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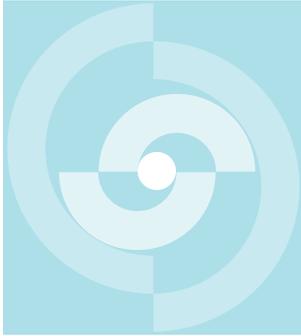
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# TECHNICAL REPORT 89-19

## EXPERIMENTS ON CONTAINER MATERIALS FOR SWISS HIGH-LEVEL WASTE DISPOSAL PROJECTS PART IV

J. P. SIMPSON

DECEMBER, 1989

Sulzer Brothers Ltd, Winterthur



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Der vorliegende Bericht wurde im Auftrag der Nagra erstellt. Der Autor hat seine eigenen Ansichten und Schlussfolgerungen dargestellt. Diese müssen nicht unbedingt mit denjenigen der Nagra übereinstimmen.

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SUMMARY

One concept for final disposal of high-level waste in Switzerland consists of a repository at a depth of 1000 to 1500 m in the crystalline bedrock of Northern Switzerland. The waste will be placed in a container which will be required to function as a high integrity barrier for at least 1000 years.

This report is the fourth and last in the current series dealing with the evaluation of potential materials for such containers. Four materials were identified for further evaluation in the first of these reports: they were cast steel, nodular cast iron, copper and Ti-Code 12.

Copper and cast steel were chosen for further evaluation without prejudice as to the technical merits of the other two materials. The bulk of the experimental work concentrated on the latter material as the data basis for the adoption of copper as a candidate material was more complete.

The main effort so far reported concentrated upon establishing that the general corrosion and the localized corrosion rates of cast steel in groundwaters of the type expected are acceptable. The long term corrosion rate is expected to be less than 20  $\mu\text{m/a}$  and the conditions such that large local variations in corrosion rate or pitting are unlikely.

This report touches upon two other important aspects. The first is the problem of demonstrating that cast steel containers will not fail by stress corrosion cracking. The second is the evolution of hydrogen produced by the reduction of water; the corrosion product hydrogen may be a problem if it is produced faster than it can escape as a dissolved species by diffusion, i.e. if gas pockets or bubbles are formed which could lead to pressure build-up or alter the near-field transport processes by displacement, venting or buoyancy effects.

The experimental results on pre-cracked specimens revealed no susceptibility of cast steel to stress corrosion cracking under model repository conditions. No crack growth was detected on compact DCB specimens exposed in aerobic and anaerobic groundwaters at 80 and 140°C for 16-24 months. This suggests that the maximum possible crack growth rates are below 0.1 mm/a or incubation times are exceptionally long under all test conditions. Constant extension rate test results showed a possible effect of inclusions on stress corrosion behaviour. Cast steel remains a candidate material for high-level waste containers.

As expected from thermodynamic considerations no hydrogen could be detected from copper immersed in model groundwaters at 50°C.

Hydrogen is evolved from corroding steel under anaerobic conditions. The highest steady state rate observed in a model groundwater was  $2.5 \text{ ml(NTP) } \times \text{ m}^{-2} \times \text{ h}^{-1}$  at 50°C in the model Böttstein groundwater, corresponding to a corrosion rate of 7  $\mu\text{m/a}$ ; it was lower at both 25°C and 80°C. Higher values were however obtained in dilute bentonite slurries. The hydrogen evolution rate is independent of chloride concentration between 0 and 8000 mg/l but falls by a factor of 10 on increasing the pH from 7 to 10.

Hydrogen evolution due to corrosion of iron or steel in waste repositories has to be considered in any safety analysis; the amounts produced can be significant.

The report concludes the current phase of corrosion testing for Swiss high-level waste repositories. Evidence to date suggests that both cast steel and copper are suitable container materials. Because the corrosion behaviour of both materials is sensitive to service conditions, in particular length of the aerobic phase, groundwater chemistry and temperature, further testing should be undertaken when a specific site has been identified.

### Zusammenfassung

In der Schweiz ist vorgesehen, die hochaktiven Abfälle in einem Endlager in einer Tiefe von 1000 bis 1500 m im kristallinen Grundgebirge der Nordschweiz zu beseitigen. Die Abfälle werden in Behältern, die als sehr wirksame Sicherheitsbarrieren während mindestens 1000 Jahren standhalten müssen, eingelagert.

Dieser Bericht ist der vierte und letzte in einer Reihe, die sich mit der Evaluation potentieller Materialien für solche Endlagerbehälter beschäftigt. Im ersten Bericht wurden vier Werkstoffe für eine weitere Evaluation identifiziert: Stahlguss, Sphäroguss, Kupfer und Ti-Code 12. Kupfer und Stahlguss wurden dann für eine nähere Charakterisierung ausgewählt, ohne die anderen zwei Materialien als technisch ungeeignet zu bewerten. Der Grossteil der Arbeiten konzentrierte sich auf Stahlguss, weil die Datenbasis für Kupfer als potentielles Behältermaterial bereits vollständiger war als diejenige für Stahlguss.

Hauptziel der bis jetzt dokumentierten Arbeiten war nachzuweisen, dass sowohl die allgemeine Korrosion als auch die lokalen Korrosionsgeschwindigkeiten des Stahlgusses in den zu erwartenden Grundwässern tolerierbar sind. Die erwartete Langzeit-Korrosionsgeschwindigkeit sollte nicht mehr als 20  $\mu\text{m/a}$  betragen und grosse Schwankungen in der Korrosionsgeschwindigkeit oder Lochfrass-Korrosion sind nicht zu erwarten.

Dieser Bericht behandelt zwei weitere wichtige Aspekte. Der erste Aspekt ist der Nachweis, dass die Stahlgussbehälter nicht durch Spannungsrisskorrosion versagen werden. Der zweite Aspekt ist die aus der Reduktion des Wassers stammende Wasserstoffproduktion. Dieses Phänomen könnte zu Problemen führen, wenn mehr Wasserstoff pro Zeiteinheit entsteht als durch Diffusion als gelöste Spezies entweichen kann, d.h. wenn sich Gas-Einschlüsse oder -Blasen ausbilden, die zu einem Druckaufbau führen oder die Nahfeld-Transportprozesse durch örtliche Verdrängung, Blasenbildung oder Auftriebseffekte verändern könnten.

Die Resultate der Experimente an Proben mit künstlich erzeugten Rissen haben keine Anfälligkeit des Stahlgusses für Spannungsrisskorrosion unter Modell-Endlagerbedingungen aufgezeigt. In kompakten DCB-Proben, die über 16 - 24 Monate bei Temperaturen von 80 und 140 °C sowohl aeroben als auch anaeroben Grundwässern ausgesetzt wurden, wurde kein Risswachstum beobachtet. Aus diesem Befund kann geschlossen

werden, dass die maximalen möglichen Risswachstumsraten weniger als 0.1 mm/a betragen oder dass die Inkubationszeiten unter allen Versuchsbedingungen ausserordentlich lang sind. Die Ergebnisse der Versuche mit konstanter Dehngeschwindigkeit weisen auf eine mögliche Beeinflussung von Einschlüssen auf das Spannungsrissskorrosionsverhalten hin. Stahlguss bleibt damit ein Kandidat für die Endlagerbehälter für hochaktive Abfälle.

Wie aufgrund thermodynamischer Ueberlegungen erwartet, konnte im Fall von Kupfer in Modellgrundwässern bei einer Temperatur von 50 °C keine Wasserstoffentwicklung festgestellt werden.

Korrozierender Stahl unter anaeroben Bedingungen produziert Wasserstoff. Die maximale Gleichgewichts-Produktionsrate, die in einem Modellgrundwasser beobachtet wurde, betrug 2.5 ml (NTP)  $\times$  m<sup>-2</sup>  $\times$  h<sup>-1</sup> bei 50 °C (Modellwasser Böttstein), was einer Korrosionsgeschwindigkeit von 7  $\mu$ m/a entspricht; für 25 °C und 80 °C waren die Werte noch tiefer. Höhere Werte wurden aber in verdünnten Bentonit-Schlämmen gefunden. Zwischen 0 und 8000 mg/l ist die Wasserstoffentwicklungsrate nicht von der Chlorid-Konzentration abhängig, wird aber um einen Faktor 10 verkleinert bei einem pH-Anstieg von 7 auf 10.

Die aus der Korrosion von Eisen oder Stahl stammende Wasserstoffentwicklung in Endlagern muss in jeder Sicherheitsanalyse berücksichtigt werden, da die entstehende Menge durchaus bedeutend sein kann.

Der Bericht schliesst die aktuelle Phase der Korrosionsuntersuchungen für schweizerische Endlager für hochaktive Abfälle ab. Die bis heute vorliegenden Resultate zeigen, dass sowohl Stahlguss als auch Kupfer als Behältermaterialien geeignet sind. Da das Korrosionsverhalten beider Materialien von den Endlager-Betriebsbedingungen beeinflusst wird, vor allem von der Dauer der aeroben Phase, dem Grundwasserchemismus und der Temperatur, sollen weitere spezifische Untersuchungen angestellt werden, wenn einmal ein Endlagerstandort ausgewählt worden ist.

