

Nagra

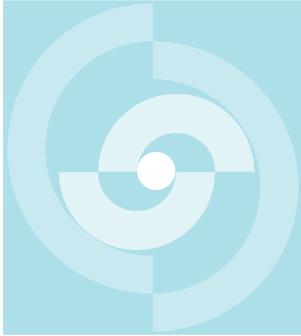
Nationale
Genossenschaft
für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
nationale
pour l'entreposage
de déchets radioactifs

Cisra

Società cooperativa
nazionale
per l'immagazzinamento
di scorie radioattive



TECHNICAL REPORT 88-02 E

**THE CORROSION BEHAVIOUR OF CARBON
STEEL IN PORTLAND CEMENT**

ROLF GRAUER

JANUARY 1988

PSI, Würenlingen and Villigen

Nagra

Nationale
Genossenschaft
für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
nationale
pour l'entreposage
de déchets radioactifs

Cisra

Società cooperativa
nazionale
per l'immagazzinamento
di scorie radioattive

TECHNICAL REPORT 88-02 E

**THE CORROSION BEHAVIOUR OF CARBON
STEEL IN PORTLAND CEMENT**

ROLF GRAUER

JANUARY 1988

PSI, Würenlingen and Villigen

This report was prepared as an account of work sponsored by Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

Der vorliegende Bericht wurde im Auftrag der Nagra erstellt. Die Autoren haben ihre eigenen Ansichten und Schlussfolgerungen dargestellt. Diese müssen nicht unbedingt mit denjenigen der Nagra übereinstimmen.

Le présent rapport a été préparé sur demande de la Cédra. Les opinions et conclusions présentées sont celles des auteurs et ne correspondent pas nécessairement à celles de la Cédra.

ABSTRACT

The production of hydrogen can cause problems in a repository for low- and intermediate-level waste. Since gas production is mainly due to the corrosion of carbon steel, it is important to have as reliable data as possible on the corrosion rate of steel in anaerobic cement.

A review of the literature shows that the corrosion current densities lie in the range 0.01 to 0.1 $\mu\text{A}/\text{cm}^2$ (corresponding to corrosion rates between 0.1 and 1.2 $\mu\text{m}/\text{a}$). This implies hydrogen production rates between 0.022 and 0.22 $\text{mol}/(\text{m}^2 \cdot \text{a})$.

Corrosion rates of this order of magnitude are technically irrelevant, with the result that there is very little interest in determining them accurately. Furthermore, their determination entails problems of measurement technique.

Given the current situation, it would appear somewhat risky to accept the lower value for hydrogen production as proven. Proposals are made for experiments which would reduce this element of uncertainty.

ZUSAMMENFASSUNG

In einem Endlager für schwach- und mittelaktive Abfälle kann die Bildung von Wasserstoff zu Problemen führen. Da die Gasentwicklung zur Hauptsache auf die Korrosion von unlegiertem Stahl zurückzuführen ist, sollte ein möglichst gesicherter Wert für die Korrosionsgeschwindigkeit in sauerstofffreiem Zement bekannt sein.

Die Durchsicht der Literatur ergibt, dass die Korrosionsstromdichten im Bereich von 0,01 bis 0,1 $\mu\text{A}/\text{cm}^2$ liegen, entsprechend einem Materialabtrag von 0,1 bis 1,2 μm pro Jahr. Daraus ergeben sich Wasserstoffproduktionsraten von 0,022 bis 0,22 $\text{mol}/(\text{m}^2 \cdot \text{a})$.

Korrosionsgeschwindigkeiten dieser Grössenordnung sind für die Technik irrelevant; deshalb besteht an ihrer exakten Festlegung wenig Interesse. Ausserdem stellen sich bei ihrer Ermittlung Messprobleme.

Es erscheint deshalb in der gegenwärtigen Situation gewagt, den kleineren Wert der Wasserstoffproduktionsrate als gesichert anzunehmen. Es werden Vorschläge für experimentelle Untersuchungen gemacht, um diese Unsicherheit abzubauen.

RESUME

La production d'hydrogène peut conduire à des problèmes dans un dépôt final pour déchets faiblement et moyennement radioactifs. Du fait que la production d'hydrogène est principalement due à la corrosion des aciers non alliés, il est important de pouvoir se baser sur une valeur du taux de corrosion aussi bien fondée que possible.

L'étude de la littérature montre que les densités de courant de corrosion se situent dans le domaine de 0,01 à 0,1 $\mu\text{A}/\text{cm}^2$ (correspondant à un taux de corrosion entre 0,1 et 1,2 $\mu\text{m}/\text{a}$). Il en résulte des taux de production d'hydrogène dans l'intervalle 0,022 jusqu'à 0,22 $\text{mol}/(\text{m}^2 \cdot \text{a})$.

Des taux de corrosion de cet ordre de grandeur sont sans importance pour les applications techniques; il s'ensuit qu'il n'y a que peu d'intérêt à les déterminer exactement. D'autre part une telle détermination pose des problèmes de technique de mesure.

Pour ces raisons il serait risqué de considérer la valeur inférieure ci-dessus comme assurée. On propose des essais expérimentaux propres à réduire cette incertitude.

TABLE OF CONTENTS

	Page
Abstract	I
Zusammenfassung	II
Résumé	III
Table of contents	IV
1. Introduction	1
2. The passivity of iron	1
3. Determination of low corrosion rates	5
4. Survey of available experimental results	7
5. Theoretical considerations	11
6. Calculation of the hydrogen evolution rate	14
7. Possible influence of anions	16
8. Conclusions and recommendations	18
9. Literature references	20

Appendix:

Comments on the potential-pH diagram of the iron/water system

1. INTRODUCTION

Significant gas production is to be expected in a repository for low- and intermediate-level waste, mainly due to corrosion reactions. In this respect, Nagra assumes that $8.2 \cdot 10^7$ Nm³ of hydrogen will be released in a type B repository in the first 10,000 years (NAGRA 1985). Around 90% of this gas production can be attributed to the corrosion of reinforcing steel and the reaction of steel wastes in the cement matrix.

Given the environment in the repository, the corrosion rate of steel in anaerobic cement should be determined as accurately as possible with a view to estimating the associated gas production rate. In Project Gewähr, Nagra relies on the data provided in a single report (PREECE, 1982) and reckons with a corrosion rate of 0.1 to 1 μ m per year.

The present report will summarise and comment on the corrosion of steel in cement as it is understood today, the aim being to define as narrow and accurate a range as possible for the corrosion rate of steel in Portland cement.

There is a comprehensive body of literature on steel corrosion in concrete, but interest tends to be focussed on increased corrosion in carbonated concrete and the effect of chlorides (CRANE, 1983). The low corrosion rate of passive steel in alkaline, chloride-free concrete is of little interest in the field of civil engineering.

2. THE PASSIVITY OF IRON

The basic information required for understanding corrosion reactions is presented briefly in (GRAUER, 1984). A more in-depth treatment of the subject, particularly of passivity, can be found in the text-book by Kaesche (KAESCHE, 1979).

