



TECHNICAL REPORT 91-21

**HYDROGEN EVOLUTION FROM
CORROSION OF IRON AND STEEL IN
LOW/INTERMEDIATE LEVEL WASTE
REPOSITORIES**

P. KREIS

AUGUST 1991

SULZER INNOTECH, Winterthur, Switzerland

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HYDROGEN EVOLUTION FROM CORROSION OF IRON AND STEEL IN LOW/INTERMEDIATE LEVEL WASTE REPOSITORIES

SUMMARY

The production of hydrogen from the corrosion of iron or steel is an important issue in low/intermediate level nuclear waste repositories where large quantities of iron and steel (e.g. as drums and reinforcing steel) accompany the waste.

Most of the iron in low/intermediate level repositories is in a cementitious environment. A review of the literature on the corrosion of iron and steel at high pH values, in particular in cementitious environments, points to hydrogen evolution rates between 22 and 220 mmol(H₂)/(m²*a). There is some indication that the rates might be lower but for normal engineering applications there has been no practical need to demonstrate this, and hence a lower rate cannot be assumed on current evidence.

Near field analysis shows that hydrogen evolved at these rates will not be dissipated by diffusion of dissolved hydrogen. This may have various consequences, for example displacement of water from the near field and, if the gas cannot escape, mechanical disruption of the host formation cannot be ruled out because of equilibrium pressures in excess of 500 bar.

In the present work the hydrogen evolution rates of corroding iron in strongly alkaline and neutral media were measured during a period of at least 6000 hours, using a volumetric method. The sensitivity of this method is sufficiently high (0.1 mmol/(m²*a)) to determine lower hydrogen evolution rates than those previously assumed for iron and steel in cement.

Selected as alkaline media were on the one hand solutions of the free bases NaOH, KOH, Ca(OH)₂, and on the other hand three synthetic cement pore waters. The pH of the solutions ranged from 12.5 to 13.

In general the hydrogen evolution rates found were below the 22 - 220 mmol (H₂)/(m²*a) postulated above. Nevertheless despite similar pH there were distinct differences between the corrosion behaviour of the monovalent (NaOH, KOH) and bivalent Ca(OH)₂ solutions.

While the Ca(OH)₂ solution shows a practically constant hydrogen evolution rate of 1 - 2 mmol/(m²*a) throughout the measuring period, the monovalent solutions reach a maximum around 13 mmol/(m²*a) after about 2000 hours, dropping below 4 mmol/(m²*a) in the course of 6000 h.

Accordingly an aged cement pore water containing only Ca(OH)₂ as free base produces hydrogen at a constant value of 0.5 - 1 mmol/(m²*a). It must be assumed that new cement pore waters containing much free NaOH and KOH behave according to the free bases, although the measuring time of 6000 hours was too short for any exact statements.

Employed as neutral media for the tests were Boettstein water (a synthetic granitic deep water), bidistilled water and a solution of pH 8.5 containing 8000 ppm chloride. All three media revealed a similar picture in principle, qualitatively and quantitatively. After a starting phase of about 1000 hours with hydrogen evolution rates of 80 - 100 mmol/(m²*a), the values begin to fall in the course of 6000 hours to 10 - 20 mmol/(m²*a). The results measured during the starting phase agree in order of magnitude with earlier results (Schenk 1988), but since corrosion measurements covering several thousand hours are rare or non-existent, a comparison with results from earlier published works is difficult.

Keywords: Corrosion, Hydrogen evolution, Cement pore water, anaerobic corrosion

ZUSAMMENFASSUNG

Die Produktion von Wasserstoff durch Korrosion von Eisen und Stahl ist ein wichtiger Aspekt bei Endlagern für schwach- und mittelradioaktive Abfälle, da grosse Mengen an Eisen und Stahl in den Lagern enthalten sind.

Der grösste Teil des Eisens in Endlagern für schwach- und mittelaktive Abfälle befindet sich in einer zementhaltigen Umgebung. Literaturangaben betreffend die Korrosion von Eisen und Stahl bei hohen pH-Werten, d.h. speziell in zementhaltiger Umgebung, deuten auf Wasserstoffentwicklungsraten von 22 - 220 mmol (H₂)/(m²*a) hin. Es gibt Hinweise, dass die Korrosionsraten sogar eher noch tiefer liegen. Bisher war allerdings kein Bedarf vorhanden, dieser Vermutung nachzugehen, da für normale technische Anwendungen die oben erwähnten Korrosionsraten nicht von Bedeutung sind.

Sicherheitsanalysen zeigen hingegen, dass in einem Endlager für schwach- und mittelaktive Abfälle der Wasserstoff, in diesen Raten produziert, nicht genügend schnell durch Diffusion abgebaut wird. Dies kann verschiedene Konsequenzen haben. Einerseits können sich Gastaschen bilden, die das Wasser verdrängen, andererseits, falls die Gasblasen nicht entweichen können, kann bei einem Gleichgewichtsdruck von mehr als 500bar bereits eine mechanische Zerstörung des Felsens resp. eine Beschädigung des Endlagers erfolgen. Aus diesen Gründen ist eine genaue Bestimmung kleiner Korrosionsraten sehr wichtig.

In der vorliegenden Arbeit wurden mit einer volumetrischen Methode die Wasserstoffentwicklungsraten von korrodierendem Eisen in stark alkalischen und neutralen Medien über einen Zeitraum von mindestens 6000h gemessen. Die Empfindlichkeit der Methode ist genügend hoch (0.1 mmol/(m²*a)), um kleinere Wasserstoffentwicklungsraten als jene für Eisen und Stahl in Zement bisher angenommen, zu bestimmen.

Als alkalische Medien wurden einerseits Lösungen der freien Basen NaOH, KOH, Ca(OH)₂, andererseits drei synthetische Zementporenwasser gewählt. Der pH der Lösungen lag zwischen 12.5 - 13.

Generell liegen die gefundenen Wasserstoffentwicklungs-raten unter den oben postulierten 22 - 220 mmol(H₂)/(m²*a). Hingegen ergaben sich trotz ähnlichem pH deutliche Unterschiede im Korrosionsverhalten zwischen den einwertigen Basen (NaOH, KOH) und der zweiwertigen Ca(OH)₂.

So weist die Lösung mit Ca(OH)₂ in der gesamten Messperiode eine praktisch konstante Wasserstoffentwicklungsrate von 1 - 2 mmol/(m²*a) auf. Demgegenüber weisen die einwertigen Basen nach ca. 2000h ein Wasserstoffentwicklungsmaximum von ca. 13 mmol/(m²*a), das aber im Verlauf von 6000h unter 4mmol/(m²*a) sinkt.

Ein gealtertes Zementporenwasser, das nur Ca(OH)₂ als freie Base enthält, produziert dementsprechend eine konstante Wasserstoffmenge von 0.5 - 1 mmol/(m²*a). Bei jungen Zementporenwässern, die viel freie NaOH und KOH enthalten, ist anzunehmen, dass sie sich entsprechend den Lösungen mit freien Basen verhalten. Für eine genaue Aussage erwies sich allerdings die Messzeit von 6000h als zu kurz.

Als neutrale Medien für die Versuche dienten Boettsteinwasser (ein synthetisches granitisches Tiefenwasser), bidestilliertes Wasser und eine Lösung mit pH 8.5, die 8000ppm Chlorid enthält. Grundsätzlich zeigten alle 3 Medien qualitativ und quantitativ ein ähnliches Bild. Nach einer Startphase von ca. 1000h mit Wasserstoffentwicklungs-raten von 80 - 100 mmol/(m²*a) sinken die Werte im Verlauf von 6000 h auf 10 - 20 mmol/(m²*a). Die in der Startphase gemessenen Werte stimmen grössenordnungsmässig mit früher gefundenen Resultaten (Schenk 1988) überein. Da jedoch Korrosionsmessungen im Bereich von mehreren tausend Stunden selten bzw. inexistent sind, ist ein Vergleich mit Resultaten aus früheren, publizierten Arbeiten schwierig.

Stichwörter: Korrosion, Wasserstoffentwicklung, Zementporenwasser, anerobe Korrosion

RESUME

La production d'hydrogène résultant de la corrosion du fer et de l'acier présents en quantités importantes dans un dépôt final pour déchets de faible et moyenne activité doit être prise en compte dans toute analyse de sûreté.

La plus grande partie du fer présent dans un dépôt pour déchets de moyenne activité se trouve dans un environnement contenant du ciment. Selon la littérature, les vitesses de formation d'hydrogène lors de la corrosion du fer et de l'acier à des pH élevés, en particulier en présence de ciment, sont de l'ordre de 22 à 220 mmol H₂/(m²*a). Certains auteurs mentionnent des vitesses de corrosion encore plus basses. Jusqu'à présent toutefois, l'intérêt à étudier des vitesses de corrosion aussi basses était pratiquement nul, vu que dans les applications techniques normales elles ne jouent aucun rôle.

Les analyses de sûreté montrent cependant que la diffusion dans les dépôts pour déchets moyennement et faiblement actifs est insuffisante pour éliminer l'hydrogène produit selon une cinétique comme celle citée ci-dessus. Ceci peut avoir des conséquences diverses. D'un côté, des poches de gaz déplaçant l'eau de la surface métallique peuvent se former, d'un autre côté, des pressions d'équilibre de gaz de l'ordre de 500 bar peuvent conduire à une destruction mécanique du rocher, voir même du dépôt final. Voilà pourquoi la détermination exacte de vitesses de corrosion faibles est, dans le présent cas, très importante.

Dans la présente étude on a utilisé une méthode volumétrique pour déterminer la cinétique d'évolution de l'hydrogène lors de la corrosion du fer en milieu neutre resp. alcalin sur une période de plus de 6000 heures. La sensibilité de la méthode est suffisante pour déterminer des vitesses de corrosion du fer dans le ciment plus faibles que celles généralement admises jusqu'à présent.

