approximately 50°C may in the long-term be somewhat artificial, since in a closed system with a stable hydroxide film it cannot be ruled out that on a long timescale that the growth of magnetite might occur on the outside of the film, producing a structure similar to that postulated at higher temperatures. However in view of the slow rate of magnetite formation at low temperatures, it may not be possible to generate a film with such a structure within the timescale of laboratory studies at temperatures below 50°C.

Considering the first possibility, control by iron diffusion through the inner phase oxide film, it is possible to eliminate this on two grounds. Firstly, in flowing systems, for example the work of Berry¹¹, the corrosion rates were far higher than found in static experiments e.g. Jelinek and Neufeld⁵. Since the inner phase oxide layer would be expected to exist in both cases, with only the thickness of the deposited layer differing between the two sets of conditions, if iron diffusion through the outer layer was the rate controlling step, no difference in corrosion rate should have existed between flowing and static conditions. Secondly, the dissolution rate was shown to be flow rate dependent in the work of Berry¹¹ thereby indicating that reaction through the inner layer was capable of keeping pace with the mass transport processes in the adjoining boundary layer.

The possibility that the inner film does achieve total coverage of the metal and that water reduction on the outside of this inner layer is rate controlling is a possibility that must be considered by the experimental programme.

It is possible to argue against water access to the surface being the rate controlling mechanism since in the work of Simpson et al.^{12,13} in pressurised systems, where access of water to the surface should have been greater, the corrosion rates were in agreement with those of other workers measured at ambient pressures⁵.

Next the possibility of ferrous ion diffusion out through the porous oxide film is considered. Since the porous oxide is thought to be hydroxide / carbonate, so long as a porous oxide exists, the solution at the metal / oxide interface and throughout the hydroxide layer should be saturated with ferrous iron. Therefore, at temperatures below 50°C there should be no diffusion gradient for iron out through the film, especially in the capsule type corrosion experiments where the whole solution rapidly became saturated with ferrous hydroxide⁵. Even though a diffusion gradient can exist within the film at higher temperatures, the concentration at the metal / oxide interface will remain at the saturation point for ferrous hydroxide.

The fact that corrosion still occurs would mean that the iron dissolution reaction would have to be capable of occurring in the presence of a solution saturated in ferrous hydroxide. This is very unlikely on thermodynamic grounds. Hence if the concentration of ferrous ions at the metal to oxide interface is unlikely to be rate limiting, then diffusion of ferrous ion within the thickening film cannot explain the reduction in the corrosion rate below the 1 µm/year measured by the workers quoted above⁵⁻⁸. However the higher corrosion rates found in flowing systems can only be explained (assuming this is rate controlling) if no porous film was present so that corrosion rates became controlled by mass transport through the boundary layer.

If the concentration of Fe^{2+} at the metal / oxide interface, and hence $\text{Fe}(\text{OH})^+$ diffusion, is not rate controlling, then the concentration of the other soluble corrosion product, hydrogen gas, may be. Since it requires approximately 14 bar of hydrogen¹ to suppress the production of ferrous hydroxide under all practical situations of interest it is always going to be possible to achieve a diffusion gradient for hydrogen gas out through the porous layer. The thicker "oxide" layers built up under static conditions would produce slower mass transport and hence higher hydrogen concentrations at the metal surface and so may produce the lower corrosion rates found in practice.

Therefore of the possible rate controlling steps it seems possible to discount options (i) and (iii). Also option (iv), ferrous ion mass transport control, seems unlikely. This leaves options (ii) and (v) as the mechanisms requiring further investigation³².

5. Summary

It is important to understand the corrosion mechanism, and to identify the rate controlling steps, since if the rate limiting step is mass transport control of the anodic dissolution reaction, then the corrosion process at 25°C will occur at a steady rate of approximately 1 µm/year. Whereas if mass transport control of the cathodic reaction is rate limiting, then the continuously thickening oxide film should stifle the corrosion reaction, giving ever decreasing corrosion rates. In the latter case, irrespective of whether the film is carbonate or hydroxide/magnetite based, it seems likely that film growth will ultimately suppress the corrosion process to very low levels. However, any loss of ferrous ion from the system, e.g. from either absorption or precipitation as a less soluble species, for example Fe_3O_4 , or due to the system being not truly closed, will promote dissolution of the film, leading to renewed corrosion. Hence the corrosion rate may ultimately be proportional to the rate of removal of iron from the system.