In its passive state, iron is covered by a non-porous oxide film only a few nanometers thick. The net anodic current density is therefore more or less independent of potential, being determined in the steady-state by the dissolution rate of the passive film in the surrounding electrolyte. As the passive film is electron-conducting, cathodic reactions can occur on the passive metal and produce a stable condition (Fig. 1).

The dissolution rate of the passive film depends in the first instance on the pH of the solution and the film stoichiometry. The passive film in the case of iron consists of an oxide with composition $Fe_{3-x}O_4$ with spinel structure. The limiting compositions are Fe_3O_4 and $\gamma-Fe_2O_3$ ($= Fe_{2.67}O_4$) which form a continuous crystalline solid solution. In the acidic range, magnetite dissolves very rapidly and only an Fe_2O_3 -film with slow dissolution kinetics can have a passivating effect.

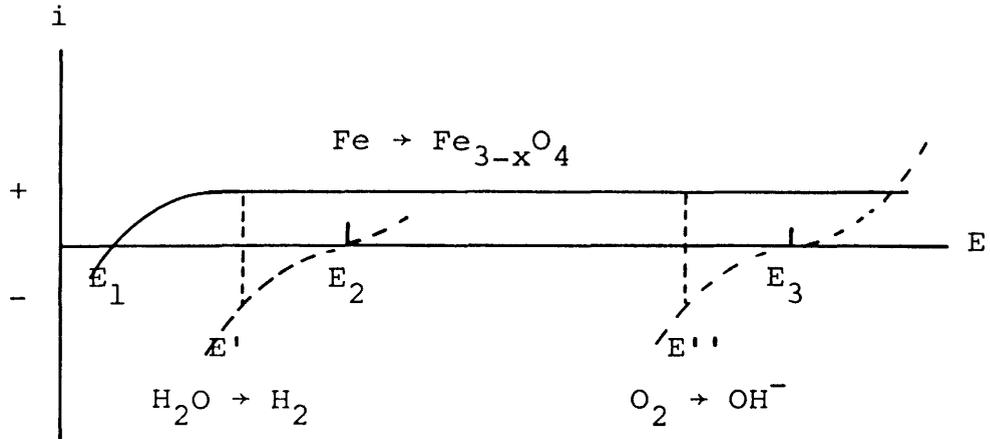


Figure 1: Schematic polarisation diagram for a passive iron electrode. E_1 : equilibrium potential iron/magnetite; E_2 : equilibrium potential H_2/H_2O ; E_3 : equilibrium potential O_2/H_2O . Because the net anodic reaction is independent of potential, a stable corrosion potential with constant corrosion rate occurs in both anaerobic (E') as well as aerated (E'') solutions.

Magnetite is thermodynamically stable in alkaline solutions (Fig. 2) and also dissolves extremely slowly under such conditions. Passivity within the stability range of the magnetite is therefore possible in alkaline solutions. The composition of the passive film varies from Fe_3O_4 in anaerobic solution to $Fe_{2.67}O_4$ in the presence of oxygen.

The thermodynamic condition for stable passivity in anaerobic alkaline solutions (that the equilibrium potential H_2O/H_2 should be higher than the potential value for Fe/Fe_3O_4) is fulfilled. From the point of view of kinetics, it is required that the corrosion current density in the passive range should be supplied by the current density of the hydrogen production.

Before the iron can be passivated, a critical current density must be overcome; this becomes smaller with increasing pH (Figs. 3 and 4). At sufficiently high pHs, this critical value is identical to the dissolution current density in the passive range, so that even extremely small cathodic currents can produce a stable passive condition.

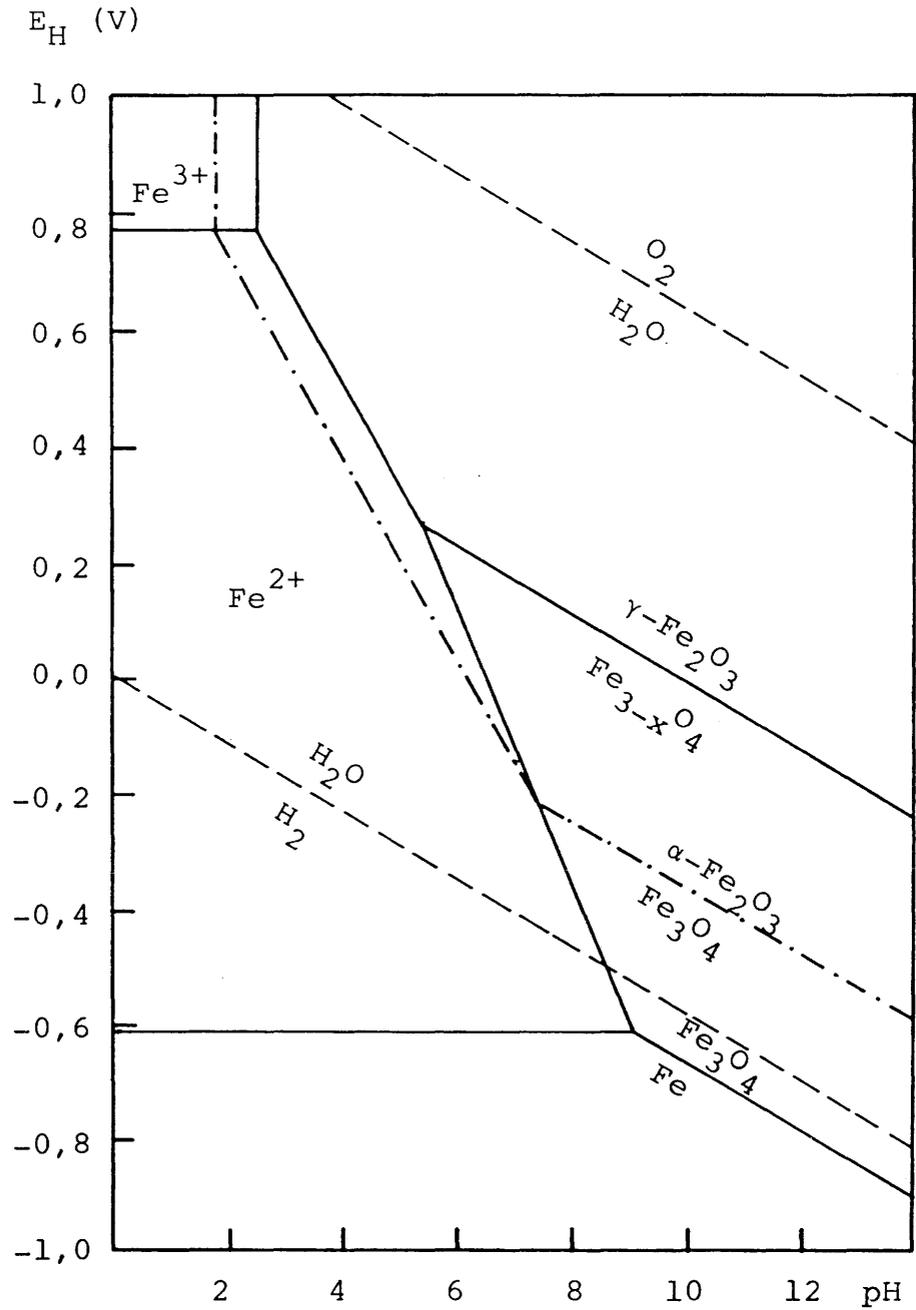


Figure 2: Potential-pH-diagram for the system iron/water at 25°C. Completed according to GARRELS and CHRIST, 1965, see Appendix.