Les études ont été réalisées dans des milieux contenant les bases libres NaOH, KOH et Ca(OH)₂ ainsi que dans trois solutions synthétiques simulant l'eau dans les pores du béton. Le pH des solutions était de 12,5 à 13.

Les vitesses de production d'hydrogène déterminées sont inférieures de 22 à 200 mmol H₂/(m²*a) citées ci-dessus. Toutefois, des différences manifestes ont été observées entre les bases monovalentes (NaOH, KOH) et bivalentes (Ca(OH)₂).

Ainsi, la solution Ca(OH)₂ produit pendant toute la durée d'essai de l'hydrogène à une vitesse constante de 1 à 2 mmol/(m²*a), alors que les bases monovalentes montrent un maximum de la production d'hydrogène de l'ordre de 13 mmol/(m²*a) après 2000 heures, tombant à 4 mmol/(m²*a) pour des temps d'exposition de 6000 heures.

Une eau de pore conditionnée ne contenant que du Ca(OH)₂ comme base libre produit en conséquence 0,5 à 1 mmol d'hydrogène par m² et année. Une eau de pore "jeune" contenant encore des bases monovalentes NaOH et KOH en quantités importantes devrait en principe se comporter comme les bases libres correspondantes. Cependant, la durée des essais était insuffisante pour vérifier cette hypothèse.

Pour simuler une solution neutre, on a utilisé de l'eau de Böttstein (eau synthétique en provenance d'un gisement granitique en grande profondeur), de l'eau bidistillée ainsi qu'une solution à pH 8,5 contenant 8000 ppm de chlorures. En principe ces trois solutions conduisent à des résultats similaires: Après une phase de démarrage d'environ 1000 heures, caractérisée par une vitesse d'évolution d'hydrogène de 80 à 100 mmol/(m²*a); cette dernière s'abaisse à 10 à 20 mmol/(m²*a) au cours de 6000 h. L'ordre des valeurs déterminées dans la phase initiale correspond à celui trouvé dans une étude antérieure (Schenk 1988); toutefois comme des essais de corrosion sur des durées de plusieurs milliers d'heures sont rares resp. inexistantes, une comparaison avec des résultats publiés dans la littérature est difficile.

Mots clef: Corrosion, formation d'hydrogène, eau de pore de ciment, corrosion anaerobique

1. INTRODUCTION

Gas generation from the waste itself and other components of the near-field of a repository is an important issue in the design and safety analysis of deep repositories (Zuidema & Höglund 1988; Neretnieks 1985), in particular for the case of low/intermediate level wastes: it has been shown (Zuidema et al. 1989 and references therein) that in this type of waste the corrosion of metals, particularly of iron and steel (e.g. waste drums and rebars), will be the dominant gas generation mechanism even for general corrosion rates between 1 and 0.1 $\mu\text{m/a}$; the gas generation rate in this case will be such that the other near field components (backfill, cavern lining) have to be specially designed to ensure that this gas can leave the near-field before an appreciable gas pressure builds up (Iriya et al. 1990).

In current projects in Switzerland for instance one requirement is that the intrinsic permeability of the cementitious backfill material will be at least 10^{-15} m^2 (considerably higher than that of ordinary concrete). In order to be able to optimize the backfill material composition, and for safety analysis purposes, it is essential to be able to quantify as accurately as possible the hydrogen evolution from corrosion processes in the repository environment as well as understand the mechanisms involved in order to be able to extrapolate short-term experimental results to repository time scales.

2. OBJECTIVES

The purpose of this work was on the one hand to provide a brief overview of the already existing results concerning corrosion in alkaline media, and on the other hand by using suitable methodology to determine as accurately as possible the corrosion rates of iron in a medium corresponding to that in an ultimate repository for wastes of low and medium-level radioactivity.

3. CORROSION MECHANISM OF IRON AND STEEL IN CEMENT PORE WATER AND SURVEY OF AVAILABLE EXPERIMENTAL RESULTS

Iron and steel are in the passive state in alkaline solutions such as cement pore water, even under fully anoxic conditions (Grauer 1988). In the passive condition, iron is covered by a non-porous oxide film only a few nanometers thick. The corrosion rate is thus practically independent of the electrochemical potential and is governed by the dissolution rate of the passive layer in the surrounding medium. The passive layer is an electron conductor which means that cathodic partial reactions (e.g. hydrogen evolution, or oxygen reduction if oxygen is present) can occur with the surface in dynamic equilibrium.

Danish authors assume that steel in cement under anoxic conditions is corroding in the active state, i.e. there is no passive layer (Hansson 1984; Preece 1982). They did however conclude that the corrosion current density was of the same order of magnitude as that for the passive state. This is not in agreement with the German school who maintain that steel in alkaline oxygen-free conditions is in a stable passive state (Grubitsch et al. 1970; Heusler et al. 1958).

On first impressions, this contradiction may appear to be purely academic, as the relevant parameter for the repository, the corrosion rate, is predicted to be the same for both mechanisms. Despite this, the argument does have a practical relevance. If the steel was corroding in the active state, then the corrosion rate would be expected to be dependent upon the material, since the exchange current density for the H_2/H_2O reaction is strongly affected by impurities. If hydrogen evolves on a passive surface then the effect of steel composition would only be slight.

Stable passivity in anoxic conditions in the pH range 12.5 to 13 is supported by numerous observations. The first point to note is that there is no significant difference between pure iron and technical steels. Further evidence for stable passivity is the form of the polarization diagrams (Grubitsch et al. 1970; Heusler et al. 1958; Kaesche 1965) which indicate no change in mechanism; an active-passive transition is only observed at significantly higher pH levels in sodium hydroxide.

There is a comprehensive body of literature on the corrosion of steel in concrete, but interest tends to be focused upon carbonated concrete and the effect of chloride (Crane 1983). For engineering purposes, the corrosion rate in alkaline, chloride-free concrete of the order of a few $\mu\text{m}\cdot\text{a}^{-1}$ is low enough to be neglected, and there is, therefore, little interest in determining it accurately.

Low corrosion rates are most readily measured by electrochemical methods, but these are not straightforward on passive systems. It should be noticed that at a typical current density of $0.1 \mu\text{A}\cdot\text{cm}^{-2}$ (equivalent to a corrosion rate of ca. $1.2 \mu\text{m}\cdot\text{a}^{-1}$) only a very small amount of material reacts in normal experimental time scales. Per hour only 0.14 nm of iron corrode, equivalent to only about half an unit cell! It is clear that a constant passive layer thickness and corrosion rate will only be reached in days rather than hours.

Since corrosion studies in anoxic alkaline solutions are few, values obtained in the presence of oxygen have also been evaluated. This is justifiable for steel in the passive state as the current density on passive steel has been shown to be independent of potential (e.g. Heusler et al. 1958).

Heusler et al. (1958) report a steady state current density for passive iron in a borate buffer at pH 9.3 of $7 \mu\text{A}\cdot\text{cm}^{-2}$, and the same value for 0.1N NaOH at 50°C. Kaesche (1965) and Grubisch et al. (1970) produced stationary polarization curves for pure iron and steel in anoxic saturated $\text{Ca}(\text{OH})_2$, using holding times of 5 and 16.7 h respectively. The corrosion current densities were found to be $< 0.2 \mu\text{A}\cdot\text{cm}^{-2}$ and $0.05\text{-}0.1 \mu\text{A}\cdot\text{cm}^{-2}$. Active-passive transitions were not observed. Iron would appear to be in the stable passive state at the corrosion potential. No difference was found between the behaviour of pure iron and technical steels. A Spanish group used the polarization resistance technique to determine the corrosion rate for steel in cement (Gonzales et al. 1980). Oxygen was present. The measured values for non-carbonated cement without additives were in the range of $0.05\text{-}0.1 \mu\text{A}\cdot\text{cm}^{-2}$. Hansson (1981) also used the polarization resistance technique and obtained a current density after 10 months of $0.1 - 0.3 \mu\text{A}\cdot\text{cm}^{-2}$ for specimen under anoxic conditions. Extrapolation of stationary polarization

curves yielded a current density of $0.1 \mu\text{A}\cdot\text{cm}^{-2}$. Preece et al. (1981) reported a corrosion current density of about $0.01 \mu\text{A}\cdot\text{cm}^{-2}$ using the stationary polarization technique on specimen embedded in cement under anoxic conditions.

The measured corrosion current densities for steel in cement are in the range $0.01\text{-}0.1 \mu\text{A}\cdot\text{cm}^2$, whereby no significant differences were found between the values in aerated and oxygen free environments. This is equivalent to a hydrogen evolution rate of $22 - 220 \text{ mmol}/(\text{m}^2\cdot\text{a})$. However, from the evidence available it is not safe to assume that the lower rate is correct for iron and steel in repositories even in the longterm. Nevertheless, as corrosion current densities around $10 \mu\text{A}\cdot\text{cm}^{-2}$ were measured independently on several occasions, further effort to reduce this uncertainty appears worthwhile. Electrochemical methods are not well suited for the longterm measurements required, whereas direct measurement of the hydrogen evolved becomes more accurate with increasing sensitivity as the observation time increases.

4. EXPERIMENTAL

4.1 Measuring technique and apparatus

The corrosion rates of iron were determined by direct measurement of the evolving hydrogen. Whereas in earlier experiments a gas chromatography method had been used (Schenk 1988), in this work a volumetric method was employed. This method was described for the first time by Schikorr in 1929.