RESUME

L'un des concepts de stockage définitif des déchets de haute activité en Suisse consiste en un dépôt final implanté à une profondeur de 1000 à 1500 m dans le socle cristallin du nord de la Suisse. Les déchets seraient enfermés dans des conteneurs qui devraient constituer des barrières de haute intégrité durant 1000 ans au moins.

Le présent rapport est le quatrième et dernier de la série en cours relative à l'évaluation des matériaux potentiels pour la réalisation de ces conteneurs. Dans le premier de ces rapports quatre matériaux avaient été retenus pour une évaluation plus poussée, à savoir l'acier coulé, la fonte nodulaire, le cuivre et le Ti-code 12. Le cuivre et l'acier coulé ont fait l'objet d'une évaluation supplémentaire, sans préjudice à l'égard des qualités techniques des deux autres matériaux. La plus grande partie des travaux expérimentaux se sont concentrés sur ce dernier matériau, les données relatives au cuivre étant plus complètes.

Les principaux efforts ayant jusqu'ici fait l'objet de rapports se sont appliqués à démontrer que les taux de corrosion généralisé et local de l'acier coulé dans des eaux souterraines des types prévus étaient acceptables. On s'attend à trouver des taux de corrosion à long terme inférieurs à 20µm/a et des conditions telles que d'importantes variations locales des taux de corrosion ou la formation de crevasses soient peu probables.

Le présent rapport traite deux autres aspects très importants. Le premier était de démontrer que des conteneurs en acier coulé ne seraient pas menacés par corrosion sous tension. Le second concerne l'évolution de l'hydrogène produit par la réduction de l'eau; l'hydrogène produit par la corrosion peut constituer un problème s'il est formé plus rapidement qu'il ne peut s'échapper par diffusion comme substance en solution, si par exemple il forme des poches ou bulles de gaz qui pourraient entraîner une augmentation de pression ou modifier le processus de transport dans le champ proche par des phénomènes de déplacement, de dégazage ou de force ascensionnelle.

Les résultats expérimentaux sur des échantillons préalablement fissurés n'ont pas révélé de susceptibilité de l'acier coulé à la corrosion sous tension dans des conditions modélisant un dépôt final. On n'a pas détecté de croissance de fissures sur des échantillons DCB exposés sous conditions aérobies et anaérobies dans des eaux souterraines

de 80 et de 140°C durant 16-24 mois. Cela suggère que le taux de croissance de fissures maximum possible se situe en-dessous de 0.1 mm/a ou que les durées d'incubation sont exceptionnellement longues dans toutes les conditions d'essais considérées. Les résultats des essais à taux de déformation constant démontrent la possibilité que les inclusions aient une influence sur le comportement en corrosion sous tension. L'acier coulé est retenu comme matériau candidat pour la réalisation de conteneurs pour déchets de haute activité.

Ainsi qu'on s'y attendait suite à des considérations thermodynamiques, on n'a pu détecter d'hydrogène provenant de cuivre immergé dans des eaux souterraines modèles à 50°C

De l'hydrogène est dégagé par la corrosion de l'acier sous conditions anaérobies. Le taux de dégagement le plus élevé, sous conditions d'équilibre dans une eau souterraine modèle, était de 2,5 ml(NTP)m<sup>-2</sup>h<sup>-1</sup> à 50°C pour l'eau modèle de Boettstein, ce qui correspond à un taux de corrosion de 7 µm/a; il était plus faible à 25°C comme à 80°C. On a toutefois obtenu des valeurs plus élevées dans des boues de bentonite diluées. Le taux d'évolution d'hydrogène est indépendant de la teneur en chlorures pour des concentrations de 0 à 8000 mg/litre, mais il diminue d'un facteur 10 lorsque le pH passe de 7 à 10.

L'évolution d'hydrogène causée par la corrosion du fer ou de l'acier dans un dépôt final pour déchets radioactifs doit être prise en compte dans toute analyse de sûreté: les quantités produites peuvent être significatives.

Ce rapport met un point final à la phase présente des essais de corrosion concernant les dépôts finals suisses pour déchets de haute activité. Les résultats obtenus à ce jour suggèrent que l'acier coulé, ainsi que le cuivre, conviennent comme matériaux pour la réalisation de conteneurs. Comme le comportement en corrosion des deux matériaux dépend des conditions de service, particulièrement de la durée de la phase aérobie, du chimisme et de la température de l'eau souterraine, des essais complémentaires devraient être entrepris lorsqu'un site spécifique aura été identifié.

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## 1. INTRODUCTION

One concept for the disposal of high-level waste in Switzerland involves a repository at a depth of around 1200 m in a stable granite formation away from large fault zones in the crystalline basement of north Switzerland. Engineered barriers include the waste solidification matrix (glass), corrosion resistant steel containers and back-filling with bentonite followed by sealing of the access tunnels and shafts /1/.

This report is the fourth and last of the current series of reports dealing with the choice and evaluation of materials for high level waste containers in a crystalline formation. The design criteria for the containers are discussed in Part I /2/. The most important of these are:

- i) Expected life of container to be 1000 years or more
- ii) Chloride bearing granitic groundwater
- iii) Initial temperature ca. 140°C falling to ambient ca. 55°C after 1000 years
- iv) Anaerobic conditions except for the first few years after closure
- v) Container to withstand external pressure of 300 MPa.

Materials that were identified as candidate materials for high level waste containers are:

- a) iron or steel (unalloyed or low alloy)
- b) copper
- c) titanium or titanium alloy
- d) a nickel-chromium-molybdenum alloy
- e) alumina

This material selection was made primarily on the basis of corrosion resistance to the groundwater under repository conditions. At this stage in the waste disposal programme there was a preference for simple massive container designs to be manufactured by well proven techniques. With these points in mind the number of candidate materials was reduced to the first three in the above

list. An experimental programme was initiated to provide corrosion data for these materials under conditions closer to those expected in the repository than was available in the literature.

The materials tested were a cast steel (GS 40), a nodular cast iron (GGG 40), copper and a titanium alloy (Ti-Code 12). Part II /3/ contains the results of the experimental programme as they were available before the submission of the "Projekt Gewähr" (Guarantee Project) final reports, which were prepared to fulfil legal requirements on the demonstration of permanent, safe management and final disposal of nuclear waste. On the basis of this data and further data available from other sources two container materials for high level waste were considered; a thick walled cast steel container for vitrified reprocessed high level waste and copper for the direct disposal of spent fuel elements.

It was concluded in a corrosion assessment for "Projekt Gewähr" /4/ that the evidence for the use of copper as a container material was very strong, and that no aspects needed to be further investigated in the framework of the feasibility study for safe disposal from the point of view of corrosion. Iron was expected to be as suitable as copper but the evidence was not as complete. A container design was proposed /5/ on the basis of the available data but further work is required to optimize this design and improve the container life expectancy estimates.

"Projekt Gewähr" was a feasibility study for nuclear waste management and disposal in Switzerland. In the case of high level waste, although a possible host geological formation was identified and used as a basis in "Projekt Gewähr". Alternative host rocks are currently being considered but no site has yet been identified. This in turn means that a definitive groundwater chemistry for the repository is not available although experimental results from investigations of the geochemistry and hydrogeology of the candidate host rock was used to define a model groundwater for "Projekt Gewähr".

Corrosion processes can be sensitive to small changes in groundwater composition. One of the reasons for choosing copper and cast steel for the containers was the conclusion from the literature that the corrosion behaviour of these materials was not strongly dependent upon the likely compositional variation in groundwater chemistry. Nevertheless, before a site is identified it would be useful to know in more detail how variations in the groundwater chemistry effect the corrosion behaviour and hence the life expectancy of a container. The experimental programme was thus extended to investigate the effects of some constituents of groundwaters on the susceptibility of cast steel to suffer from localized corrosion. This work was described in detail in Part III /6/.

The bulk of the work so far reported has /2,3,5,6/ concentrated upon establishing that the general corrosion rate was low enough to establish a container life of 1000 years and that, at least in the two model waters, the conditions were such that the containers were corroding under conditions unlikely to cause large local variations or pitting.

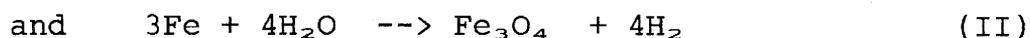
This report touches upon two other important aspects. The first is the problem of demonstrating that the containers will not fail by stress corrosion cracking, which like pitting could cause premature failure. The second is the production of hydrogen produced by the oxidation of iron by water; the corrosion product hydrogen could become a factor which would need to be considered in the safety analysis if it is produced at a rate faster than it can escape by diffusion as a dissolved gas, i.e. if gas bubbles or pockets were produced which could lead to pressure build-up or alter the near field transport processes by displacement, venting or buoyancy effects.