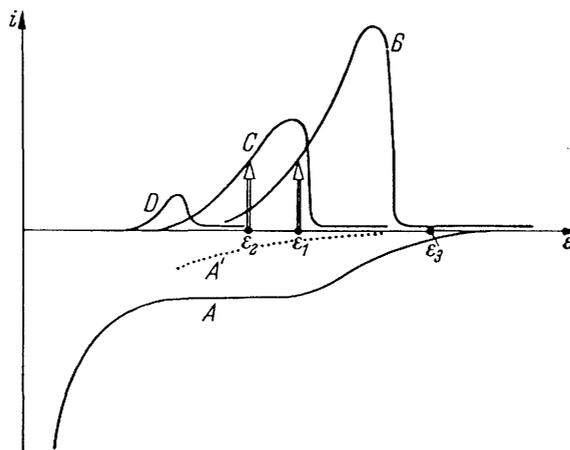


Figure 3: For passivating iron, a critical current density which becomes smaller with increasing pH has to be overcome (B, C, D). A is the curve for oxygen reduction. $\epsilon_1, \epsilon_2, \epsilon_3$: corrosion potentials when A is combined with B, C and D. The combination A/D (and also A'/D) give stable passive conditions (KAESCHE, 1979). The level of the critical current density also depends on the anion.

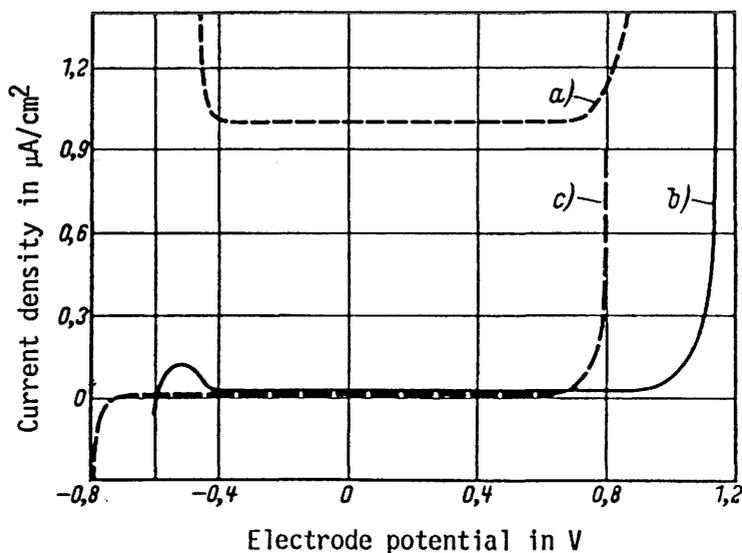


Figure 4: Stationary polarisation diagram for pure iron at 50°C in anaerobic solutions of a) glycol buffer, pH = 9.3; b) borate buffer, pH = 9.3; c) 0.1 M sodium hydroxide solution. After HEUSLER et al., 1985.

3. DETERMINATION OF LOW CORROSION RATES

Corrosion rates in the order of a few micrometres per year are practically insignificant from the point of view of the technical application of unalloyed steels and there is therefore very little interest in determining them with any degree of accuracy. Measurements of changes in dimension and weight losses are not applicable in the case of low corrosion rates because of the limited sensitivity of the techniques used and errors caused by adhesive corrosion products. Electrochemical measurement methods therefore have to be used.

a) Stationary polarisation diagrams

The corrosion current density of oxide-passive metals is constant over a wide potential range. In a potential range which permits no cathodic reactions, the measured total current density is therefore identical to the corrosion current density (Fig. 1). Since it takes several hours to achieve stationary conditions at low current densities, it is necessary to carry out long-term experiments at constant potential.

In principle, corrosion current densities can also be determined by extrapolating the stationary polarisation diagrams to the corrosion potential (Fig. 5). This method finds particular application in the case of actively corroding metals.

A prerequisite to applying this method is a linear shape for at least one of the partial curves in semi-logarithmic notation. It also has to be assured that the system is not affected by the measurement. This second requirement in particular is almost impossible to fulfil in the case of passive iron in anaerobic solution. Cathodic polarisation involves a drop below the Fe/Fe₃O₄ potential and the passive film is reduced. This alters the kinetics of hydrogen production and thus the shape of the cathodic partial curve.

b) Polarisation resistance

It can be deduced theoretically (HEITZ and SCHWENK, 1976; KAESCHE, 1979; MORELAND and RAWLANDS, 1977) that the gradient of the polarisation diagram at rest potential is a measure of corrosion current density. The relationship

$$\Delta E / \Delta i = R_p = B / i_{\text{korr}}$$

applies; R_p is the polarisation resistance. The proportionality constant B can be derived from electrode kinetic parameters, but some of these are only estimates themselves (GRAUER et al., 1982). The corrosion current densities can therefore be determined only to within a factor of 2 to 3.

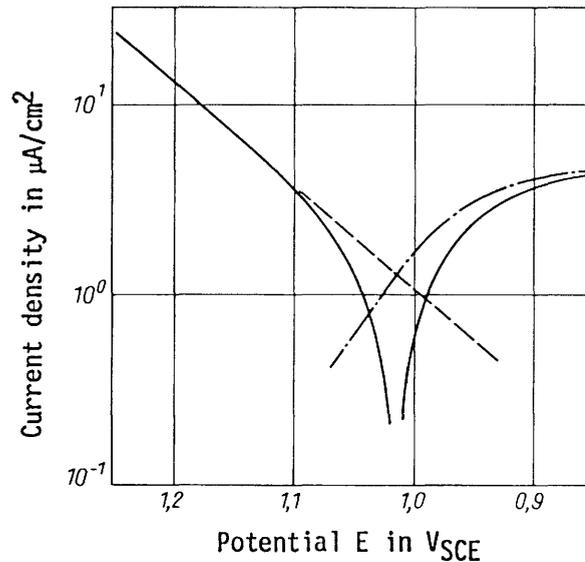


Figure 5: Polarisation diagram for pure aluminium in an anaerobic acetate buffer. The corrosion current density can be determined by extrapolation of the cathodic branch of the curve to the corrosion potential. —: measured total current density; ----: extrapolated net cathodic current density; -·-·-: calculated net anodic current density (GRAUER and WIEDMER, 1980).

The great advantage of the method is that, because of the low polarisation of $\Delta E \leq \pm 10$ mV required, the system is not disturbed electrochemically. Measurement problems can occur in the case of passive metals and in high-resistance systems (cemented samples), see HEITZ and SCHWENK, 1976.