Here the evolving hydrogen is determined in a closed glass cell containing an iron specimen and a corresponding corrosion medium, by measuring the build-up of gas pressure. This method allows very long measuring times, because even the tiniest escape of hydrogen is virtually ruled out.

The glass cell used is shown in Fig. 1. It consists of the actual corrosion chamber on the right and a U-tube serving to measure the pressure rise.

The volume of the left hand chamber (5) is about 27 ml and that of the right hand corrosion chamber (1) is 85 - 90 ml. The U-tube has an internal diameter of 3mm.

The volumes are determined for each individual cell. 50 - 60 ml of test solution and several metres in total in cut lengths of wire to give a surface area of about 0.08 m^2 are placed in the right hand chamber (1). Mercury is then introduced into the U-bend section (3) and some water above the mercury on the left hand side. The cells are evacuated for 2 hours to degas the solution before the two arms are sealed under vacuum. The maximum usable mercury column is about 190 mm. In the initial evacuated state the pressure on both sides of the mercury is equal to the vapour pressure of water. Any hydrogen evolved will be detected by a rise in the pressure on the right hand side. The cells are held at room temperature which over the long measurement period was $21 \pm 3 \text{ }^\circ\text{C}$.

The presence of water on both sides of the mercury column provides automatic correction for variation in vapour pressure with temperature. Corrections were made for the thermal expansion of the gas in the corrosion chamber and the increase in volume in this chamber due to depression of the mercury column. No corrections were made for thermal expansion of the solution, mercury or glass, changes in the gas solubility due to temperature and vapour pressure differences between water and the test solutions. These errors are below 1% and were thus neglected.

The mercury column could be read to $\pm 0.5 \text{ mm}$ equivalent to $\pm 0.007 \text{ mmol}(\text{H}_2) \cdot \text{m}^{-2}$ for 0.08 m^2 iron surface in the cell.

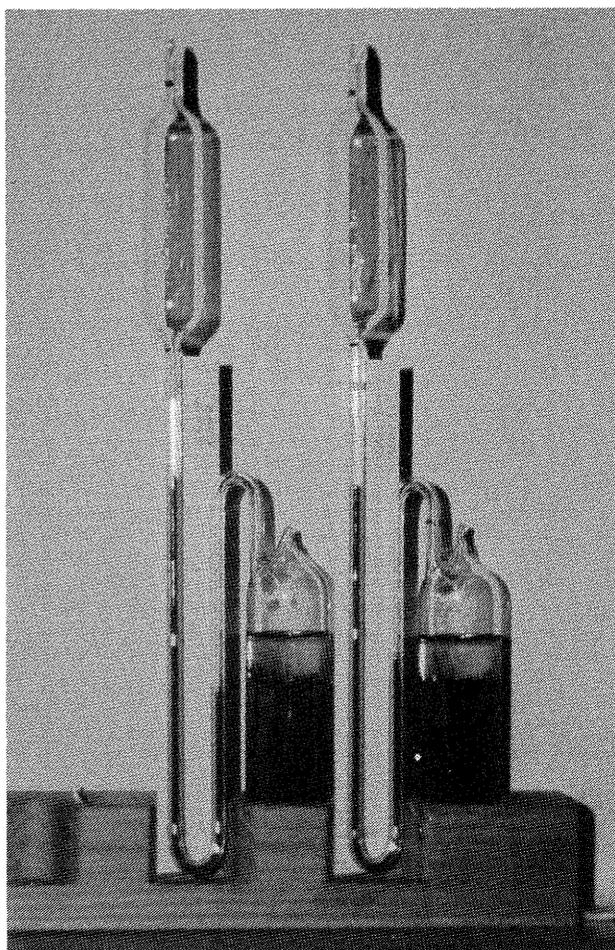
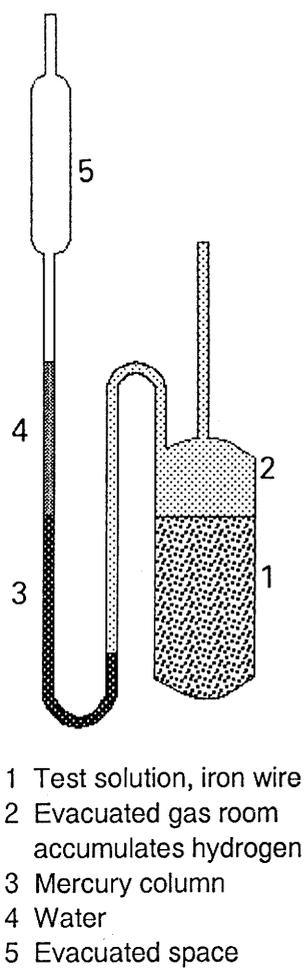


Fig. 1: Corrosion test cell

4.2 Experimental program

4.2.1 Media

The test media employed are indicated in Tables 1, 2 and 3.

Table 1: Test media

	Series 1	Series 2
A) Boettstein water (Table 2)	X	X*
B) 8000 ppm Cl pH 8.5 (Table 2)	X	X*
C) Bidistilled water	X	
D) 0.1 N NaOH pH 13	X	
E) Ca(OH) ₂ saturated pH 12.8		X
F) NaOH pH 12.8		X
G) KOH pH 12.8		X
H) Cement pore water Ia pH 13.2		X
I) Cement pore water Ib pH 12.9	X	X
J) Cement pore water II pH 12.5	X	X

* with these media, two different types of iron were tested (cf. 4.2.2)

Table 2: Chemical composition of Boettstein water (a) and 8000 ppm chloride solution, pH 8.5 (b) (in µg/g).

	Na	K	Mg	Ca	Cl	F	SO ₄
(a) Boett.	4800	54	3	1100	8100	3.8	1820
(b) Chloride	5188	--	--	--	8000	--	--

 The pH of this solution was adjusted to 8.5 by a buffer system in contact with air (log pCO₂ = - 3.5)
 0.1% Na₂CO₃ : 0.1% NaHCO₃ 1 : 100

Table 3: Chemical composition of the synthetic cement pore waters.

mmol/l	KOH	NaOH	Na ₂ SO ₄	CaSO ₄	Ca(OH) ₂	CaCO ₃	Mg(OH) ₂
Pore water Ia	180	114	3	-	sat.	sat.	sat.
Pore water Ib	60	34	3	-	sat.	sat.	sat.
Pore water II	3	-	-	3	sat.	sat.	sat.

The three synthetic cement pore waters correspond to different aging stages with the free alkalinity reduced by the diluting effect of groundwater flow. The chemical composition of the pore waters are based on model calculations carried out by Berner (1987).

4.2.2 Specimen material

The majority of the tests were performed on lengths of pure iron wire of 0.57 mm in diameter, with a carbon content of 0.91% and at least 99% iron.

To enable the influence of the purity of the specimen material on the hydrogen evolution to be assessed, in test series 2 (Boettstein water and solution with 8000 ppm Cl^-) a wire grade with 0.36% carbon was tested additionally (marked * in Table 1). This wire had a diameter of 1 mm.

The wires were cut into lengths of 80 mm and degreased with Chlorothene and alcohol, pickled in 10% HCl and rinsed thoroughly in water and alcohol, before being dried under vacuum and put into the cell.

4.2.3 Tests performed

The tests for measuring the hydrogen production by corroding iron under anaerobic conditions and alkaline pH were divided into two series (cf. Table 1). Each test consisted of three individual measurements.

In a **first series** measurements were performed in 0.1 N sodium hydroxide solution at pH 13 and two synthetic cement pore waters with pH between 12.5 and 13 (Table 1, solutions D, I and J). It was to be investigated whether the corrosion depends solely on the pH, or whether the cations and anions present in the cement pore waters (K^+ , Ca^+ , SO_4^{2+}) exercise a decisive influence on the corrosion behaviour of the iron.

Besides these alkaline media, neutral media were tested as well, i.e.:

- Boettstein water (synthetic depth water) (A)
- a solution with 8000 mg Cl^- /l buffered with carbonate (B)
- bidistilled water (C)

These media provided a comparison between the results obtained by this method and those arrived at by the gas chromatography measurements performed earlier (Schenk 1988).

Cells with high corrosion rates (neutral media and sodium hydroxide solution) reached their maximum hydrogen capacity before the planned minimum measuring time of 6000 hours. In this **first measuring series** the measuring time was extended by carefully shaking the glasses before the hydrogen came through the mercury column, in order to transfer the gas into the other vessel under control. The measurements from these cells were then corrected for the gas compression on the left-hand side.

Because the different corrosion behaviour of the cement pore water II (J) and the 0.1 N NaOH (D) could not be explained in the first test series, the influence of the cations Na, K and Ca on the corrosion behaviour was investigated in a **second series** with alkaline media at the same pH. The measurements with the synthetic cement pore waters were repeated and supplemented by another strongly alkaline medium.

In this phase the tests with neutral media were confined to the Boettstein water (A) and the 8000 ppm Cl/l solution at pH 8.5 (B). The influence of the test material on the hydrogen evolution was to be examined in this series, i.e. iron specimens with two different carbon contents were tested.

In this **second test series** the measuring time of the corrosion cell with high hydrogen evolution rates was extended by an other procedure: after reaching its maximum hydrogen pressure the capillary of the reaction chamber was broken under vacuum and the cell evacuated anew. Through this procedure the hydrogen pressure alternated several times between 0 and 0.25 bar during the measuring phase. In this way an attempt was made to estimate the influence of the hydrogen partial pressure on the reaction.

Paralleling these two long-time series, a few **blank cells** were employed in a **third series** aimed at establishing the sensitivity of the methodology. In particular it was to be ascertained that no parasitic reactions in the test cells were falsifying the measured hydrogen formation.

No iron specimens were put into the test cell for these blank tests, but the hydrogen was filled straight into chamber (2) in Fig. 1 in gaseous form to simulate a cell at its maximum hydrogen capacity. The hydrogen partial pressure was adjusted to about 180 mm Hg.