6. Conclusions

1. Protective films form on carbon steel corroding under anaerobic conditions in neutral and alkaline condition solutions.
2. The composition of the films formed on carbon steel in granitic groundwaters may be either hydroxide/magnetite or hydroxide/carbonate.
3. The structure of either of these oxides is expected to be porous.
4. The literature suggests that the cathodic reaction is rate controlling. The rate controlling process can take two forms:
 - (a) hydrogen diffusion through the oxide is rate controlling. As the corrosion process proceeds and the corrosion film thickens then hydrogen evolution on the metal will be less favoured and the rate will be retarded.
 - (b) the oxide structure is duplex with a magnetite outer layer, the hydrogen evolution reaction occurring on this outer layer.
5. Further work is required before the mechanism of film formation and the nature of the film is fully understood but there is a significant body of concurring evidence that the films are protective and, therefore, reduce corrosion rates and hydrogen gas production rates to relatively small long-term values.

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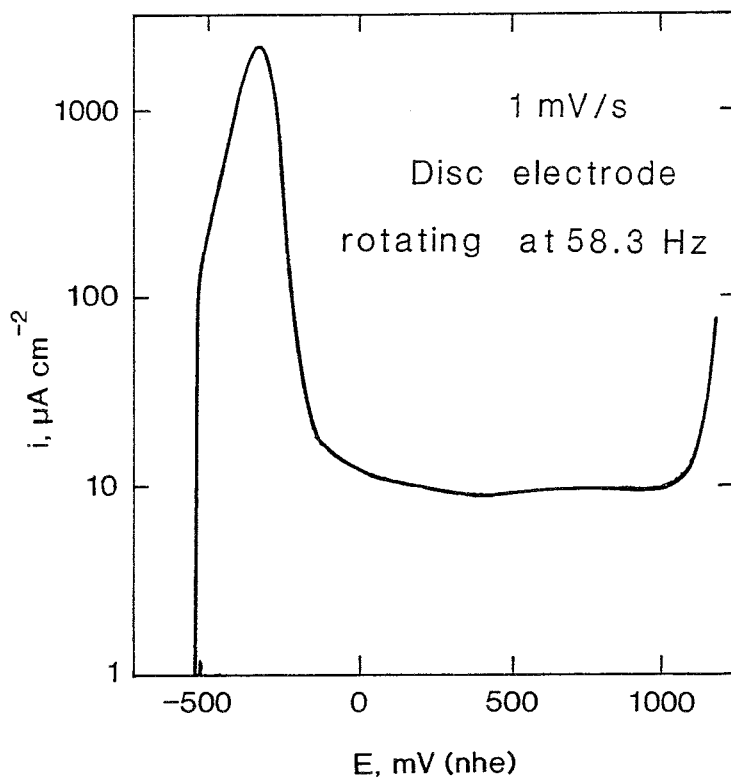


FIG. 1A.

Anodic polarisation scan for iron in $0.75 \text{ KHCO}_3 / 0.05 \text{ K}_2\text{CO}_3$ pH 8.8