## 2. CORROSION INDUCED HYDROGEN EVOLUTION ON HIGH LEVEL WASTE OVERPACK MATERIALS IN SYNTHETIC GROUNDWATERS AND CHLORIDE SOLUTIONS

### 2.1 INTRODUCTION

In the reference scenario for Projekt "Gewähr", the waste enclosed in its overpack is to be placed in 3.7 m diameter horizontal tunnels surrounded by compacted bentonite clay as a backfill. The overpack is required to function as a high integrity barrier for at least 1000 years /5/.

After sealing the repository, groundwater will seep into the repository leaving the container in water saturated compacted bentonite. On closure some oxygen will be trapped in the repository which will be consumed by corrosion of the iron container. The groundwater is oxygen free so as soon as the trapped oxygen has been consumed, corrosion will continue under anoxic conditions. In anoxic sulfide-free groundwaters the most probable iron corrosion reactions are:



Both of these reactions produce hydrogen. The equilibrium pressure is calculated to be about 100 atm for reaction I and 500 atm for reaction II at 25°C [2]. Magnetite ( $\text{Fe}_3\text{O}_4$ ) is expected to be the corrosion product on iron under Swiss repository conditions; this reaction is favoured by the higher temperatures expected in the repository with a maximum of about 150°C early in the life of the repository falling to close to the ambient 50°C at 1000 years; the average temperature for the first 1000 years is about 80°C. The pressure is temperature dependent and Neretnieks /7/ gives the following hydrogen equilibrium pressures:

25°C	516 atm,
55°C	618 atm,
80°C	699 atm,
120°C	819 atm

There is some uncertainty in the thermodynamic data and the pressures may vary by several 10's of percent, but nevertheless the equilibrium pressures will be well in excess of the 120 atm hydrostatic pressure.

Hydrogen evolved by corrosion may escape by diffusion. Neretnieks /7/ estimated that the rate of loss of dissolved hydrogen by diffusion through compacted bentonite could support a corrosion rate of 0.03 to 0.8  $\mu\text{m/a}$ . The corrosion rate assumed for container design purposes was 20  $\mu\text{m/a}$  /3,4,6/, although the long term rate is expected to be nearer 10  $\mu\text{m/a}$  /6/.

Since hydrogen cannot escape by diffusion, it must be expected that a considerable pressure can, in principle, be generated. It could, however, be shown /8/ that the hydrogen will in fact be able to escape through the bentonite buffer by a percolation process. In order to assess further the effect of hydrogen on the repository near-field it is nevertheless essential to have accurate data on the evolution rate.

As it became clear that the corrosion product hydrogen was an important issue with cast steel containers, an experimental programme was initiated to measure the hydrogen evolution rate directly.

As no specific site (as opposed to the geological formation) has been identified for a Swiss HLW repository, the experimental programme included both model reference waters and buffered sodium chloride solutions. The latter were used in a parameter study to look at the effects of chloride ion concentration, pH and temperature /9/.

The reader is referred to the report by Schenk /9/ for a more detailed discussion of the method and results of measurements on carbon steel. The results on copper were published in reference /10/. The results from these two references are quoted in this report along with some new results of hydrogen evolution measurements on carbon steel in miscellaneous environments relevant to high level waste disposal.

## 2.2 EXPERIMENTAL: CARBON STEEL

### 2.2.1 Measuring technique

The specimens are placed in three glass flasks along with the deaerated test medium. The flasks are immersed in a water bath for temperature regulation. (Figure 1)

A nitrogen gas stream is first water saturated by bubbling it through the wash bottle and then passed over the test medium in the flasks. The gas is not bubbled through the test solution. As the carrier gas passes over the cells, it picks up any gas evolved by corrosion reactions.

The gas stream is then partially dried by passing it through a water cooled water trap before being sampled for analysis in a gas chromatograph.

The gas chromatograph was calibrated for a gas concentration of 10-100 ppm by volume hydrogen, accurate to  $\pm 1$  vol.ppm in this range. The detection limit was less than 1 vol.ppm hydrogen, i.e. the analysis is semi-quantitative from 10 down to 1 vol.ppm hydrogen.

The hydrogen evolution rate is given by:

$$N = G.T/F \quad (III)$$

where G is the volume fraction of hydrogen in the gas stream, T is the carrier gas flow rate in  $\text{ml.h}^{-1}$  and F is the total surface area of the corrosion coupons in  $\text{m}^2$  and N has the units  $\text{ml}(\text{H}_2).\text{m}^{-2}.\text{h}^{-1}$ .

The standard test conditions were a gas flow rate of  $100 \text{ ml.h}^{-1}$  and total surface area of  $78 \text{ cm}^2$ . This gives as the detection limit for hydrogen  $N_{d1}$ :

$$N_{d1} = 0.013 \text{ ml}(\text{H}_2).\text{m}^{-2}.\text{h}^{-1} \text{ at NTP.} \quad (IV)$$

This is equivalent to a corrosion rate of  $0.036 \mu\text{m/a}$  assuming oxidation of iron to the divalent state.

The measurements were continued until the hydrogen evolution rate was constant. When no hydrogen was detected the minimum test period was 380 hours. The experiments are described in detail in reference /9/.

- [1] Nitrogen gas supply
- [2] Water bottle
- [3] Specimen flasks (3)
- [4] Water bath
- [5] Cold trap
- [6] Gas chromatograph
- [7] Gas flow rate meter
- [8] Output
- [TI] Thermostat
- [PI] Pressure reduction
- [WLD] Detector
- [INT] Integrator
- [REC] Recorder

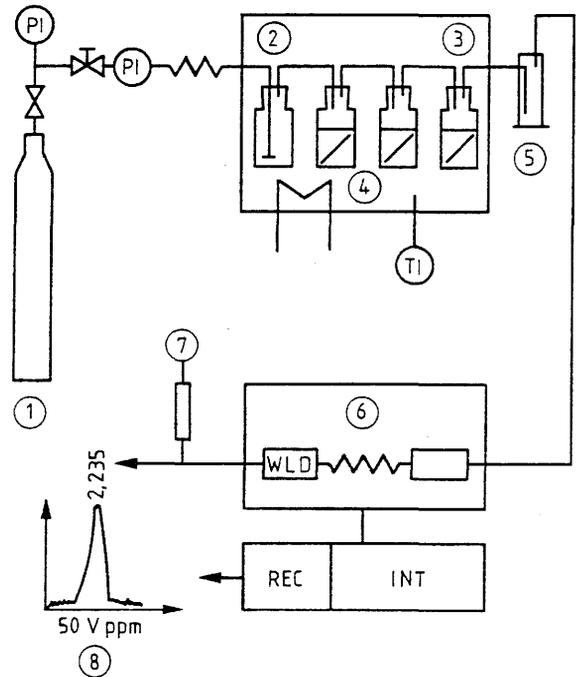


Figure 1 Experimental apparatus (schematic)

2.2.2 Materials

The carrier gas was 5 nines nitrogen with O<sub>2</sub> <2 vol.ppm, H<sub>2</sub> <1 vol.ppm, and H<sub>2</sub>O <2 vol.ppm.

The specimens were low carbon steel sheet, DIN Material Number, (W.Nr.) 1.0333 with a typical analysis:

C 0.1%, Mn 0.3%, Si 0.1%, N,P,S < 0.007%.

One coupon (50 x 24 x 1.5 mm<sup>3</sup>) was placed in each of the three specimen bottles after wet grinding to 1000 grit and degreasing in alcohol and acetone.

### 2.2.3 Media

Three series of tests were run.

#### Series 1:

The first used the two corrosion reference waters as the corrosion medium: Böttstein and Säckingen.

The compositions of the two groundwaters are given in Table 1. Böttstein water is a synthetic groundwater based on samples taken from the northern Swiss granitic base rock. Säckingen water is a natural source water; the variation in composition reflects the range of compositions observed at the source.

Table 1. Chemical Composition of Böttstein and Säckingen waters

	Säckingen µg/g	Böttstein µg/g
Na <sup>+</sup>	900 - 1070	4800
K <sup>+</sup>	75 - 86	54
Mg <sup>++</sup>	12 - 15	3
Ca <sup>++</sup>	124 - 158	1100
Cl <sup>-</sup>	1480 - 1820	8100
F <sup>-</sup>	2.3 - 2.8	3.8
SO <sub>4</sub> <sup>=</sup>	112 - 115	1820

#### Series 2

The second in a series of sodium chloride solutions of 0 (bi-distilled water), 80, 800 or 8000 mg/l Cl<sup>-</sup> unbuffered (nominal pH 7) and buffered with carbonate to pH 8.5 or 10. The temperature was 50 or 80°C.