In a first phase only three kinds of blank cells were tested:

1. filled with bidistilled water
2. filled with hydrogen on the corrosion side (chamber 2) but without water (neither in chamber 2 nor rising tube 4)
3. analogous to cell 2 but with non-degassed water on both sides of the mercury column.

The first kind of blank cell showed no change in the mercury column between 100 and 13 000 hours. The second one also gave a constant pressure reading right from the start. The third kind on the other hand revealed a constant loss of H_2 in the corrosion part of the cell, necessitating a further investigation with blank cells.

Possible reasons of the loss established were:

- a) Hydrogen dissolves partially in water or mercury
- b) Hydrogen diffuses through (moist) mercury
- c) Hydrogen is adsorbed on the cell walls
- d) Hydrogen reacts with contaminants present in the mercury (such as oxides)
- e) Hydrogen reacts with the residual dissolved oxygen present in the water.

To provide clarity on these points the following tests were made:

4. As with cell 3, but using mercury of high purity. This was to reveal any reaction of the hydrogen with impurities in the mercury.
5. As cell 3, but with large amount of mercury in the corrosion chamber (1). This was to reveal any influence of the surface mercury/water like reaction on the surface or diffusion hydrogen into mercury.

6. As cell 3, but with some air left in the hydrogen atmosphere. This was to reveal any reaction of oxygen with hydrogen or mercury.
7. As cell 3, but without water in the left-hand chamber (rising tube 4). This was to reveal any diffusion of hydrogen through moist mercury.

In all blank tests where water was present, attention was given to complete degassing of the bidistilled water (except test 6).

4.3 Calculations

The calculation of the hydrogen generated is performed with the help of the ideal gas law. As mentioned above, the values were corrected for the thermal expansion and volume increase of the gas. Regardless of the pressure the solubility of the hydrogen (Perry 1954) in the test solution amounted to 5% of the quantity produced, and was not taken into account in the calculation.

4.3.1 Calculating the hydrogen production

In a first step the height of the mercury column (+ water column) must be converted into the pressure units (pascals):

$$(P_{\text{mmHg}} * 101320) / 760 = P_{\text{Pascal}} \quad (1)$$

In a second step the volume increase of the gas chamber due to the falling mercury column is calculated:

$$V = V_0 + [(mmHg/2) * (d_K/2)^2 * \pi] \quad (2)$$

V	= volume	[m ³]
V ₀	= initial volume	[m ³]
mmHg	= mercury column	[m]
d _K	= capillary diameter	[m]

After this the mole number of the hydrogen produced is obtained directly:

$$(p \cdot V) / R \cdot T = n \quad (3)$$

R= ideal gas constant
 p= pressure [pascal]
 V= gas volume [m³]
 T= temperature [Kelvin]
 n= mole number [mol]

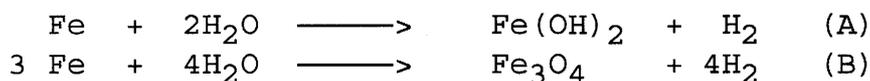
To allow a comparison of the results, the mole number is divided by the surface of the iron specimen, giving the hydrogen production in mol/m².

$$n/A = \text{mol/m}^2 \quad (4)$$

A = surface area of iron specimen [m²]

4.3.2 Calculating the corrosion rates in nanometres

From formula (4) the mole number of the hydrogen generation per square metre is already known. Assuming the iron is oxidized only to Fe²⁺ (in accordance with formula A)



this corresponds at the same time to the mole number of the corroded iron per m². A simple conversion then gives the corrosion rate in nm.

$$(n/A) * (MM/d_{\text{Fe}}) * 10^9 = \text{nm} \quad (5)$$

n = mole number (Fe = H₂)
 MM = mole mass Fe (= 0.05585kg)
 A = surface Fe [m²]
 d = density Fe [7855kg/m³]

General conversion factors:

formula A: 1mmol H₂/m² = 7.1 nm Fe corrosion *)
 formula B: 1mmol H₂/m² = 5.3 nm Fe corrosion
 1mmol H₂/m² = 22.4 ml H₂/m² (1bar; 273K)

*) used in this paper as conversion factor

4.3.3 Calculating the hydrogen production after equalization of the mercury column

As mentioned above, some of the test cells reached the maximum measurable pressure before the end of the planned test time. On these cells, in the **first test series** part of the gas was transferred under control into the top left-hand vessel (Fig. 2). To enable the pressure behaviour in these cells to be determined, the readings must be corrected with the following calculations.

The pressure in the corrosion chamber (p_A) is given then by the height of the mercury column and the gas pressure on the (p_B) in these cases.

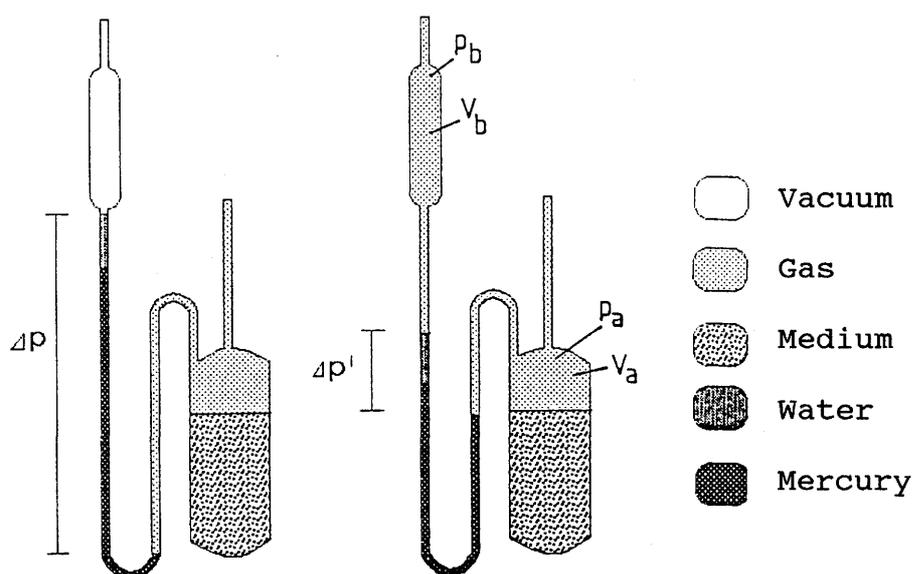


Fig. 2

We have:

$$p_A = p_B + p'$$

$$\text{i.e.} \quad \frac{n_A \cdot R \cdot T}{V_A} = \frac{n_B \cdot R \cdot T}{V_B} + p' \quad (6)$$

The sum $n_A + n_B = n_{\text{Tot}}$ is known. Likewise p' can be determined (and converted into pascals)

$$\frac{n_A \cdot R \cdot T}{V_A} = \frac{(n_{\text{Tot}} - n_A) \cdot R \cdot T}{V_B} + p' \quad (7)$$

$$n_A = \frac{n_{Tot} * V_A + (p' * V_A * V_B) / R * T}{(V_A + V_B)} \quad (8)$$

$$n_B = n_{Tot} - n_A \quad (9)$$

From n_A and n_B the gas pressure (p_B) may be calculated:

$$p_B = n_B * R * T / V_B \quad (10)$$

If these values are added in formula (1), the hydrogen evolution can be calculated as before with the formulas 2 and 3.

5. EXPERIMENTAL RESULTS

The results of the hydrogen evolution experiments are presented as both the total hydrogen evolved and the hydrogen evolution rate. The evolution rate was derived from the total hydrogen curve. The corrosion values are provided as a guide and were calculated from the hydrogen evolution values. All curves plotted are mean values from three individual determinations.

The **reproduceability** between the separate parallel tests is shown in Fig. 3, 4, 5. In these figures, curves of each individual parallel tests are plotted.

As one can see the main differences are varying corrosion at the beginning of the tests (Fig. 4) and different incubation time (Fig. 5). It is assumed that this behaviour is caused by slight variation of the remaining oxygen content in the test solution and by the preparation of the test material. But as the measuring time increases these starting effects cease and the values for the hydrogen evolution rates reach an average reproduceability of $\pm 10\%$.

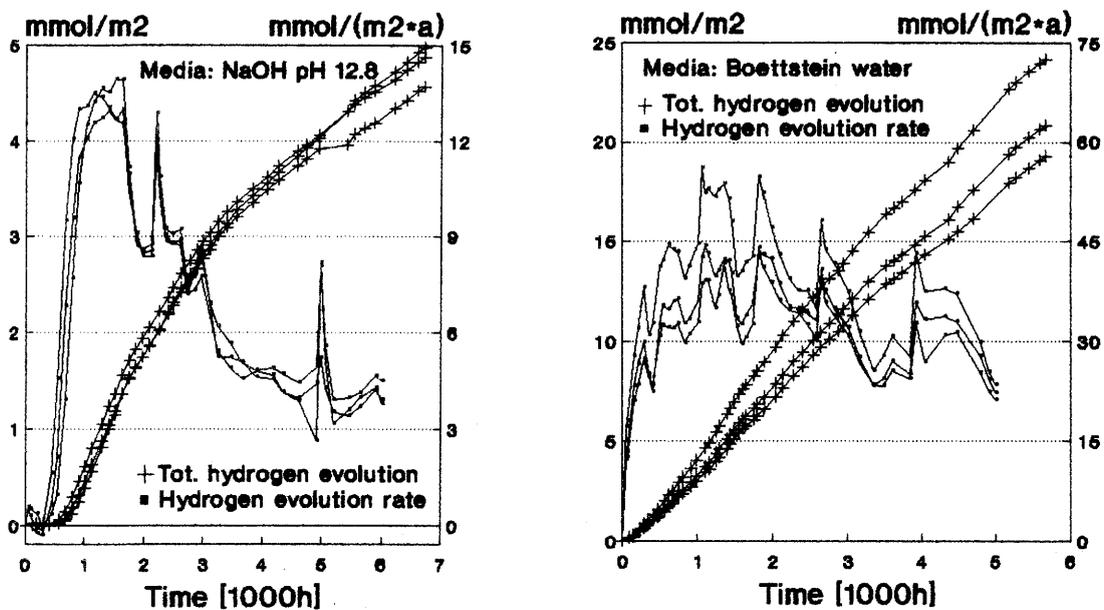


Fig. 3: Examples of total hydrogen evolution and hydrogen evolution rates with good reproducibility between individual determination.