4. SURVEY OF AVAILABLE EXPERIMENTAL RESULTS

Electrochemical investigations of passive systems are not straightforward for several reasons. For a start, it should be noted that, with a typical corrosion current density of $0.1 \mu\text{A}/\text{cm}^2$ (corresponding to a corrosion rate of around $1.2 \mu\text{m}$ per year), only extremely small amounts of material are altered during normal experimental time-periods. 0.14 nm of iron are altered per hour, which corresponds to corrosion of around 0.5 unit cells!

It is therefore easy to appreciate that setting-up of steady-state conditions takes about one day and that even traces of redox-active impurities will be affecting the total current and the potential.

In anaerobic solution, a corrosion current density of $0.1 \mu\text{A}/\text{cm}^2$ results in a hydrogen evolution rate of $2 \cdot 10^{-9}$ mol per cm^2 and hour. The hydrogen does not form bubbles but remains in solution and is removed by diffusion. This readily shows that in anaerobic solution corrosion potentials above the equilibrium line $\text{H}_2/\text{H}_2\text{O}$ are possible (HANSSON, 1985b), since the hydrogen activity is less than 1.

With respect to this problem, it is also interesting to note that embedding the samples in cement creates additional difficulties. For this reason, many authors have carried out their investigations in synthetic pore-waters (usually in saturated $\text{Ca}(\text{OH})_2$ solution). This rules out any possible influence by redox-active cement impurities.

Since only a small number of corrosion investigations have been carried out in anaerobic alkaline solutions, the following discussion will also include results obtained in the presence of air. This is acceptable for passive steel as the current density in the passive range has been shown to be independent of potential (e.g. HEUSLER et al., 1958).

BAEUMEL and ENGELL, 1959 have also shown that there is practically no difference between the polarisation diagrams for steel in saturated $\text{Ca}(\text{OH})_2$ solution and in 0.1 M NaOH (with comparable pH values). It can also be deduced from their work that cement (provided it contains no redox-active components) has no effect on the polarisation diagrams at low current densities. At high current densities, which are not of interest here, transport processes are influenced by the solid material. It therefore follows that results from tests with model solutions (NaOH, $\text{Ca}(\text{OH})_2$) can be compared directly with those for cemented samples.

The question then arises as to the **lowest corrosion current densities** ever measured for iron in alkaline solutions.

It can be deduced from the work by HEUSLER et al., 1958 that the stationary current density in the passive range in a borate buffer (pH = 9.3) is 7 nA/cm². It can be seen from Figure 4 that this value also applies for 0.1 M NaOH at 50°C (the current density in HEUSLER et al., 1958 is not given numerically for this system). The absence of the active/passive transition in the sodium hydroxide solution is worthy of note. Japanese authors have determined passive current densities of 40 nA/cm² in borate solutions (Fig. 97 in KAESCHE, 1979).

KAESCHE, 1965 and GRUBITSCH et al., 1970 have produced stationary polarisation diagrams for pure iron and steel in anaerobic saturated Ca(OH)₂ solution (Figs. 6 and 7). The experimental times were 5 and 16.7 hours. The corrosion current densities were <0.2 μA/cm² (KAESCHE, 1965) and 0.05 -0.1 μA/cm² respectively (estimated from Fig. 7).

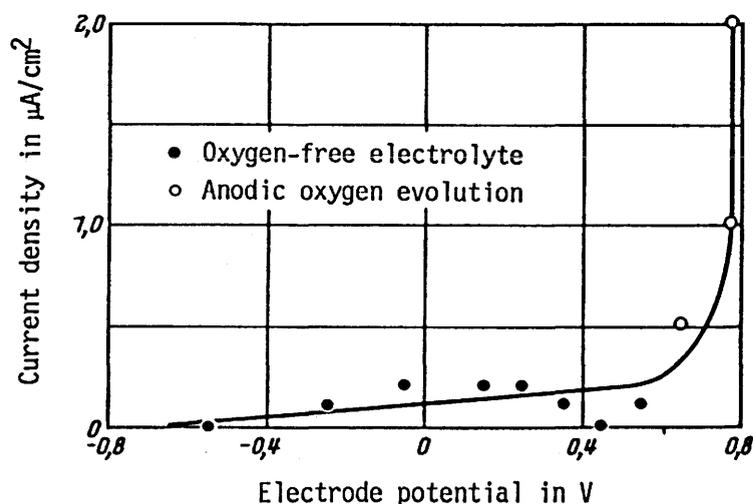


Figure 6: Stationary anodic polarisation diagram for carbonyl iron in anaerobic saturated calcium hydroxide solution at 25°C (KAESCHE, 1965).

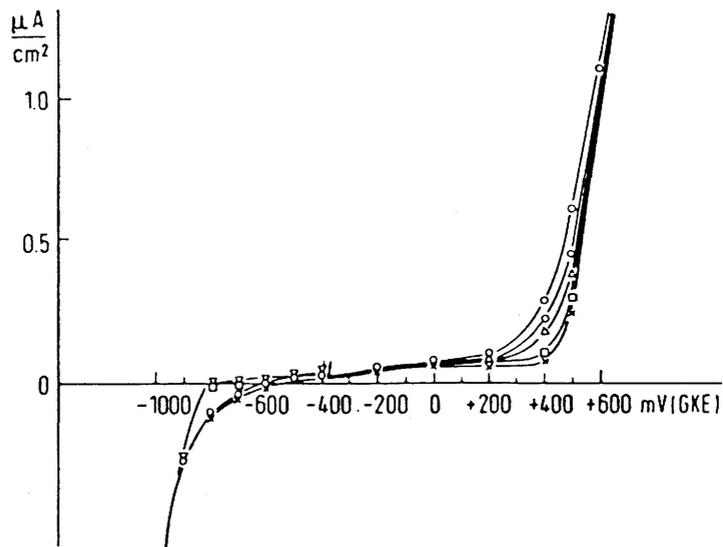


Figure 7: Stationary polarisation diagrams for steel wires in anaerobic saturated calcium hydroxide solution at 25°C. The different symbols relate to the different mechanical stresses in the wires (GRUBITSCH et al., 1970). GKE: saturated calomel electrode, $E_H = +244$ mV.

An active/passive transition was not detected in either work; the iron appears to be in the stable passive state at the corrosion potential. These studies also indicate that there is no significant difference between the behaviour of pure iron and that of technical steels.

A Spanish group has carried out a wide range of experiments to determine the corrosion rate of cemented steel by measurement of the polarisation resistance (ANDRADE and GONZALEZ, 1978; ANDRADE and PAGE, 1986; GONZALEZ et al., 1980). The samples were not anaerobic.

An example of the change in corrosion current density with time is given in Figure 8; after 28 days it reaches $0.06 \mu\text{A}/\text{cm}^2$. The Figure also shows the detrimental effect of chloride and the rise in corrosion rate when the cement is carbonated. Addition of nitrite as a passivator does not lower the corrosion rate significantly. The values measured by the authors for additive-free non-carbonated cement are in the range 0.05 to $0.1 \mu\text{A}/\text{cm}^2$ (with $B = 52$ mV).