The two buffer systems were:

pH 8.5; 0.1%  $\text{Na}_2\text{CO}_3$  : 0.1%  $\text{NaHCO}_3$  = 1:100

pH 10 ; 0.1%  $\text{Na}_2\text{CO}_3$  : 0.1%  $\text{NaHCO}_3$  = 1.5:1

### Series 3

A series of measurements were carried out with phosphate and bentonite additions to synthetic Böttstein water and chloride solutions.

The phosphate addition was made by adding 1000 mg/l phosphate as  $\text{Na}_2\text{HPO}_4$  to the solutions.

The bentonite addition was made by adding 5% by weight dry sodium bentonite to the test solution

#### 2.2.4 Results: Carbon Steel

The results of the hydrogen evolution experiments reported in reference /9/ are given in Table 2 for Series 1 and 2.

The results of the Series 3 experiments are given in Table 3. The experiments in the two reference waters were repeated hence the slight difference in hydrogen rates reported in Table 2 to Table 3.

#### 2.2.5 Discussion: Carbon Steel

The average corrosion rate as measured by hydrogen evolution is well below the 20  $\mu\text{m/a}$  maximum used for the Swiss container design /5/.

The results from series 2 show that the corrosion rate is strongly dependent upon pH and almost independent of chloride concentration /9/, as shown in figures 2 and 3.

The results of Series 1 and 2 experiments are discussed in detail elsewhere /9/.

Series 3 experiments were designed to explore the effects of phosphate additions which may act as an inhibitor for iron corrosion /11/, and the effects of the presence of bentonite on the corrosion rate.

There is no evidence that phosphates have any significant effect on the anaerobic corrosion rate of carbon steel in either plain carbonate buffered chloride solutions or in synthetic Böttstein water. It should be noted that in the latter most of the phosphate precipitated out immediately as a calcium phosphate ( $\text{CaHPO}_4$  has a solubility of 136 mg/l at 25°C or 95 mg/l as  $\text{PO}_4^{3-}$ ); chemical analysis of the solution gave a dissolved phosphate concentration at 25°C of ca. 62 mg/l phosphate as  $\text{PO}_4^{3-}$ .

Bentonite on the other had a noticeable effect on the corrosion rate at 80°C increasing the corrosion rate by a factor of ca. 5-8 in the plain chloride solution, and by a factor of 10-20 in Böttstein water. The effect was less marked at 50°C; the bentonite increased the corrosion rate by a factor of ca. 3 in the plain chloride solution and if anything reduced it in Böttstein water.

The effect of bentonite on the hydrogen evolution rate cannot be explained at the present time. Experiments in highly compacted bentonite at 80°C did not show an increase in corrosion rate over specimens immersed in Böttstein water /3,6/.

Table 2. Results of hydrogen evolution measurements in reference groundwaters and carbonate buffered chloride solutions. Hydrogen evolution rates at steady state (i.e. hydrogen evolution rate virtually unchanged over last 40 hours of observation). Corrosion rates are calculated from the hydrogen evolution rate assuming oxidation of Fe to Fe(II). Long incubation times are possible, measurable corrosion may occur at pH 10 at longer exposure times.

Medium	Temp. °C	Hydrogen evolution rate ml.m <sup>-2</sup> .h <sup>-1</sup>	Corr. rate µm.a <sup>-1</sup>
Säckingen	25	0.65	1.8
Säckingen	50	1.3	3.6
Säckingen	80	0.6	1.7
Böttstein	25	0.45	1.3
Böttstein	50	2.5	7.0
Böttstein	80	0.95	2.7
pH 7 ; 0 ppm Cl <sup>-</sup>	50	1.0	2.8
pH 7; 80 ppm Cl <sup>-</sup>	50	1.1	3.0
pH 7 ; 800 ppm Cl <sup>-</sup>	50	0.5	1.4
pH 7 ;8000 ppm Cl <sup>-</sup>	50	1.3	3.5
pH 7; 0 ppm Cl <sup>-</sup>	80	0.35	1.0
pH 7; 80 ppm Cl <sup>-</sup>	80	1.4	3.9
pH 7; 800 ppm Cl <sup>-</sup>	80	2.1	5.9
pH 7; 8000 ppm Cl <sup>-</sup>	80	0.3	0.8
pH 8.5; 0 ppm Cl <sup>-</sup>	50	0.3	0.8
pH 8.5; 80 ppm Cl <sup>-</sup>	50	0.3	0.8
pH 8.5; 800 ppm Cl <sup>-</sup>	50	0.5	1.4
pH 8.5;8000 ppm Cl <sup>-</sup>	50	0.5	1.4
pH 8.5 0 ppm Cl <sup>-</sup>	80	0.2	0.6
pH 8.5; 80 ppm Cl <sup>-</sup>	80	0.6	1.7
pH 8.5; 800 ppm Cl <sup>-</sup>	80	0.2	0.6
pH 8.5;8000 ppm Cl <sup>-</sup>	80	1.0	2.8
pH 10; 0 ppm Cl <sup>-</sup>	50	<0.02	<0.04
pH 10; 80 ppm Cl <sup>-</sup>	50	<0.02	<0.04
pH 10; 800 ppm Cl <sup>-</sup>	50	<0.02	<0.04
pH 10; 8000 ppm Cl <sup>-</sup>	50	<0.02	<0.04
pH 10; 0 ppm Cl <sup>-</sup>	80	0.2	0.6
pH 10 ; 80 ppm Cl <sup>-</sup>	80	1.0	2.8
pH 10 ; 800 ppm Cl <sup>-</sup>	80	0.3	0.8
pH 10; 8000 ppm Cl <sup>-</sup>	80	0.2	0.6

Table 3 Results of Series 3 hydrogen evolution experiments. Measured hydrogen evolution rates at steady state (i.e. virtually constant value over last 40 hours of observation). Long incubation times are possible, measurable corrosion may occur in bi-distilled water at longer observation times.  
(B = Böttstein water,  $\text{Cl}^-$  and  $\text{PO}_4^{3-}$  in mg/l, Bentonite 5% by weight dry sodium bentonite)

Medium mg/l	Temp °C	H <sub>2</sub> steady state ml(H <sub>2</sub> )/m <sup>2</sup> .h	Time h
Böttstein water (B)	50	3.0-3.5	156
Böttstein water (B)	80	0.5-1.0	162
-----	-----	-----	-----
B + 1000 $\text{PO}_4^{3-}$	50	0.5	156
B + 1000 $\text{PO}_4^{3-}$	80	0.5-1.0	162
-----	-----	-----	-----
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=7	50	1.0-2.0	134
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=7	80	0.5	164
-----	-----	-----	-----
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=8.5	50	1.5-2.5	134
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=8.5	80	1.5-2.0	164
-----	-----	-----	-----
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=10	50	0.8-1.3	195
8000 $\text{Cl}^-$ + 1000 $\text{PO}_4^{3-}$ pH=10	80	2.0-2.5	160
-----	-----	-----	-----
B + 5% Bentonite pH=8.2	50	1.8-2.3	195
B + 5% Bentonite pH=8.2	80	10.0-13.5	195
-----	-----	-----	-----
8000 $\text{Cl}^-$ + 5% Bentonite *	50	1.3-1.8	163
8000 $\text{Cl}^-$ + 5% Bentonite *	80	5.5-8.5	182
-----	-----	-----	-----
Bi-distilled water	50	<0.02	163

\* pH ca. 8.2

Figure 2

Average and standard deviation of hydrogen evolution rate as a function of pH (excluding transients) for all media and temperatures.

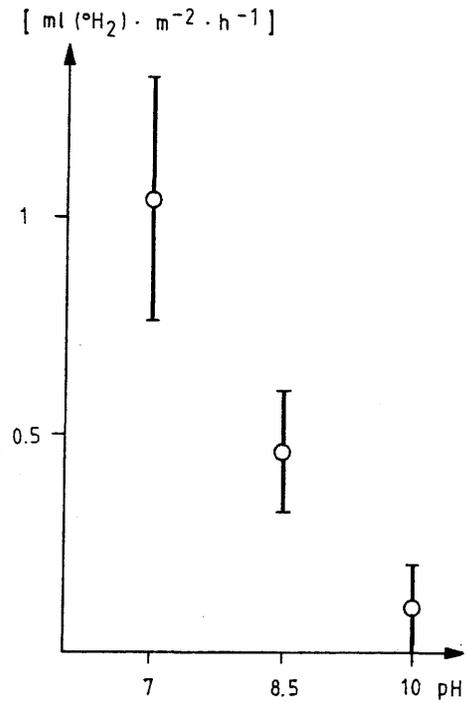
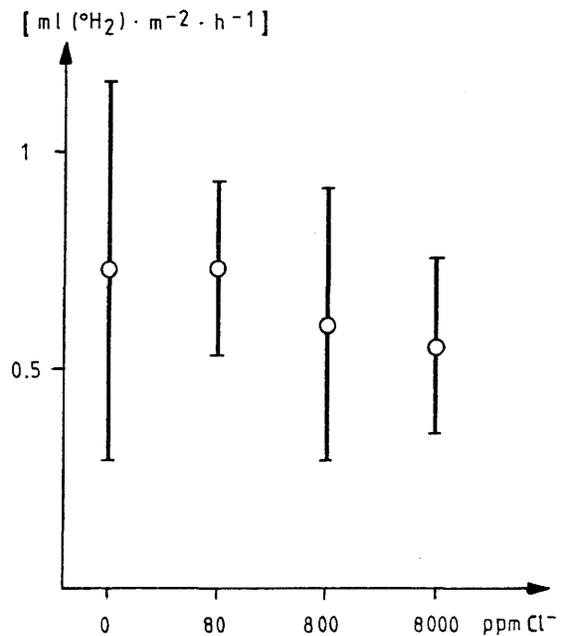


Figure 3

Average and standard deviation of hydrogen evolution rate as a function of Cl<sup>-</sup> concentration for all media and temperatures.