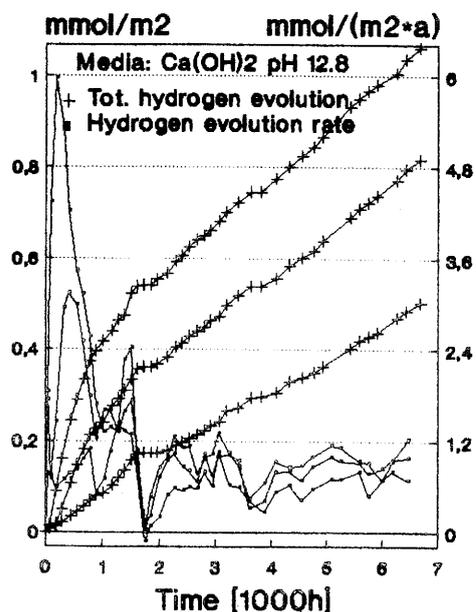


Fig. 4:

Total hydrogen evolution and evolution rate of $\text{Ca}(\text{OH})_2$. Different behaviour in starting phase of test.

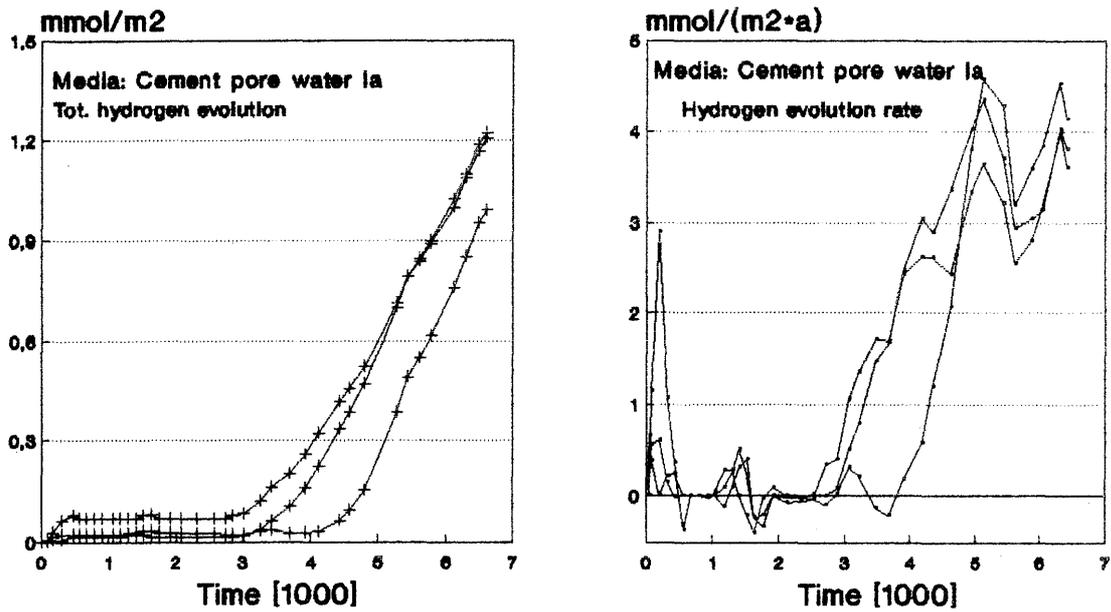


Fig. 5: Total hydrogen evolution and evolution rate of cement pore water Ia. Different incubation time between individual cells.

5.1 Tests with blank cells

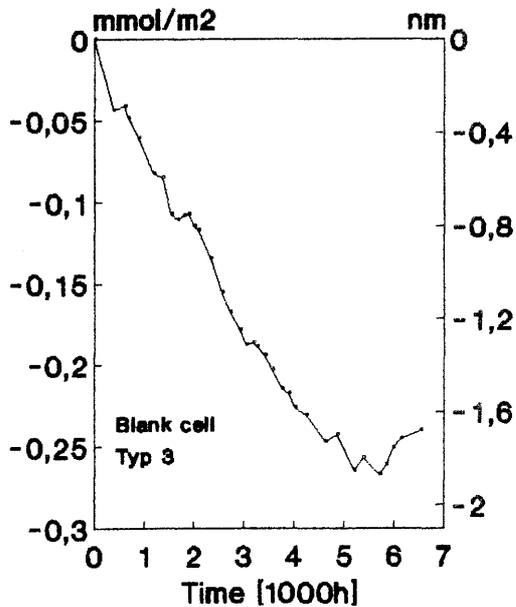


Fig. 6 depicts the hydrogen evolution of a blank cell (type 3) containing bidistilled water and hydrogen in its corrosion chamber. Within 1000 hours the offtake is 4 μmol , equivalent to a hydrogen consumption of 0.05 mmol/m² or a negative hydrogen evolution rate of 0.43 mmol/(m²*a) referred to the standard surface of 0.08 m². After 5000 hours the loss becomes stabilized.

Fig. 6: "Hydrogen evolution" in a blank cell with non-degassed water (type 3).

Fig. 7 depicts the results of blank cell types 4 to 7, also containing water and hydrogen in their corrosion chambers. Special interest attaches to the combinations

- 4) hydrogen/high-purity mercury reaction
- 5) hydrogen/mercury reaction
- 6) hydrogen/oxygen reaction
- 7) diffusion of hydrogen through moist Hg

As will be shown, only the cell still containing oxygen residues reveals a constant and significant loss of oxygen. All other cells still show a constant mercury column after some days.

On the strength of these results it may be concluded that any disturbances, such as diffusion of hydrogen through mercury, adsorption of hydrogen on cell walls, dissolution of hydrogen in water or mercury, affect the measuring accuracy of the method only to a subordinate degree after a starting phase lasting a few days. On the other hand, great attention must be given to complete degassing. Apparently blank cell 3 still contained 5 ppm O_2 , which was completely transformed only after 5000 hours.

This effect may have minor importance at cells which contain iron specimen. The oxygen present there is consumed rapidly by the corrosion of iron. But there is the possibility that the incubation time is influenced by oxygen.

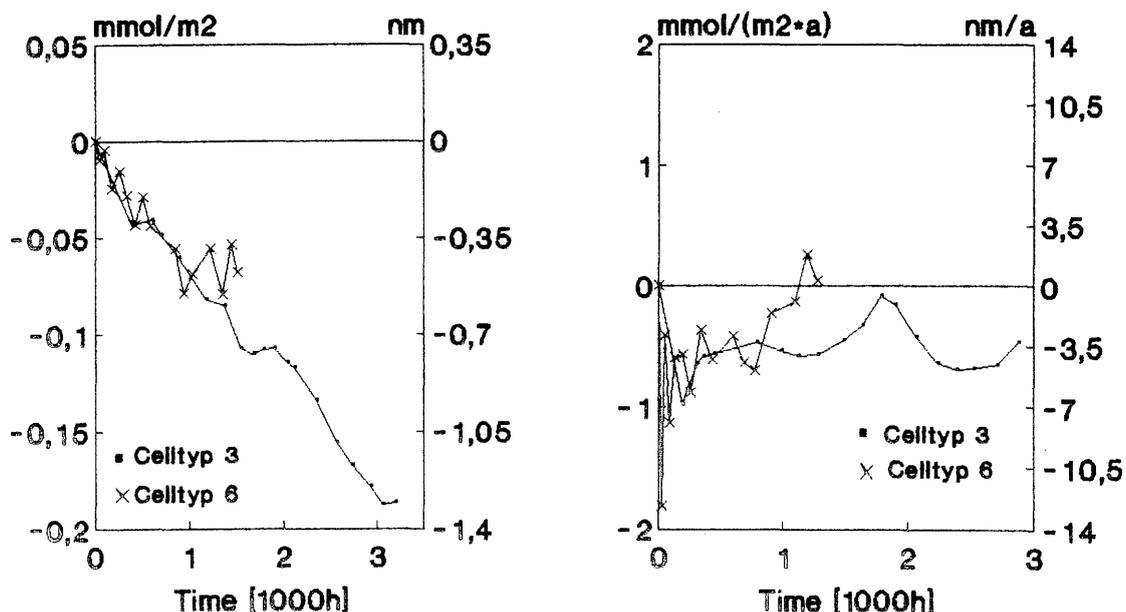


Fig. 7a: "Hydrogen evolution" of different blank cells containing small amounts of oxygen.