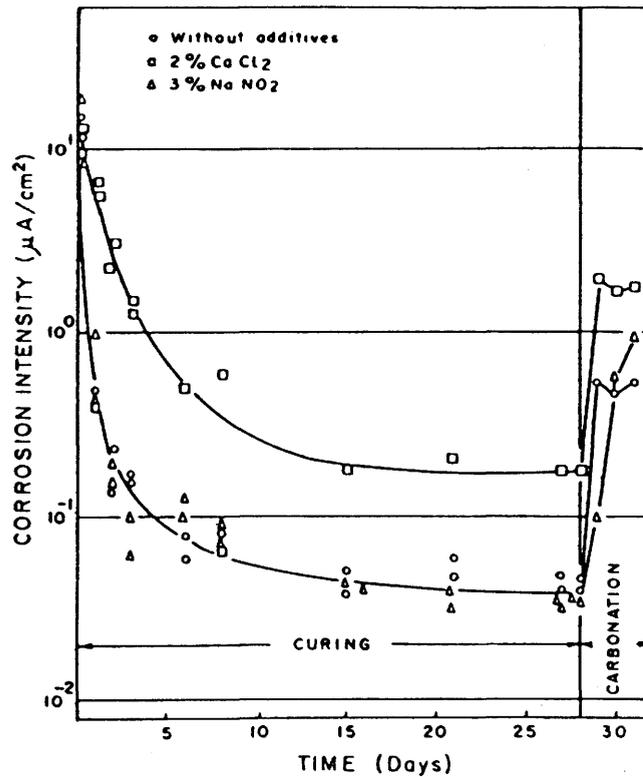


Figure 8: The variation with time of the corrosion current density - determined from polarisation resistance - in a cemented steel rod at ambient temperature in contact with air (CRANE, 1983).

HANSSON, 1985b also used the polarisation resistance to determine corrosion current densities of 0.1 to 0.3 $\mu\text{A}/\text{cm}^2$ ($B = 26 \text{ mV}$) after a period of 10 months. The samples were stored under exclusion of oxygen. Extrapolation of the stationary polarisation diagrams gave corrosion current densities of 0.1 $\mu\text{A}/\text{cm}^2$.

ARUP, 1983 gives a corrosion rate of 0.1 $\mu\text{m}/\text{year}$ for passive steel in concrete; this corresponds to a current density of around 0.01 $\mu\text{A}/\text{cm}^2$. There are no references to the test methods used.

Preece et al. (PREECE et al., 1981; PREECE et al. 1983) also determined corrosion current densities in the order of 0.01 $\mu\text{A}/\text{cm}^2$ for cemented samples under exclusion of oxygen using stationary polarisation diagrams. However, on reading through this work, it is apparent that these values are somewhat optimistic and that 0.05 $\mu\text{A}/\text{cm}^2$ would be more accurate.

Hansson's measurements (HANSSON, 1985a) with steps in potential of 20 mV every 10 minutes give values which are too high.

5. THEORETICAL CONSIDERATIONS

Danish authors assume that, with corrosion potentials around -750 mV, steel in anaerobic cement no longer has a passive film and can therefore corrode actively (ARUP, 1983; HANSSON, 1984; HANSSON, 1985b; PREECE, 1982; PREECE et al., 1983). They ascertain that the corrosion current density in the active state has about the same value as in the passive state. This contradicts the German school of thought (work has already been discussed), according to which steel in alkaline solutions is also in a stable passive state under oxygen exclusion (GRUBITSCH et al., 1970; HEUSLER et al., 1958; KAESCHE, 1979;). It is worth noting that the German work is not cited by the Danish group.

The first impression is that this contradiction comes down to a purely academic discussion since - and only this is relevant for a repository situation - the corrosion rates have the same low values and are not affected by the controversy.

However, the question does have a practical aspect. If active corrosion is assumed, the corrosion rate would be expected to depend on the material involved since the exchange current density for the H_2/H_2O reaction is strongly affected by metal purity. If, on the other hand, the hydrogen evolution is on the passive oxide, the effect of the steel composition should no longer be important.

Many results point in favour of stable passivity under exclusion of oxygen in the pH range 12.5 to 13. The first thing to be noted is that there is no significant difference between pure iron and technical steels. A further argument for stable passivity is the shape of the polarisation diagrams (GRUBITSCH et al., 1970; HEUSLER et al., 1958; KAESCHE, 1965) which shows no change in the corrosion mechanism (Figs. 4 and 7). An active/passive transition can be detected only at significantly higher NaOH concentrations (HEUSLER, 1985; SCHWARZ and SIMON, 1963). Under these conditions, passivation is preceded by metal dissolution to the hydroxy complex $Fe(OH)_3^-$ (in the corrosion literature this still has the historically interesting formula $HFeO_2^-$).

As shown in the Appendix, the Flade potential in alkaline solutions is not a critical limiting value for the active/passive transition. It is however a characteristic value since, at values higher than the Flade potential, the passive film is completely oxidised. For every cathodic sweep, there is a reduction of the passive oxide. In the case of a low corrosion rate, the anodic current density can be supplied by this reduction so that a corrosion potential in the vicinity of the Flade potential can be set up. The polarisation diagrams in (PREECE et al., 1983) can be explained in this way (Fig. 9). The shift of several 100 mV in the corrosion potential between anodic and cathodic sweeps is thus an artefact caused by the measurement.

In practice, corrosion potentials close to the Flade potential are also expected to be a transient phenomenon. A steel passivated originally in the presence of oxygen is covered by a completely

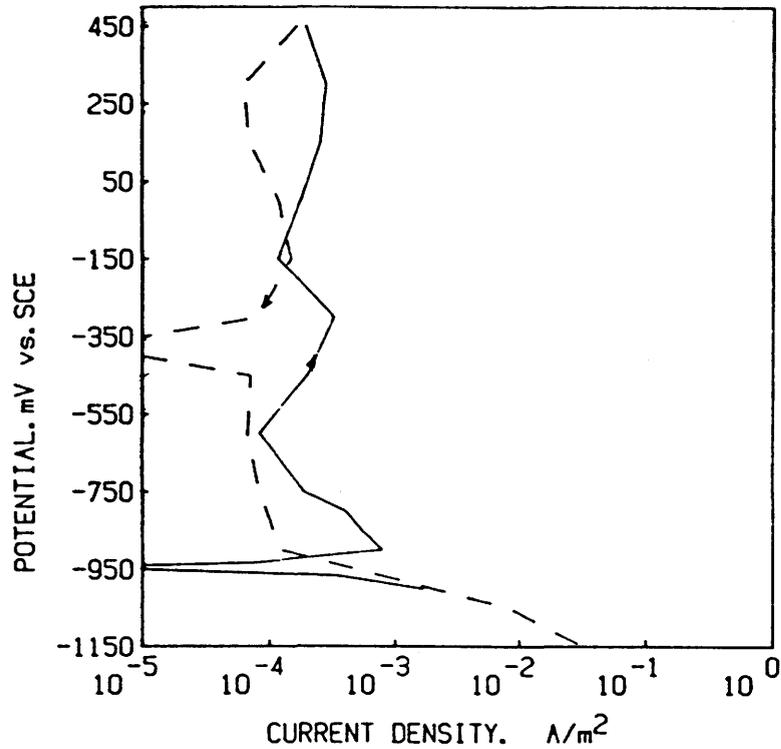


Figure 9: Stationary polarisation diagrams for cemented steel in $\text{Ca}(\text{OH})_2$ solution at 35°C . In the case of the cathodic sweep (dashed), there is a rest potential in the vicinity of the Flade potential. The potential values relate to the saturated calomel electrode ($E_{\text{H}} = +224 \text{ mV}$), PREECE et al., 1983. oxidised passive film and possibly by other iron(III) corrosion products which are partly reducible (GRAUER, 1981). If the system becomes anaerobic during the course of time, the iron(III) compounds will be reduced before hydrogen production begins; this results in corrosion potentials in the vicinity of the Flade potential.