### 2.3 HYDROGEN EVOLUTION FROM CORROSION OF COPPER

Hultquist /12/ reported that hydrogen was evolved from copper corroding in pure water at 25°C at a rate of  $15 \cdot 10^{-6} \text{ g(H}_2\text{)} \cdot \text{h}^{-1} \cdot \text{m}^{-2}$ , equivalent to a corrosion rate of 0.96  $\mu\text{m/a}$  if copper is oxidised to the cuprous state by water via the reaction:



The amount of hydrogen reported to be in the corrosion cell after ca. 1100 h exposure was 0.8 mg in a volume of 0.02  $\text{dm}^3$  equivalent to a hydrogen partial pressure ( $P_{\text{H}_2}$ ) of about 0.45 bar. /12/

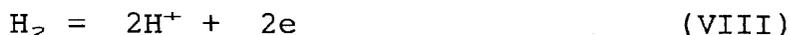
The partial reactions involved are :



where /13/

$$E(\text{V nhe}) = 0.471 - 0.0591\text{pH} \quad \text{at } 25^\circ\text{C} \quad (\text{VII})$$

and:



where /13/

$$E(\text{V nhe}) = -0.0591\text{pH} - 0.0295\log(P_{\text{H}_2}) \quad \text{at } 25^\circ\text{C} \quad (\text{IX})$$

From equations VII and IX, the equilibrium partial pressure for hydrogen over copper/cuprous oxide in water at 25°C is ca.  $10^{-16}$  bar. Nevertheless, Hultquist claims that reaction V is irreversible and that the hydrogen evolved can thus accumulate and reach any partial pressure given time.

Corrosion rates of the magnitude reported by Hultquist and the amounts of hydrogen evolved are not to be expected for copper immersed in pure water.

### 2.3.1 Experimental

#### 2.3.1.1 Measuring technique.

Identical to that for carbon except as mentioned below.

#### 2.3.1.2 Materials

The copper was 0.1 mm thick foil of > 99.7% purity.  
(Sb <0.005, As <0.002, Pb <0.05, Fe <0.005, Mn <0.005,  
Ag <0.002, Sn <0.005 % by weight.)

The carrier gas was 5 nines nitrogen with:  
O<sub>2</sub> <2 vol.ppm, H<sub>2</sub> <1 vol.ppm, and H<sub>2</sub>O <2 vol.ppm.

Two different test solutions were used:

A: a synthetic granitic groundwater;

B: a sodium chloride solution.

The compositions of the solutions are given in Table 4.

Table 4. Composition of the test solutions.

Test medium	mg/l	Cl <sup>-</sup>	SO <sub>4</sub> <sup>=</sup>	F <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>++</sup>	Mg <sup>+</sup>
A		8100	1820	4	4800	54	1100	3
B		8000	-	-	5408	-	-	-

The copper sheet was washed, degreased, dried and weighed before the experiments. Fresh sheet was used for each experiment. The sheet was washed, dried and weighed after the experiment.

The sample flasks each hold about 100 ml of test solution, the top ends of the copper coil are about 10 mm below the water surface. The total gas volume is ca. 100 ml.

The conditions for each experiment are given in Table 5.

Table 5. Details of the experiments performed. Hydrogen evolution would be detected by the gas chromatograph if the hydrogen evolution rate from copper exceeds the value given in the last column of the table. The detection limit was calculated using equation (VI) assuming the detection limit for the gas chromatograph to be 1 vol. ppm H<sub>2</sub>.

Test	Medium	Temp. °C	Test Period h	Area of copper m <sup>2</sup>	Gas flow rate l.h <sup>-1</sup>	H <sub>2</sub> detection limit g(H <sub>2</sub> ).h <sup>-1</sup> .m <sup>-2</sup>
1	A	50	1008	0.24	0.1	0.037.10 <sup>-6</sup>
2	B	50	1008	0.24	0.1	0.037.10 <sup>-6</sup>
3	A	80	672	0.12	0.1	0.073.10 <sup>-6</sup>
4	B	80	672	0.12	0.1	0.073.10 <sup>-6</sup>

#### 2.4.1 Results

Hydrogen evolution was not detected under any of the conditions investigated.

After 1008 h the gas flow in experiments 1 and 2 was interrupted. The copper was left to corrode for another 50 h. The gas above the copper specimens was then collected by displacing with 400 ml nitrogen. The displaced gas was collected in a balloon and analyzed in the gas chromatograph. This is equivalent to a gas flow rate of 500 ml in 50 h, compared to the standard condition of 5000 ml in 50 h, i.e the sensitivity was increased by a factor of about 10 by this means. No hydrogen was detected.

Weight gains of about 1 mg at 50°C and 0.5 mg at 80°C (±0.5°C) were found in medium A and a weight loss of about 0.4 mg (±0.5) in medium B at 50°C.

### 2.4.2 Discussion

The measurements show that the rate of hydrogen production on copper in neutral chloride solutions containing about 8000 mg/l chloride ion at 50°C is less than  $0.0037 \cdot 10^{-6}$  g(H<sub>2</sub>).h<sup>-1</sup>.m<sup>-2</sup> (balloon experiment). This is 4000 times lower than that reported by Hultquist for copper in pure water at 25°C. The corrosion rate of copper is therefore < 0.0003 µm/a in these oxygen free chloride solutions.

According to Bjorndahl and Nobe /14/ the corrosion of copper in chloride solutions is controlled by the reaction:



$$E(\text{V nhe}) = -0.277 + 0.059 \log[\text{CuCl}_2^-]/[\text{Cl}^-]^2 \quad (\text{XI})$$

The cathodic partial reaction is the same as that in the absence of chloride ions, i.e.:



Reaction X is thus also oxidation by water producing hydrogen. Assuming that the solubility of copper as CuCl<sub>2</sub><sup>-</sup> is 10<sup>-5</sup> mol/l (15), the hydrogen partial pressure in equilibrium with copper would be of the order of 10<sup>-13</sup> bar using equations 9 and 11. This is higher than the partial pressure in the absence of chloride but is still well below detectable levels. The formation of copper chloride complexes only becomes significant in concentrated chloride solutions.

The weight changes are near the resolution of the technique used. Assuming that the weight gain in solution A at 50°C is due to Cu<sub>2</sub>O formation via reaction (V), 0.125 mg of hydrogen would be produced. If produced continuously this corresponds to a production rate of  $0.5 \cdot 10^{-6}$  g(H<sub>2</sub>).h<sup>-1</sup>.m<sup>-2</sup>. This would be detected by the gas chromatograph. The weight gain is probably due to reaction of copper with residual oxygen initially present in the cells. The corresponding steady state hydrogen production rate for solution B at 50°C assuming loss of copper is  $0.05 \cdot 10^{-6}$  g(H<sub>2</sub>).h<sup>-1</sup>.m<sup>-2</sup>. Copper chloride complex solubility would account for a 0.64 mg weight loss. The

weight change determinations cannot be used as a control for the hydrogen evolution as they are not precise enough and both weight losses and weight gains are possible.

In summary, it can be stated that the results presented here do not support the observations of Hultquist. No hydrogen evolution could be detected from the corrosion of copper in dilute chloride solutions, supporting the thermodynamic evidence that water cannot be an oxidant for copper in pure water or dilute chloride media.

Eriksen et al. /16/ also failed to confirm Hultquist's observations.

### 3. STRESS CORROSION CRACKING

#### 3.1 INTRODUCTION

Pitting corrosion and stress corrosion cracking are the two corrosion mechanisms which could lead to premature failure of a container. Pitting has been considered within the NAGRA programme, initial experimental work on stress corrosion cracking of carbon steels relevant to Swiss repository conditions is presented in this report.

#### 3.2 EXPERIMENTAL

Two experimental techniques were used to investigate the behaviour of cast steel GS 40 in the reference synthetic Böttstein groundwaters. These were Constant Extension Rate Testing (CERT) and immersion tests on wedge loaded Double Cantilever Beam (DCB) fracture mechanics specimens.