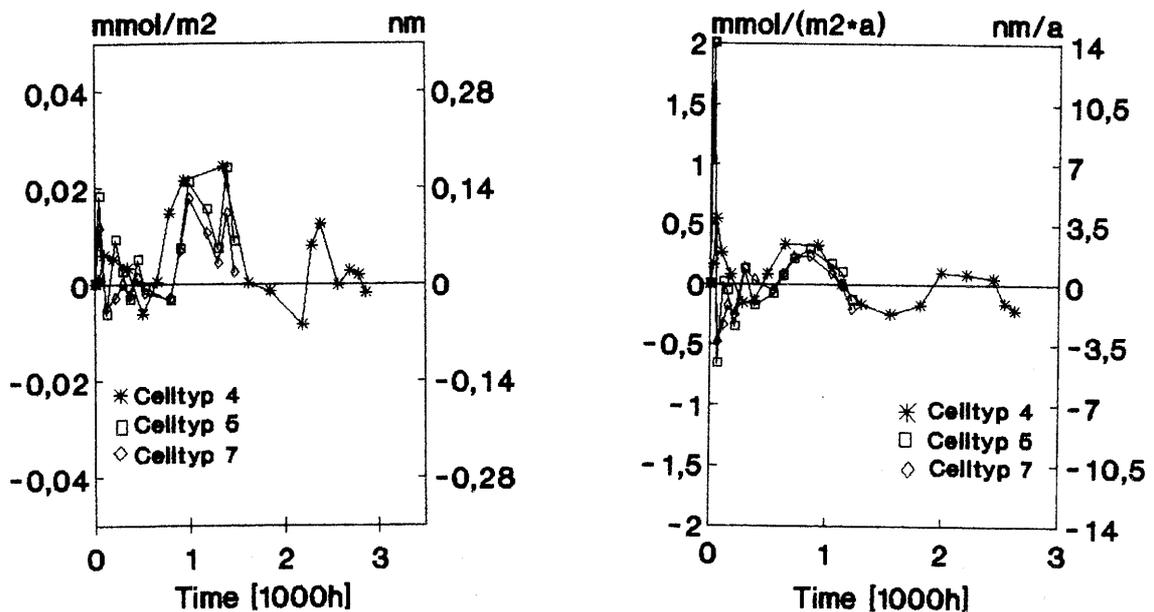


Fig. 7b: "Hydrogen evolution " of blank cells without traces of oxygen

From the evaluation of all blank tests it can thus be assumed that under the boundary conditions adopted here the **sensitivity** of the method is about $0.4 \text{ mmol}/(\text{m}^2 \cdot \text{a})$ when the values are derived from short time hydrogen evolution measurements (cf. Fig 7b). At longer test periods (cf. Fig. 8) and larger derivation interval, the sensitivity increases to about $0.1 \text{ mmol}/(\text{m}^2 \cdot \text{a})$.

5.2 Tests with alkaline media

As expected the corrosion rates of iron in alkaline media are very low and well below the $22 - 220 \text{ mmol}/(\text{m}^2 \cdot \text{a})$ postulated in the literature. All the same, with similar pH of the solutions but different chemical composition, very different corrosion behaviours of the media result.

In Fig. 8 the results of the first series of long-time tests in alkaline media are depicted. With 0.1N NaOH pH 13, in the first 3000 hours a hydrogen evolution rate of $10 \text{ mmol}/(\text{m}^2 \cdot \text{a})$ results, which subsequently declines steeply, however. On the other hand the iron in cement pore water II at pH 12.5 corrodes during 12000 hours at a virtually constant hydrogen evolution rate of $0.9 \text{ mmol}/(\text{m}^2 \cdot \text{a})$. Throughout the entire duration of the test (of series 1 and 2), cement pore water Ib with a pH of 12.9

generated no measurable quantity of hydrogen. With all media, the single iron wires did not stick together, so the specimen surface was constant during the whole period.

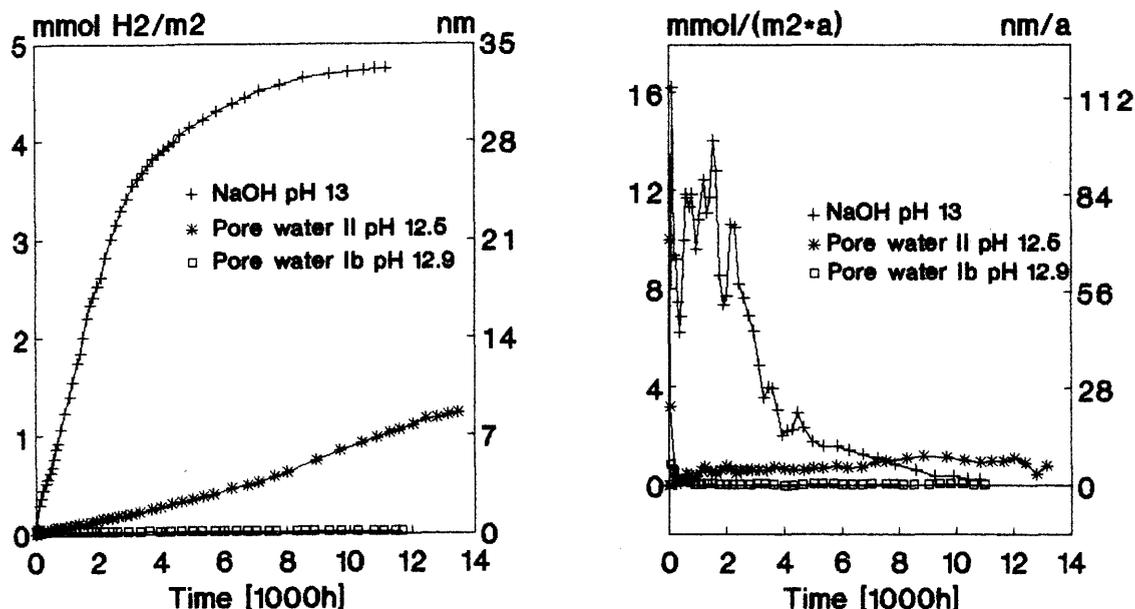


Fig. 8: Results of the first test series with alkaline media.

Fig. 9 shows the effects of the three main components of the cement pore water NaOH, KOH and $\text{Ca}(\text{OH})_2$ at pH 12.8 established in the second measuring series.

The results of the monovalent bases NaOH and KOH agree very closely with the sodium hydroxide solution of the first test. On the other hand the bivalent base $\text{Ca}(\text{OH})_2$ gives a distinctly lower, constant evolution rate similar to cement water II.

The results of the three synthetic cement pore waters from series 2 are depicted in Fig. 10. The behaviour of pore waters Ib and II is analogous to that in test series 1.

However the pore water Ia used as test medium in test series 2, equivalent to a new cement pore water, gives a qualitatively similar picture to the media based on NaOH (D) and KOH (G) in Fig. 9. After a starting phase during which no gas generation was measured, the corrosion rises suddenly above that of cement pore water II.

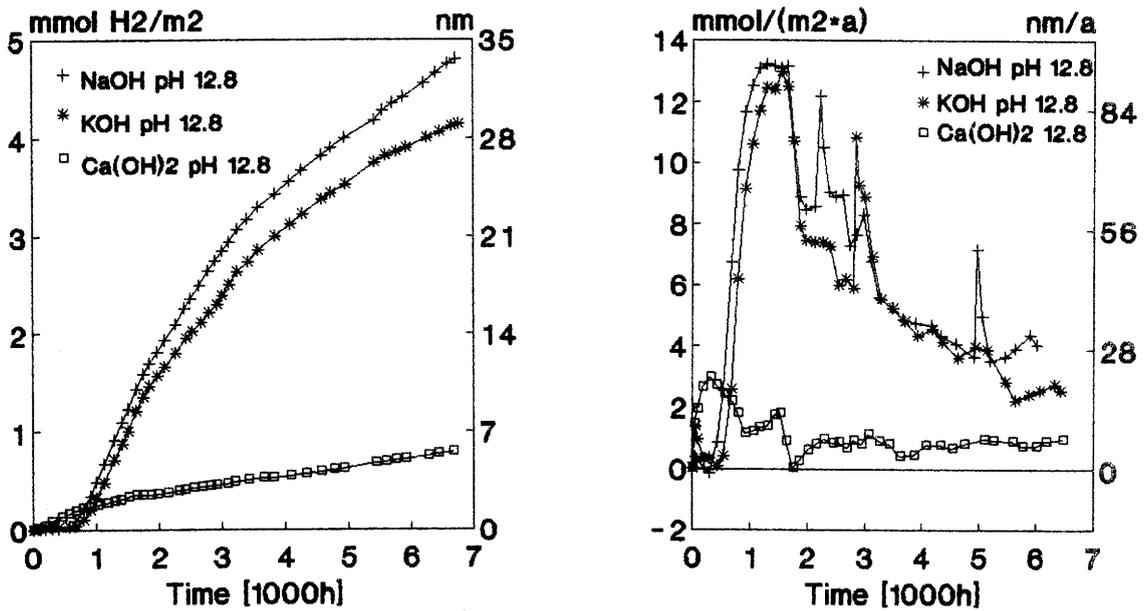


Fig. 9: Comparison of the three main components of cement pore water: NaOH, KOH, Ca(OH)₂.