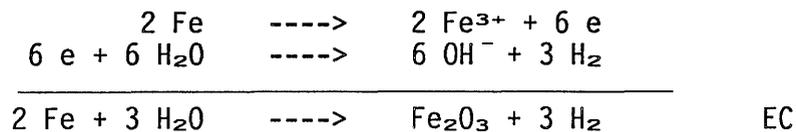
Finally, it should be mentioned that a comparison between experimentally determined potentials and equilibrium potentials is problematic because of the uncertainties in the data-base. For example, the uncertainty in the Fe/Fe₃O₄ potential is estimated as 40 mV (HEUSLER, 1985) and quantitative considerations which are based on equilibrium potentials (HANSSON, 1985b; PREECE, 1982) should therefore be interpreted with caution. This is also true for the comparison between measured corrosion potentials and the H₂/H₂O equilibrium value (HANSSON, 1985b). Such measurements are very susceptible to perturbations because of the low current densities in the case of iron; this, in turn, results in poorly reproducible or unstable measured values. A residual oxygen content of 1 ppm in the inert gas atmosphere leads to cathodic current densities of 7 nA/cm² (HEUSLER et al., 1958) which are comparable with passive current densities.

6. CALCULATION OF THE HYDROGEN EVOLUTION RATE

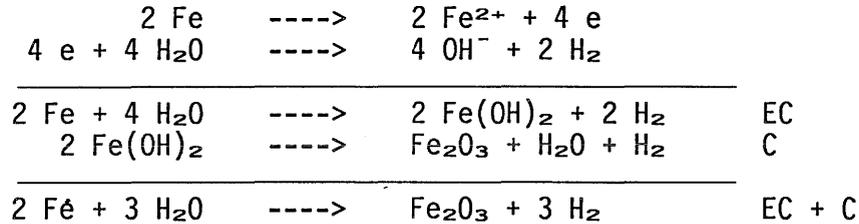
The question arises whether measured corrosion current densities can be converted directly into a hydrogen evolution rate. We therefore have to discuss whether the electrochemical charge transfer valency of the iron corresponds to its average oxidation number in the passive oxide and in the secondary corrosion products or whether a chemical oxidation (C) is coupled to the electrochemical charge transfer reaction (EC).

If, for the purpose of illustration, the limiting composition Fe_2O_3 is assigned to the corrosion products, the following limiting reactions are to be considered for anaerobic solutions:

a) Charge transfer valency 3



b) Charge transfer valency 2



In case a) it is assumed that the iron reacts electrochemically in one step to the oxidation state III. This releases an equivalent quantity of hydrogen and the measured corrosion current density gives the hydrogen production rate.

It is assumed in case b) that the iron reacts electrochemically only to the oxidation state II. In addition, there is a purely chemical oxidation in which hydrogen is released from water and is undetectable by an electrochemical measurement. The ratio $\text{H}_2(\text{C})/\text{H}_2(\text{EC})$ is 0.5 and the measured corrosion current density therefore has to be multiplied by 1.5 in order to calculate the hydrogen evolution rate. A similar process for the limiting composition Fe_3O_4 (which is realistic under the given conditions) gives a correction factor of 1.33.

The mechanism of iron dissolution, and particularly that of passivation, is very complex (BESSONE et al., 1977; MACDONALD and ROBERTS, 1978) and definitive statements about the partial reactions in the iron/cement system should be treated with caution. Nevertheless, it is certain that, in the case of the active corrosion of iron, the charge transfer valency is also 2 in aerobic solutions (KAESCHE, 1979) and iron(III)-compounds are produced through coupled chemical reactions.

For reasons of caution, this reaction sequence should also be assumed, by way of precaution, for the formation of passive films. Because of the low potential under anaerobic conditions, the composition of the passive film and that of the secondary corrosion products will lie close to the limiting composition Fe_3O_4 ; for the calculation of the hydrogen evolution rate, the corrosion current density is therefore multiplied by 1.33:

$$i_{\text{H}_2} = 1.33 \cdot i_{\text{corr.}}$$

Considering the element of uncertainty in the electrochemical measurements, this correction is purely of a cosmetic nature.

On looking through the literature, it can be seen that the the corrosion current densities for steel in cement lie between 0.01 to 0.1 $\mu\text{A}/\text{cm}^2$. It should however be noted that some of the data are based on measurement of polarisation resistance. In some of the studies, the passive current densities had to be derived from illustrations in the text, which is not conducive to accuracy.

Nevertheless it appears justified to take the upper value as 0.1 $\mu\text{A}/\text{cm}^2$, which gives a

maximum hydrogen evolution rate of 0.22 mol/(m²•a).

If it is considered that the lowest corrosion current density of around 7 nA/cm² was measured in a clean system under laboratory conditions (HEUSLER et al., 1958), it would be risky under the present circumstances to take a value below 10 nA/cm² as the lower limit. For the hydrogen evolution rate, this gives

a minimum value of 0.022 mol/(m²•a).

For conservative estimates, these evolution rates would have to be multiplied by a safety factor.

7. POSSIBLE INFLUENCE OF ANIONS

The corrosion investigations discussed in this report were carried out in pure hydroxide solutions and generally do not take account of anion influences. The potential effect of the most important anions will now be discussed briefly. Chloride, sulphate and hydrogen sulphide can occur in considerable concentrations in formation waters and nitrates are one of the waste components.

Chlorides can cause pitting in passive steel. The occurrence of this type of corrosion is linked to a concentration-dependent critical potential - KAESCHE, 1965 - (Fig. 10). These potentials lie in a range which is not reached in anaerobic cement and pitting is therefore possible only in the presence of oxygen or some other oxidant (e.g. nitrate).