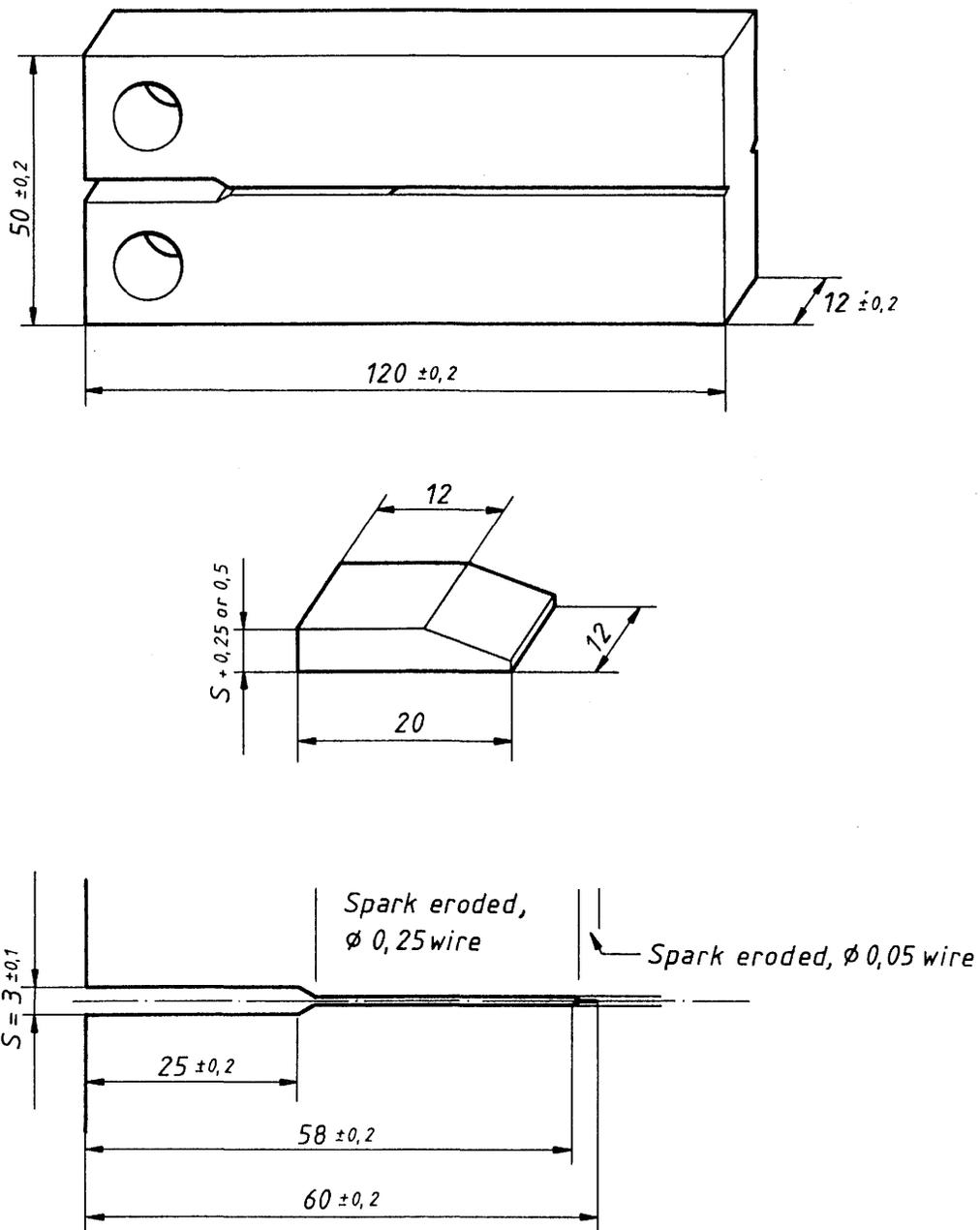
The CERT method consists of a tensile test performed on tensile specimens at a slow strain rate (the method is often called slow strain rate testing) in the corrosive medium. The tensile properties, in particular elongation and reduction of area, are compared with values obtained at the same temperature and strain rate in a neutral medium, in this case air.

The method is particularly suited to testing whether or not stress corrosion cracking is a possibility. Positive CERT indications do not always correlate to stress corrosion problems in service, but provided the test conditions are relevant, absence of an indication in the CERT test indicates that stress corrosion is extremely unlikely. The advantages and limitations of the test method are discussed by Parkins in a review article /17/.

The wedge loaded DCB specimens were immersed in the same apparatus used in this project /2,3,6/ for immersion testing.

The DCB specimens were cast steel GS40 standard 12 mm thick DCB specimens (Fig. 4), the specimens were pre-cracked by fatigue loading in air before the load wedge was inserted. Two nominal K-values 20 or 40 MPa.m<sup>-½</sup> were used. Duplicate 40 MPa.m<sup>-½</sup> specimens were exposed for each test condition and time; Two 20 MPa.m<sup>-½</sup> loaded specimens were added for the longest time exposures.

Figure 4. The wedge loaded DCB specimen.



### 3.3 CERT RESULTS

Conditions: Synthetic Böttstein water, 80°C,  
nitrogen purged, pH 8.3 - 8.5.

Specimens: GS 40, Tensile specimens, dia. 5 mm,  
length 20mm.

Strain rate: Nominal  $2 \times 10^{-7}$ /sec.

Series 1 Specimens under potentiostatic control.  
Results in Table 6.

Series 2 Specimens at free corrosion potential,  
-450 to -500 mV nhe.  
Results in Table 6.

Series 3 Specimens at free corrosion potential,  
-450 to -500 mV nhe.  
Strained at  $1 \times 10^{-6}$  sec<sup>-1</sup> to ca. 150% yield  
strength and then held for 1420 hours.  
Results in Table 7.

### 3.4 DISCUSSION CERT RESULTS

The most sensitive tensile parameters are the elongation and reduction of area at failure. The relevant figure is that in brackets where the experimental values are expressed as a percentage of the reference air value, below 100% indicates poorer performance in the corrosive environment. A drop of more than 10% is necessary before a possible sensitivity to the test medium is to be suspected.

Table 6. Results of CERT tests on GS 40 in synthetic Böttstein water at 80°C under potentiostatic control and at the free corrosion potential.

Potential mV n.h.e.	Elong. % (%air)		R of A % (%air)		Comments (#)
Air 80°C	23.3		45		Small secondary "cracks"
	22.3		48		
*	18.7		38		Small secondary "cracks"
*	17.6		32		Small secondary "cracks"
-650	10.4	(46)	21	(45)	Small secondary "cracks"
	20.9	(92)	42	(90)	
-600	18.3	(80)	42	(90)	Large secondary "crack"
	12.5	(55)	26	(56)	Small secondary "cracks"
-550	11.6	(51)	17	(37)	Large secondary "crack"
	21.7	(95)	48	(103)	
-500	10.2	(45)	22	(47)	Small secondary "cracks"
	21.2	(93)	49	(105)	Large secondary "cracks"
-450	14.1	(62)	34	(73)	Small secondary "cracks"
	12.6	(55)	26	(56)	Large secondary "crack"
-400	15.9	(70)	51	(110)	General corrosion
	14.8	(65)	39	(84)	General corrosion
-350	11.4	(50)	61	(131)	General corrosion
	7.9	(35)	56	(120)	General corrosion
Corr Pot	20.0	(88)	48	(101)	
	19.9	(87)	42	(88)	
	18.2	(80)	45	(95)	
	21.6	(95)	45	(95)	
	22.4	(98)	45	(95)	

# Secondary cracks are apparent cracks in the specimen away from the fracture site. In most cases these features are not due to stress corrosion but are caused by surface or near surface voids (see text and Figures 5-7).

\* See explanation in section 3.4.1.

Table 7. Results of strain and hold stress corrosion cracking testing.  
Specimens at free corrosion potential,  
Strained at  $1 \times 10^{-6} \text{ sec}^{-1}$  to ca. 150% yield strength and then held for 1420 hours.

Corr. potential mV n.h.e.	Hold stress N/mm <sup>2</sup>	Hold stress % Rp	Result
-405	331	147	No cracking
-410	336	149	No cracking
-417	352	156	No cracking
-411	316	140	No cracking

#### 3.4.1 CERT specimens held at -450 to -650 mV nhe

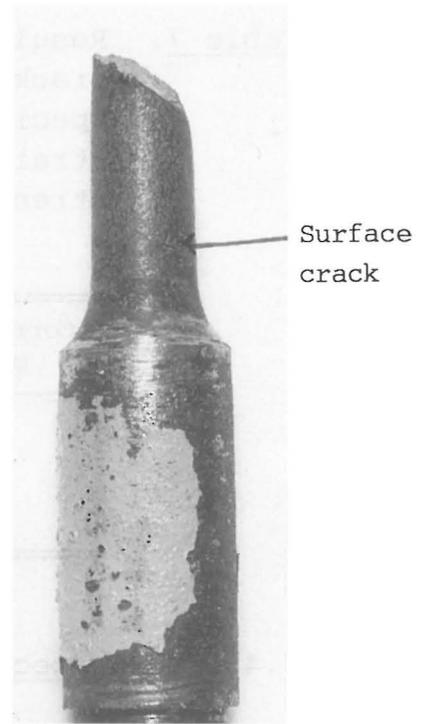
As can be seen from Table 6 most of the specimens tested at potentials cathodic to the free corrosion potential gave results below 90%. Another feature of the results is the large difference between the duplicate specimens. This first series of specimens were taken at random from the set of specimens prepared.