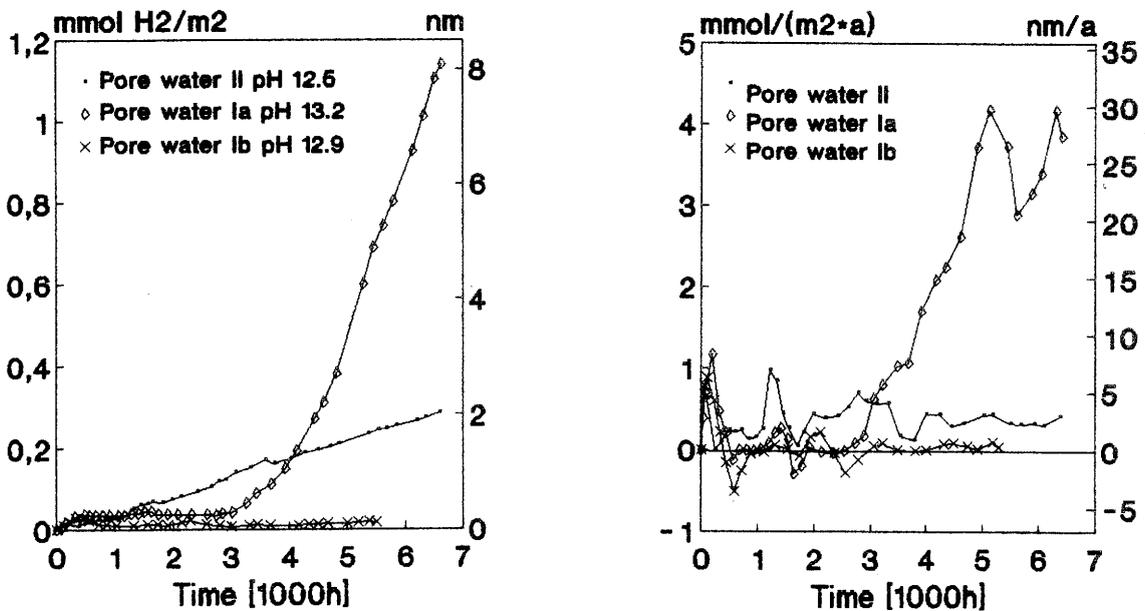


Fig. 10: Comparison of different types of cement pore water.

On the strength of the results obtained, it can be assumed that the corrosion rate of iron in alkaline media depends mainly on the components NaOH, KOH and Ca(OH)₂.

Even at higher pH values the monovalent bases NaOH and KOH cause a relatively large evolution of hydrogen after a certain incubation period, which however falls off again after a certain time, as may be seen in Figs. 8 and 9. On the other hand the $\text{Ca}(\text{OH})_2$ solution has no incubation period, with a practically constant but low corrosion rate over 6000 hours. Apparently the $\text{Ca}(\text{OH})_2$ is involved in the formation of a passive layer which reduces the evolution of hydrogen, whereas this does not happen with the monovalent bases.

The behaviour of the synthetic cement pore waters follows a basic pattern: With cement pore water II, which as free base contains above all $\text{Ca}(\text{OH})_2$, a low and constant production of hydrogen is measured throughout the measuring period. The analogy between the monovalent bases and cement pore waters Ia and Ib is less clear. Nevertheless one might imagine that both media behave accordingly to the pattern of NaOH, though the inactive starting phase is several times longer. Under this assumption therefore, an onset of hydrogen evolution corresponding to that of NaOH should be expected with medium Ib as well as Ia.

5.3 Tests with neutral media

The corrosion rates arrived at experimentally in the first long-time series with the media Boettstein water, 8000 ppm Cl^- at pH 8.5 and bidistilled water, are depicted in Fig. 8.

The qualitative behaviour of all three media is roughly similar. In a starting phase lasting about 1000 hours, corrosion rates of 70 - 100 $\text{mmol}/(\text{m}^2 \cdot \text{a})$ occur. After this the hydrogen evolution drops continually, reaching a constant minimum of about 5 - 9 $\text{mmol}/(\text{m}^2 \cdot \text{a})$ after about 4000 hours.

In previous gas chromatography measurements carried out on iron specimen containing 0.1%C, a corrosion rate of 180 $\text{mmol}/(\text{m}^2 \cdot \text{a})$ was found for Boettstein water at 25 °C (Schenk 1988). Allowing for the fact that the measuring time was less than 500 hours and the specimens were prepared differently (polished), the values established here for the starting phase agree closely with the gas chromatography measurements.

At the end of the test, the specimen was covered by a grey-blue layer, but the single iron wires not sticking together. So the specimen surface was constant throughout the test period.

However the pH values of the different neutral media increased during the measuring period. The finally obtained values were:

Solution 8000ppm Cl ⁻ , pH 8.5	:	pH 10.1
Boettstein water	:	pH 8.7
Bidistilled water	:	pH 8.6

So the decrease of the hydrogen evolution rate can not only be explained by a build up of a covering layer, but also by a slightly increasing pH value.

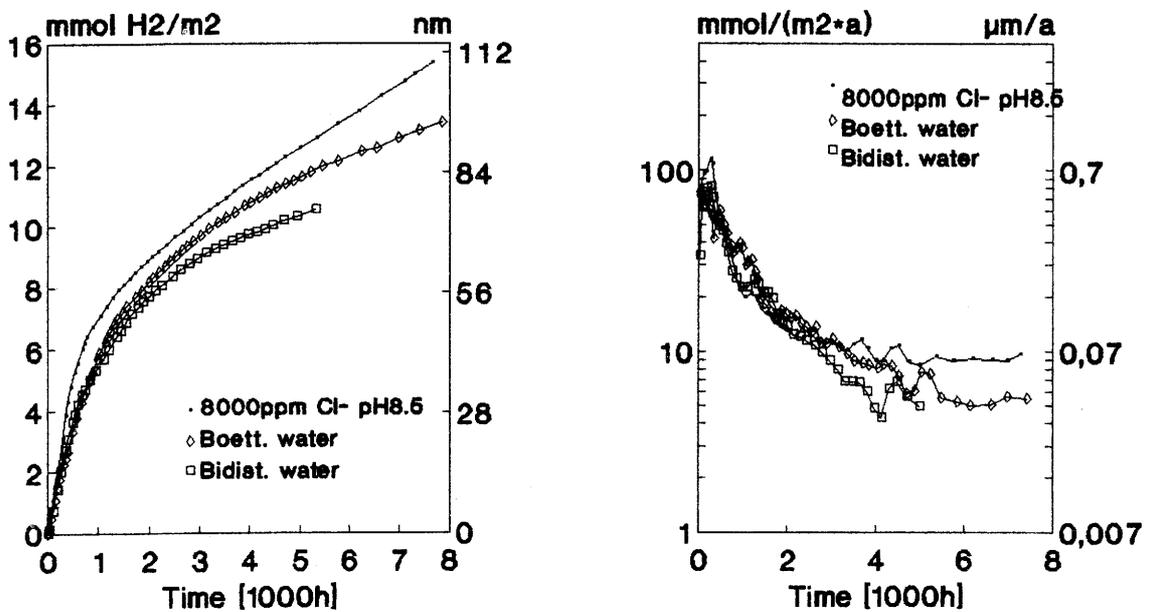


Fig. 11: Comparison of corrosion rates in three neutral media.

The influence of the purity of the iron specimens is depicted in Fig. 12.

It will be seen that both in Boettstein water and in the NaCl solution the specimen with higher carbon content (0.91 %) corrodes faster in the starting phase. On the other hand after 5000 hours these specimens tend to generate less

hydrogen than the purer iron specimen. Apparently, owing to the higher corrosion rate on the specimens with higher carbon content a more compact covering layer forms, inhibiting the hydrogen evolution more after a few thousand hours.

Nevertheless the generally higher values for the hydrogen evolution (about factor 2, cf. Figs.11 and 13) compared with series 1 are conspicuous. As mentioned before, in series 2 the measuring time of a corrosion cell was extended by exhausting the hydrogen generated upon reaching the maximum capacity. In this way the hydrogen pressure alternated several times between 0 and 0.25 bar. The disturbances possibly triggered by this are recognizable in Fig. 12 as irregularities in the curves for the hydrogen evolution rates.

Accordingly there are two possible explanations for the generally higher corrosion rates in series 2:

- the system is disturbed briefly whilst exhausting the hydrogen, possibly damaging slightly the covering layer of the iron surface,
- the hydrogen generated inhibits the reaction already at relatively modest pressures of 0.25 bar.

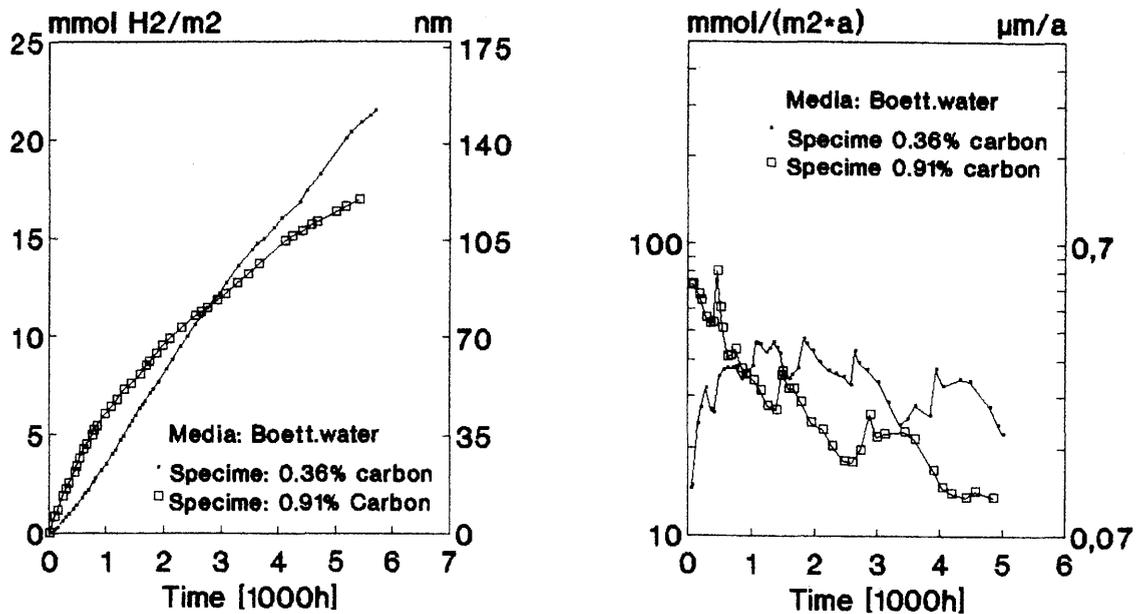


Fig. 12a: Corrosion behaviour of iron specimens with different carbon contents in Boettstein water.