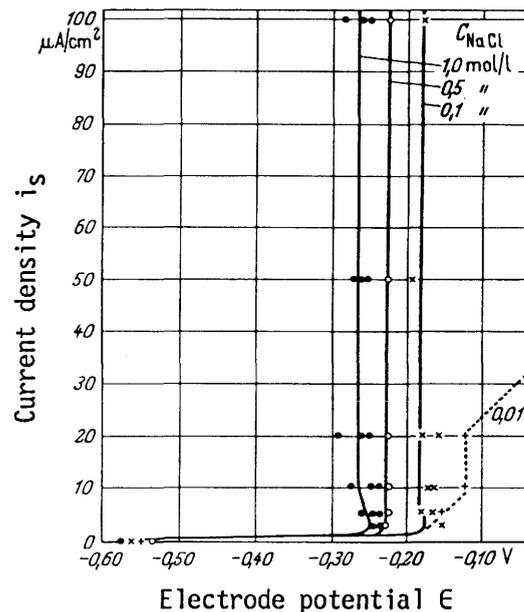
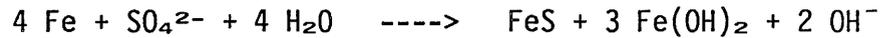


Figure 10: Stationary polarisation diagrams for a reinforcing steel in anaerobic saturated calcium hydroxide solution with various NaCl concentrations at 25°C. At a concentration-dependent critical potential, a current breakthrough is observed (KAESCHE, 1965).

Chloride can however increase the dissolution rate of oxidic phases and, consequently, of passive films (GRAUER and STUMM, 1982). This should perhaps be borne in mind when considering the discovery that adding 1 mol/litre of sodium chloride to a calcium hydroxide solution increases the passive corrosion current density from around 0.2 to 5 $\mu\text{A}/\text{cm}^2$ (KAESCHE, 1965).

Sulphate is metastable in aqueous solutions under reducing conditions. There is no reference in the literature to steel corrosion by sulphate which would occur more or less according to the reaction



The intense colour of iron sulphides would make such a reaction obvious even with low corrosion rates. In aqueous sulphate solutions which contain no other oxidant, hydrogen evolution is the only cathodic reaction.

In the presence of sulphate-reducing bacteria, sulphate can participate in corrosion reactions (GRAUER, 1984; THE METALS SOCIETY, 1983). It does not seem to be possible to predict the extent of bacterial corrosion but, in alkaline solutions such those found in cement pore-waters, such activity should be highly unlikely.

In nitrate-containing waters with oxygen contents below around 1 mg/litre, nitrate is reduced on unalloyed steel (GARRELS and CHRIST, 1964). The reduction leads via nitrite to production of ammonium and nitrogen. There do not appear to be any investigations of nitrate reduction on passive steels in alkaline solutions. It can, however, be assumed that the passive film remains intact and the corrosion rate is not increased. Pitting is possible if both nitrate and chloride are present simultaneously.

The presence of hydrogen sulphide narrows the thermodynamic stability range of iron oxide phases (GARRELS and CHRIST, 1965). Different sulphides are formed (GRAUER, 1981) and corrosion involves hydrogen production.

In concrete the corrosion rate could be restricted by the supply of hydrogen sulphide. There are also indications that the sulphidic corrosion products act as a protective layer in alkaline solutions and thus limit corrosion (KAESCHE, 1966).

8. CONCLUSIONS AND RECOMMENDATIONS

The corrosion current densities for steel in cement lie in the range 0.01 to 0.1 $\mu\text{A}/\text{cm}^2$, with no significant difference between aerated and anaerobic systems. This gives a hydrogen evolution rate of between 0.022 to 0.22 $\text{mol}/(\text{m}^2\cdot\text{a})$.

It is not certain on the basis of existing information whether the lower value can be expected in a repository situation over longer time-periods. Since corrosion current densities for unalloyed steel in the range $< 1 \mu\text{A}/\text{cm}^2$ are irrelevant from a technical point of view, few efforts have been made to determine such values with any degree of accuracy.

However, corrosion current densities in the order of 10 nA/cm^2 have been measured independently on more than one occasion and it should therefore be worthwhile attempting to reduce existing uncertainties by carrying out relevant experiments - always assuming that a hydrogen evolution rate of 0.22 $\text{moles}/(\text{m}^2\cdot\text{a})$ is in fact too high for a repository.

It should be stressed that reaching lower values by assuming that the corrosion rate will decrease with time is unjustified. The corroding agent is water and it cannot be assumed at these low corrosion rates that its supply through the cement or through a layer of secondary corrosion products will be rate-determining.

It is also wrong to speculate that corrosion practically ceases if the solution is saturated with the passive oxide. In relation to an $\text{Fe}_{3-x}\text{O}_4$ -phase, the passive film is metastable. This leads to a stationary transformation of the oxide layer to secondary corrosion products. The thickness of the passive film thus reaches a stationary value.

Repeated reference was made in the text to the measurement problems involved with low current densities, particularly in oxygen-"free" solutions. Even though these difficulties are recognised, it should still be possible to obtain reliable information with electrochemical experiments. In addition to the usual methods of gas purification, it is recommended that a large quantity of iron shavings be introduced into the test vessel as an oxygen-getter. The use of hydrogen as a protective gas would contribute to the stabilisation of the free corrosion potentials (Caution: passive metals are pure redox electrodes if $i_p < i_o$). For measurements in the cathodic range, use of a large-surface Ag/AgCl electrode (instead of platinum) as a counter-electrode is recommended in order to rule out any oxygen contamination.

The passive current density is obtained from stationary polarisation experiments with a duration of around one day. A potential jump method could be used to determine the potential of the active/passive transition.

Another basic approach is direct measurement of the hydrogen production rate. There is plenty of experience in this area (SCHENK, 1983) and the sensitivity of the method has been improved so much in recent years (SIMPSON and SCHENK, 1987) that it can be applied to the system of interest here.

Since it has been shown that steels behave in practically the same manner in Portland cement, saturated Ca(OH)_2 -solution and 0.1 M NaOH, it is recommended that experiments with a simple model pore-water be carried out and that the complexity of the medium be increased (e.g. by addition of silicate, Mg^{2+}) only during a second stage.

9. LITERATURE REFERENCES

- C. ANDRADE and J.A. GONZALEZ, 1978: Quantitative measurement of corrosion rate of reinforcing steel embedded in concrete. *Werkstoffe und Korrosion* 29 (1978) 515.
- C. ANDRADE and C.L. PAGE, 1986: Pore solution chemistry in hydrated cement systems containing chloride salts: A study of cation specific effects. *Brit. Corros. J.* 21 (1986) 49.
- H. ARUP, 1983: The mechanism of the protection of steel by concrete. In CRANE, A.P., 1983, pg. 151.
- A. BAEUMEL and H.-J. ENGELL, 1959: Korrosion von Stahl in Beton. *Arch. Eisenhüttenwesen* 20 (1959) 417.
- J. BESSONE et al., 1977: The kinetics of iron dissolution and passivation. *Electrochim. Acta* 22 (1977) 1147.
- A.P. CRANE (Ed.), 1983: Corrosion of reinforcement in concrete construction Ellis Horwood (1983).
- R.M. GARRELS and C.L. Christ, 1965: Solutions, minerals and equilibria, pg. 195, 221. Harper & Row (1965).
- H. GOEHR and E. LANGE, 1957: *Z. Elektrochem.* 61 (1957) 1291.
- J.A. GONZALEZ, S. ALGABA and C. ANDRADE, 1980: Corrosion of reinforcing bars in carbonated concrete. *Brit. Corros. J.* 15 (1980) 135.
- R. GRAUER and E. WIEDMER, 1980: Aussagefähigkeit und Anwendungsgrenzen elektrochemischer Korrosionsprüfmethoden. *Aluminium* 56 (1980) 282.
- R. GRAUER, 1981: Feste Korrosionsprodukte II: Aluminium und Eisen. *Werkstoffe und Korrosion* 32 (1981) 113.
- R. GRAUER, P.J. MORELAND and G. PINI, 1982: A literature review of polarisation resistance constant (B) values for the measurement of corrosion rate. *Nat. Assoc. of Corrosion Engineers Houston, Texas* (1982).
- R. GRAUER and W. STUMM, 1982: Die Koordinationschemie oxidischer Grenzflächen und ihre Auswirkung auf die Auflösungskinetik oxidischer Festphasen in wässrigen Lösungen. *Colloid & Polymer Sci.* 260 (1982) 959.
- R. GRAUER, 1984: Behältermaterialien für die Endlagerung hochradioaktiver Abfälle: Korrosionschemische Aspekte. NTB 84-19 and EIR-Bericht Nr. 523 (1984).