It was noticed at this stage that the specimens had been taken from a particularly poor area of the casting. Voids were visible on the machined surfaces of many of the remaining tensile test specimens. A small void in cross section is shown in figures 5-7. The specimens were then sorted and only those free of surface defects at ca 20X magnification were used for further testing. (About 70% of the remaining specimens were discarded.)

The results marked \* in Table 6 were from the first series of tests, i.e. from before the specimens had been sorted for surface defects. The first two results from specimens free of surface defects were used as the reference for calculating the change in properties when tested in the synthetic groundwater. It is clear that if the starred references had been used many of the percentage changes between air and the synthetic groundwater would have been

Figure 5

CERT test specimen tested at  
-450 mV nhe.  
El. 12.6%  
RA. 26%  
Appearance of a CERT specimen  
tested in the cathodic region  
with a lower than expected  
Elongation (El.) and reduction  
of area (RA.).



M 15860555

6 mm 

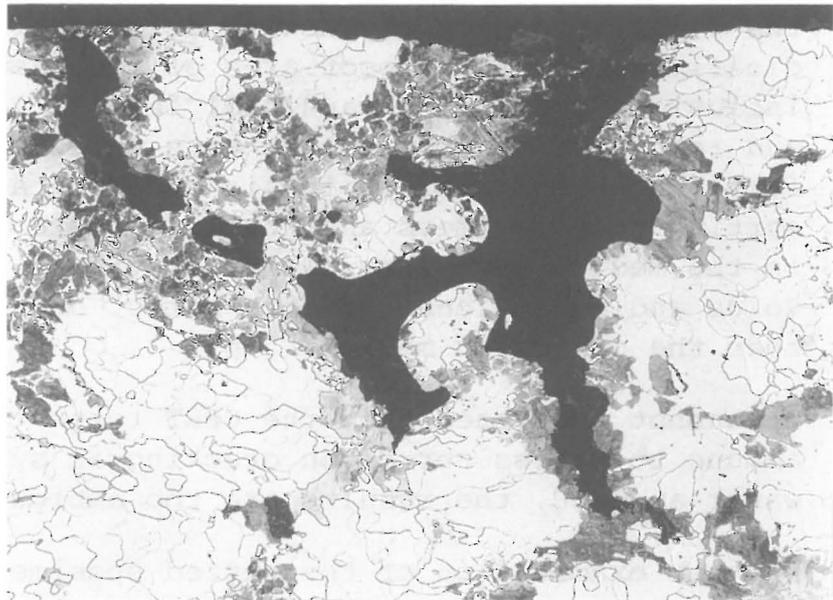
Figure 6 Detail from figure 5. Surface crack typical of those observed.



M 15860555

1 mm 

Figure 7 Section through surface feature in figure 6. The feature is a void, as indicated by the rounded contours. The crack like features at the bottom of the picture may be natural void boundaries or due to stress corrosion crack initiation in the void.



67716CD

100  $\mu\text{m}$  

closer to 100% and several way above; there is no rational explanation for values way above 100%.

The remarks in the comments column refer to cracks of the type pictured in figure 5 noticed in the post-test routine visual examination. The same feature is shown in figures 6 and 7. These features were observed away from the fracture surface. These features are often an indication of stress corrosion cracking. However, in this case the same features were observed on the air specimens (even on one of the sorted specimens), which means that the deterioration of tensile properties between the reference values is not necessarily due to stress corrosion but to the random presence of casting defects. The specimens were clearly taken from a poor area of the casting; voids and inclusions would also (and did) lead to lower elongation and reduction of area values even when tested in air. The fact that better values in air could be achieved by simply sorting the specimens and that duplicate specimens tested in the medium gave very different values suggest that the voids and inclusions had more effect on the tensile values than the corrosion medium.

It cannot be stated from the CERT tests that GS 40 is immune to stress corrosion cracking in synthetic Böttstein water at 80°C, the results are too ambiguous.

Further examination of the tested specimen does not help clarify the situation either. The detail of a void in figure 7 shows in the main the expected rounded contours of a void, however, the void extremities towards the centre of the specimen are not rounded. Although voids may have such a morphology it is also possible that these crack-like features are due to stress corrosion.

This series of tests does, however, raise the issue of the effects of material quality on the (stress) corrosion behaviour. Non-metallic inclusions are particularly detrimental to stress corrosion behaviour /18,19/.

#### 3.4.2 CERT specimens held at -350 and -400 mV nhe

These specimens were held in at potentials above the corrosion potential and actively corroded as can be seen from figures 8 and 9.

The corrosion loss decreases the cross section and explains the high values in the % reduction of area column. There is no evidence of stress corrosion on specimens held at potentials anodic to the free corrosion potential.

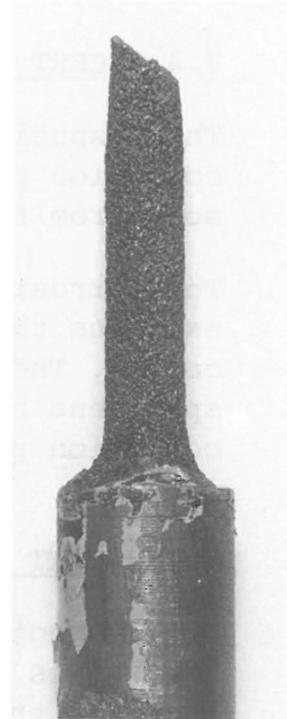
#### 3.4.3 CERT specimens held at the corrosion potential

These specimens were all taken from the sorted group. The values are all satisfactory, i.e the CERT test suggests that the material is not susceptible to stress corrosion cracking at the free corrosion potential.

This set of results would tend to support a hypothesis that the specimens held at the cathodic potentials (unsorted group) are indicating the presence of material defects rather than reacting to the environment.

Figure 8

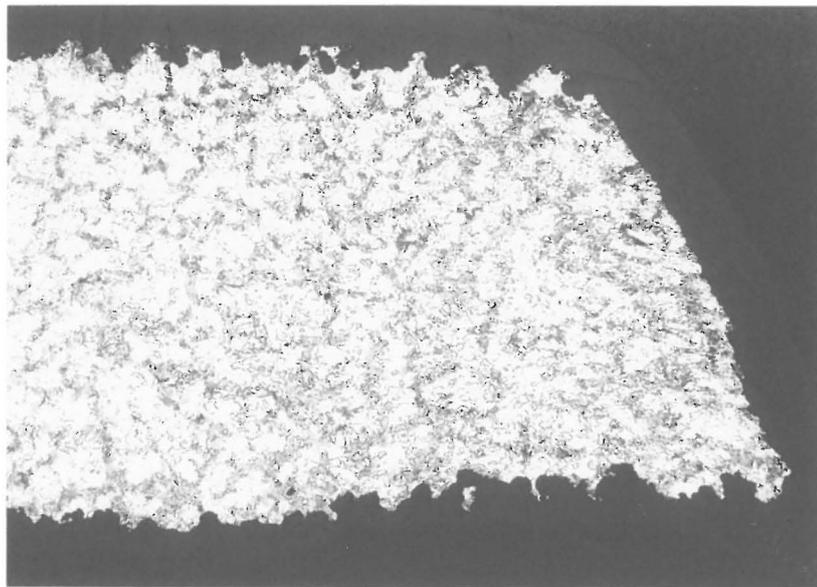
CERT test specimen tested at  
-350 mV nhe.  
El. 11.4%  
RA. 61%  
Appearance of a CERT specimen  
tested in the anodic region.  
Specimen is severely corroded.



M 15860884

6 mm 

Figure 9 Cross section of specimen in figure 8.  
Specimen is severely corroded.



67715CD

1 mm 

## 3.5 DCB RESULTS

The test conditions and times for the DCB specimens are given in Table 8

Table 8. Test conditions and test times for wedge loaded GS 40 DCB specimens.