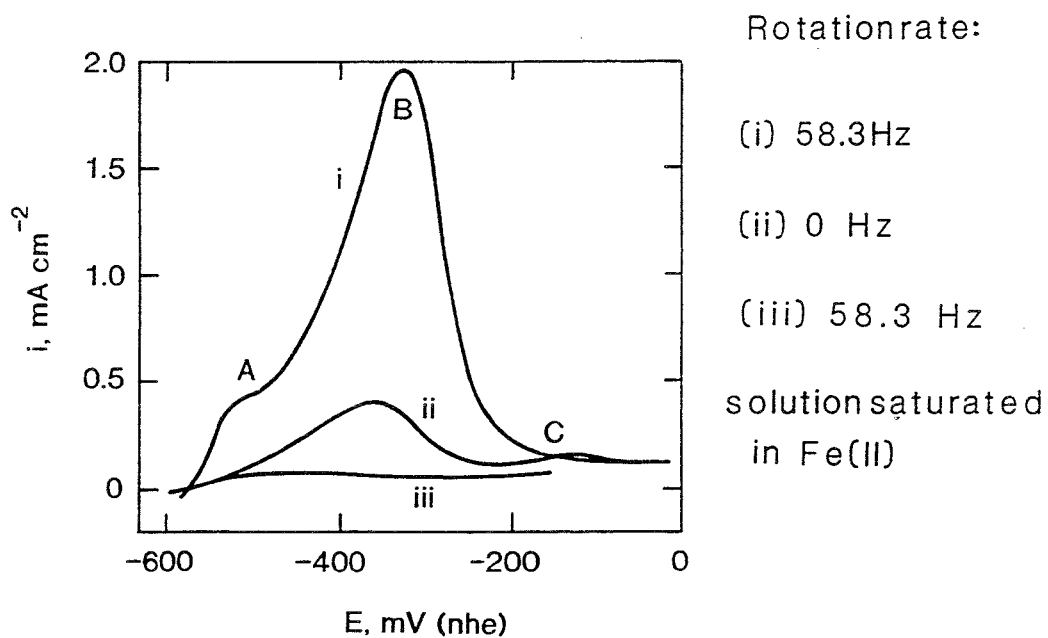


FIG. 1B.

As 1(a) but potential scan at 10 mV/s

(from reference 20)

Appendix 1

Relative solubilities of film forming species in granitic groundwaters

The Groundwaters we are concerned with are approximately 0.01M $\text{HCO}_3^-/\text{CO}_3^{2-}$ and around pH = 9

The following solubility product data, at 25°C, has been taken from the Handbook of Physics and Chemistry (68th Edition, 1987-88, CRC Press, Boca Raton, Florida, USA):

$$[\text{Fe}^{2+}][\text{OH}^-]^2 = 4.87 \times 10^{-17} \quad \text{and} \quad [\text{Fe}^{2+}][\text{CO}_3^{2-}] = 3.07 \times 10^{-11}$$

$$[\text{H}][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 5.61 \times 10^{-11}$$

$$\text{At pH}=9 \quad [\text{CO}_3^{2-}] = 5.61 \times 10^{-11} \times 0.01 / 10^{-9} = 5.61 \times 10^{-4}$$

$$\text{At pH}=10 \quad [\text{CO}_3^{2-}] = 5.61 \times 10^{-11} \times 0.01 / 10^{-10} = 5.61 \times 10^{-4}$$

Therefore at pH 9 ferrous carbonate is expected to be precipitated at:

$$[\text{Fe}^{2+}] = 3.07 \times 10^{-11} / 5.61 \times 10^{-4} = 5.5 \times 10^{-8} \text{ M}$$

and ferrous hydroxide at:

$$[\text{Fe}^{2+}] = 4.87 \times 10^{-17} / 10^{-10} = 4.87 \times 10^{-7} \text{ M}$$

Whereas at pH 10 ferrous carbonate is expected to be precipitated at:

$$[\text{Fe}^{2+}] = 3.07 \times 10^{-11} / 5.61 \times 10^{-4} = 5.5 \times 10^{-7}$$

and ferrous hydroxide at:

$$[\text{Fe}^{2+}] = 4.87 \times 10^{-17} / 10^{-8} = 4.87 \times 10^{-9}$$

Therefore at pH of 9 the film should precipitate as FeCO_3 , though the difference is marginal and only a small increase in pH will tend to favour hydroxide formation. It is not possible to say what effect the carbonate complex will have since the data presented in Davies and Burstein (reference 20, main text) is for far higher bicarbonate concentrations. This data is also at 75°C rather than 25°C. Any tendency for formation of this carbonate complex will effect both solubilities through the total iron present in solution, but is not expected to directly effect the tendency for ferrous carbonate precipitation to occur in preference to ferrous hydroxide precipitation as indicated above.

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