- H. GRUBITSCH, H. MIKLAUTZ and F. HILBERT, 1970: Potentiodynamische und potentiostatische Messungen an gespannten Drahtelektroden in gesättigten Ca(OH)_2 -Lösungen mit verschiedenen Zusätzen. Werkstoffe und Korrosion 21 (1970) 485.
- C.M. HANSSON, 1984: Comments on electrochemical measurements of the rate of corrosion of steel in concrete. Cement and concrete Res. 14 (1984) 574.
- C.M. HANSSON, 1985a: The corrosion rate of mild steel in deaerated synthetic cement pore solution. SKB Teknisk PM Nr. 29, January 1985.
- C.M. HANSSON, 1985b: Hydrogen evolution in anaerobic concrete resulting from corrosion of steel reinforcement. SKB Teknisk PM Nr. 30, January 1985.
- E. HEITZ and W. SCHWENK, 1976: Theoretische Grundlagen zur Ermittlung von Korrosionsstromdichten aus Polarisationswiderständen. Werkstoffe und Korrosion 27 (1976) 241.
- K.E. HEUSLER, K.G. WEIL and F. BONNHoeffER, 1958: Die Bedeutung des Flade-Potentials für die Passivität des Eisens in alkalischer Lösung. Z. phys. Chem. N.F. 15 (1958) 149.
- K.E. HEUSLER, 1985: Ueberlegungen zur Thermodynamik und Kinetik der Reaktion zwischen Eisen und Wasser in Bentonit. NTB 85-22 (1985).
- H. KAESCHE, 1965: Untersuchungen über die Korrosion unlegierter Stähle in Kalziumhydroxydlösung und in feuchtem Beton. Arch. Eisenhüttenwesen 36 (1965) 911.
- H. KAESCHE, 1966: Die Korrosion der Metalle. 1. Aufl., Anhang d. Springer 1966.
- H. KAESCHE, 1979: Die Korrosion der Metalle. 2. Aufl. Springer 1979.
- GARRELS and CHRIST, 1965: Einflussgrößen der Nitratreduktion durch feuerverzinkten und unverzinkten unlegierten Stahl. gwf - Wasser/Abwasser 124 (1983) 378.
- D.D. MACDONALD and B. ROBERTS, 1978: A potentiostatic transient study of the passivation of carbon steel in 1 M NaOH. Electrochim. Acta 23 (1978) 557.
- THE METALS SOCIETY, 1983: Microbiological corrosion. ISBN 0-904357-58-9 (London 1983).
- P.J. MORELAND and J.C. RAWLANDS, 1977: Methode und Instrumentierung bei Polarisationswiderstandsmessungen. Werkstoffe und Korrosion 28 (1977) 249.

- NAGRA, 1985: Projekt Gewähr 1985. Endlager für schwach- und mittelaktive Abfälle. Das System der Sicherheitsbarrieren. Pg. 44, 46. NGB 85-07 (1985).
- C.M. PREECE, H. ARUP and F.O. GRONVOLD, 1981: The influence of hydrogen and carbon dioxide on the corrosion of steel in anaerobic waste storage. SKB/KBS. SFR 81-09 (1981).
- C.M. PREECE, 1982: Corrosion of steel in concrete. Report to SKBF, 28.5.1982. Issued subsequently (with redactional changes) under the same title as KBS TR 82-19.
- C.M. PREECE, F.O. GRONVOLD and T. FROLUND, 1983: The influence of concrete type on the electrochemical behaviour of steel in concrete. In CRANE, 1983, pg. 393.
- R. SCHENK, 1983: Experimente zur korrosionsbedingten Wasserstoffbildung in Endlagern für mittelaktive Abfälle. NTB 83-16 (1983).
- W. SCHWARZ and W. SIMON, 1963: Untersuchungen zum elektrochemischen Verhalten des Eisens in Alkalilösungen. Ber. Bunsenges. 67 (1963) 108.
- J-P. SIMPSON and R. SCHENK, 1987: Hydrogen evolution from corrosion of pure copper. Corrosion Science, 27 (1987)1365.

APPENDIX

COMMENTS ON THE POTENTIAL-pH DIAGRAM OF THE IRON/WATER SYSTEM

The potential-pH diagrams for the iron/water system published in the corrosion literature consider only haematite (α -Fe₂O₃) as a solid phase besides iron and magnetite. This phase is not formed during corrosion reactions in the ambient temperature range. If the corrosion product is produced via the solution, goethite (α -FeOOH) is the stable iron(III) phase (GRAUER, 1981).

Potential-pH diagrams are mostly used to define the stability ranges of passivity. In this respect, they have only a limited application because kinetic effects are not taken into account in an equilibrium diagram.

Haematite is not a component of passive films. As already mentioned in section 2, the passive film of iron consists of a spinel phase with composition Fe_{3-x}O₄ ($x \leq 1/3$). Older concepts which saw the passive oxide as consisting of a metal-sided film of Fe₃O₄ and a solution-sided γ -Fe₂O₃ layer are no longer valid. It would also cause difficulties to assume a phase boundary between two oxides whose lattice constants are 0.85 nm within a layer 4nm in width.

If the γ -Fe₂O₃ is taken into consideration in the potential-pH diagram (Fig. 2), the stability range of the partly oxidised magnetite is widened considerably. The somewhat uncertain value of -718.5 kJ/mol was used for the free enthalpy of formation of the γ -Fe₂O₃ (GOEHR and LANGE, 1957).

The equilibrium line Fe₃O₄/ γ -Fe₂O₃ corresponds more or less to the critical potential for passivity (Flade potential) found in acid solutions:

$$E_p = 580 - 59 \text{ pH (mV)}.$$

At low pH values, passivity is ensured by the low dissolution rate of the γ -Fe₂O₃ (compared with that of Fe₃O₄). In alkaline solutions, the dissolution rate of magnetite is also low and passivation below the Flade potential is therefore possible. The Flade potential is no longer a critical boundary value but it can be shown that, at this potential value, the oxidation of the passive oxide to γ -Fe₂O₃ is complete (HEUSLER et al., 1958; SCHWARZ and SIMON, 1963).