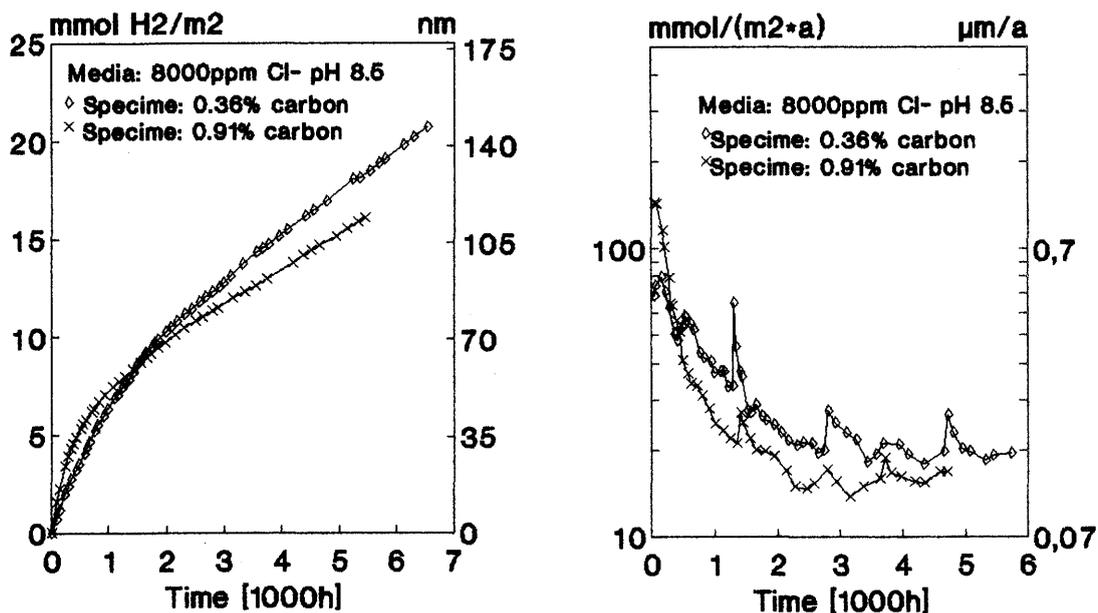


Fig.12b: Corrosion behaviour of iron specimen with different carbon content in NaCl-solution pH 8.5

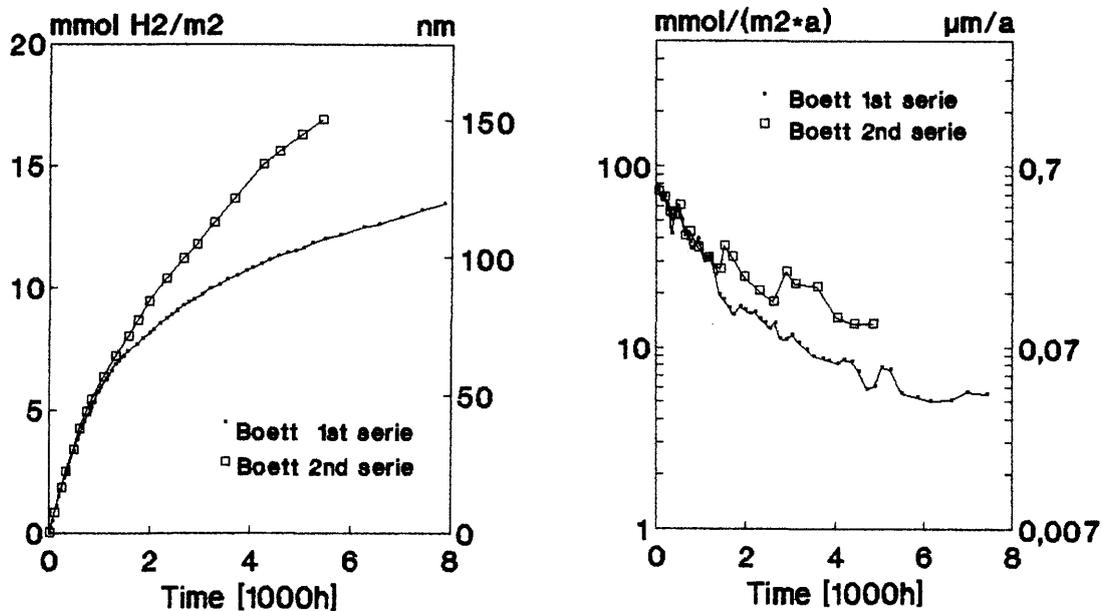


Fig. 13a: Comparison between 1st and 2nd measuring series with Boettstein water

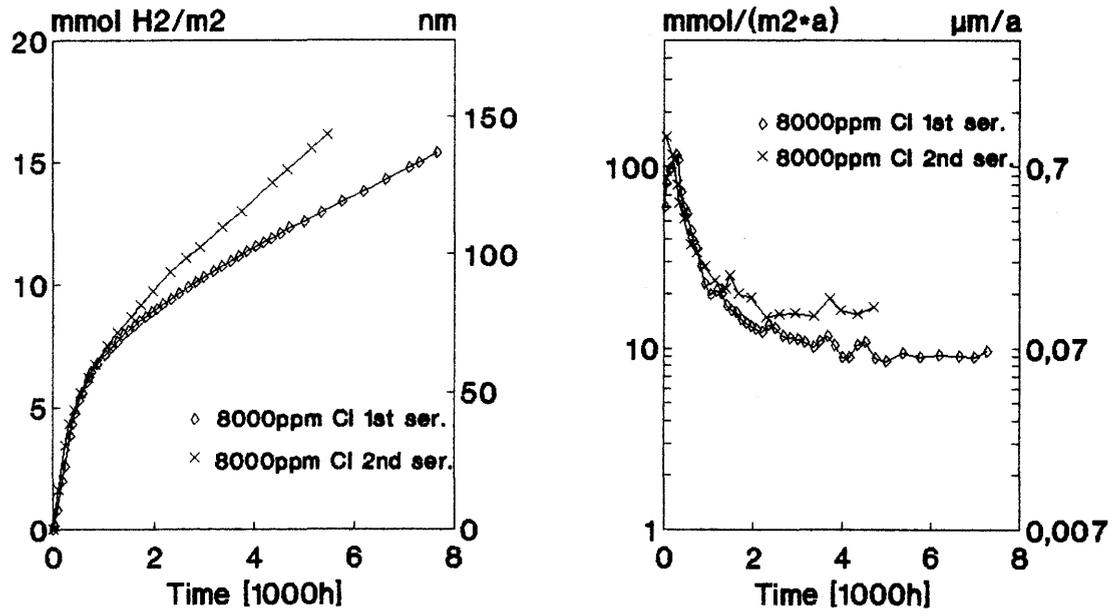


Fig. 13b: Comparison between 1st and 2nd measuring series with NaCl-solution pH 8.5

6. DISCUSSION AND CONCLUSIONS

The results show that it takes several thousand hours for many of the hydrogen evolution rates to even approach a constant value. This point is important when evaluating values from other work where time scales in the thousand hour range are rarely considered. This is also a reason for the considerably lower hydrogen evolution rates found for iron in Böttstein water in this paper than the 185 mmol/(m².a) reported from short term experiments (Schenk 1988). Initial rates reported here are lower at ca. 70 mmol/(m².a) but within expected experimental scatter. The corrosion rate should not be expected to decrease with time since the corroding agent is water itself in a reducing environment, and the corrosion is not regulated by solubility effects due to secondary transformation of the corrosion products as the passive film is metastable with respect to an Fe_{3-x}O₄ phase.

However it must be assumed that the hydrogen generated begins to inhibit the corrosion of the iron as the pressure rises. But further measurements would be needed to establish the order of magnitude of a possible pressure influence on the iron oxidation, because no more exact statements can be made on the strength of the results to date.

Of prime interest within the scope of this work are the results with the alkaline media, since they represent the conditions in ultimate repositories for low- and medium-level active wastes.

Surprisingly the corrosion behaviour with similar pH depends very much on the chemical composition of the corrosion medium.

With Ca(OH)₂ as base, at pH 12.8 there is a constant hydrogen evolution rate of 1 - 2 mmol/(m²*a) during the whole measuring period. As the free bases NaOH and KOH in an ultimate repository may be expected to get washed out by the flowing groundwater after a certain time, and the pH is controlled mainly by the Ca(OH)₂, this value would appear to be of importance in final repositories.

Accordingly the cement pore water II, equivalent to an aged water virtually free of NaOH and KOH, generates hydrogen at a constant rate of 0.5 - 1 mmol/(m²*a) throughout the measuring time of 12 000 hours.

However it must not be overlooked that with the monovalent bases NaOH and KOH, likewise at pH 12.8, hydrogen evolution rates of 10 mmol/m²*a also were measured during a relatively short time. Nor can the behaviour of new cement pore waters, containing larger amounts of KOH and NaOH, be estimated accurately as yet, because in this case even the measuring time of 6000 hours appears to be too short.

Since the mechanism for the different behaviour of mono- and bivalent bases is unclear, it would be wise to assume conservatively a hydrogen evolution rate of 10 mmol/(m²*a) in alkaline media.

Generally speaking the analysis method employed allows the measurement of very low hydrogen evolution rates over a period of some thousands of hours. Although the results of blank tests show that in the absence of oxygen the measuring accuracy is retained over several thousand hours, it must be assumed that the method tends to underestimate rather than overestimate the evolution of hydrogen due to diffusion of hydrogen into iron. In view of this, the measured values should be regarded as the minimum corrosion rates to be expected.

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