Medium	Exposure time months
Böttstein + 0.1 mg/l O <sub>2</sub> 80°C	3
Böttstein anaerobic 80°C	3
Böttstein + 0.1 mg/l O <sub>2</sub> 140°C	3
Böttstein anaerobic 140°C	3
Böttstein + 0.1 mg/l O <sub>2</sub> 80°C	8
Böttstein anaerobic 80°C	8
Böttstein + 0.1 mg/l O <sub>2</sub> 140°C	6
Böttstein anaerobic 140°C	8
Böttstein + 0.1 mg/l O <sub>2</sub> 80°C	24
Böttstein anaerobic 80°C	27
Böttstein + 0.1 mg/l O <sub>2</sub> 140°C	16
Böttstein anaerobic 140°C	16

Specimens were evaluated in three ways after testing.

1. The specimens were opened in a tensile machine until a change in slope of the load displacement trace indicated that the wedge had been unloaded. The stress intensity could be calculated from this value. All specimens were still loaded (within ±10%) at the initial stress intensity. After the wedge was unloaded the specimens were broken open in liquid nitrogen.

2. The fracture surface of all specimens was examined at 50X magnification under a binocular microscope for signs of stress corrosion crack propagation between the fatigue pre-crack and the low temperature fracture surface. No such region could be identified on any of the specimens.
3. The fracture surfaces of the longest exposed specimens were examined in the scanning electron microscope (SEM) for evidence of stress corrosion crack propagation, both before and after chemical cleaning of the surface corrosion layer. Stress corrosion crack propagation could not be identified.

The best preserved fatigue crack regions were on the anaerobic specimens exposed at 140°C, see figure 10. The most difficult to evaluate was the aerated specimen at 80°C.

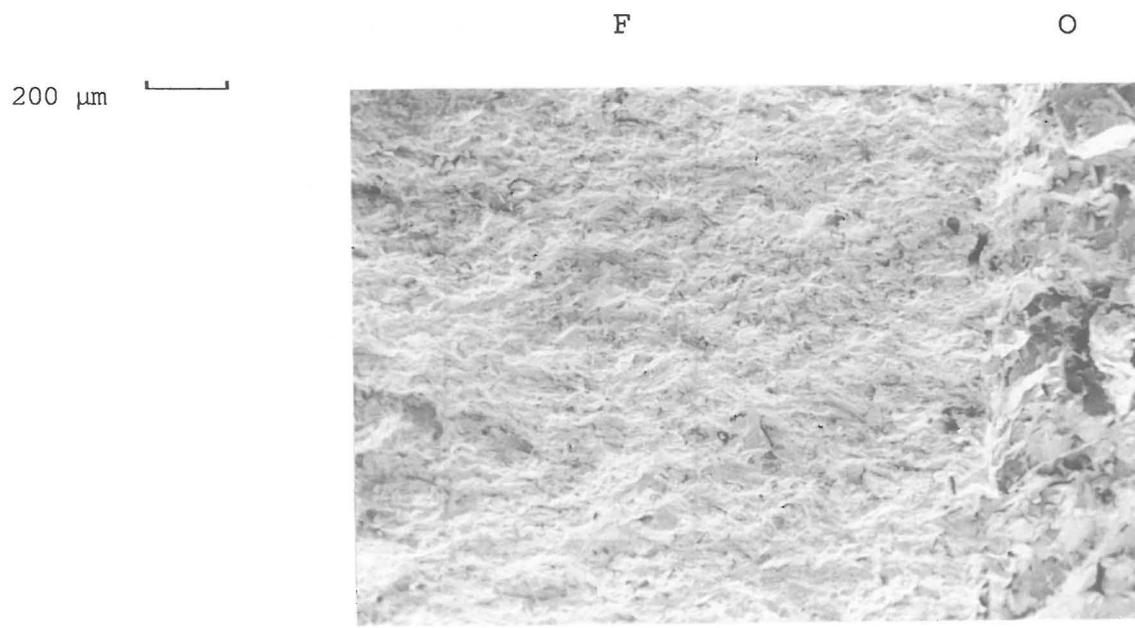
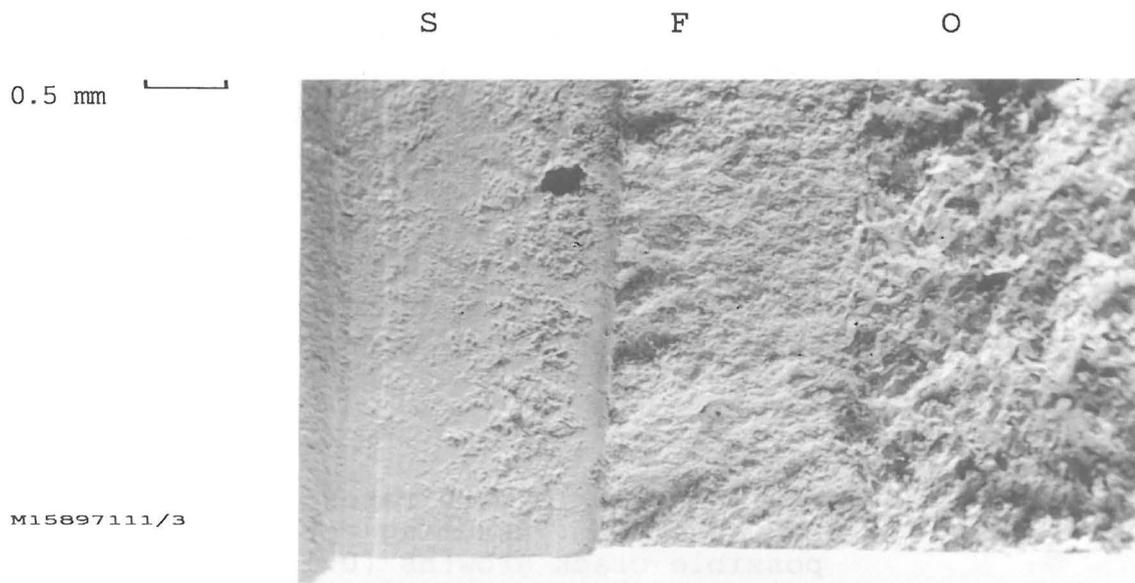
As no stress corrosion region could be identified, it is difficult to give an upper bound for the crack propagation rate as this depends on the estimate of the smallest stress corrosion crack advance which should be visible and/or detected.

The lift-off tests indicate that the crack growth (if any) was less than 0.5 mm.

This should easily be seen in the binocular microscope particularly as the fatigue crack end was marked by a scratch which was still clearly visible on the anaerobic specimens. A crack growth of > 0.5 mm would be noticed. No increase in crack length was noticed.

The SEM examination of all the 40 MPa.m<sup>-3/2</sup> loaded longest exposure time specimens revealed no evidence of crack propagation due to stress corrosion. No change in fracture surface morphology could be detected between the air fatigued pre-crack and the post test low temperature brittle fracture. The appearance of the fracture was similar for both aerated and anaerobic exposures except that the outer edge of the crack was more severely corroded in the former case.

Figure 10 Surfaces of DCB specimen tested at 80°C in Böttstein water under anaerobic conditions, 27 months exposure. The area marked "S" was spark eroded, that marked F is the air fatigue crack and that marked "O" is the overload fracture under liquid nitrogen. No change in surface morphology is visible between the fatigue crack region and the nitrogen fracture surface.



It is useful to express these results as a "maximum crack growth rate", (i.e. the DCB results show that the crack growth rate must be lower than this "maximum crack growth rate"). The most sensitive of the evaluation techniques is the SEM examination. It is assumed that stress corrosion would produce a different crack surface morphology and that this would be visible despite the effects of corrosion on the fracture surface. Bearing in mind these two assumptions, it is estimated from the SEM examination that the crack growth could not have been greater than 0.1 mm for anaerobic exposures. This value was arbitrarily increased to 0.2 mm for aerobic exposures to take account of possible masking of stress corrosion at the outer edges of the crack by corrosion.

Maximum crack growth rates for GS 40 are given in Table 9, assuming either 0.1 or 0.2 mm maximum crack extensions from SEM examination or 0.5 from the visual or lift-off estimate.

Table 9. Maximum crack growth rates from longest exposure DCB specimens. Assuming either SEM maximum possible crack growths (0.1 mm anaerobic, 0.2 mm aerobic) or lift-off/visual value (0.5 mm).

Medium	Maximum crack growth rate			
	SEM		Lift-off/visual	
	m/sec <sup>-1</sup>	mm/a	m/sec <sup>-1</sup>	mm/a
<u>aerated:</u>				
Böttstein 80°C	3.2 x 10 <sup>-12</sup>	0.1	8.0 x 10 <sup>-12</sup>	0.25
Böttstein 140°C	4.8 x 10 <sup>-12</sup>	0.15	12.0 x 10 <sup>-12</sup>	0.38
<u>anaerobic</u>				
Böttstein 80°C	1.4 x 10 <sup>-12</sup>	0.05	7.0 x 10 <sup>-12</sup>	0.25
Böttstein 140°C	2.4 x 10 <sup>-12</sup>	0.08	12.0 x 10 <sup>-12</sup>	0.4

### 3.6 DISCUSSION DCB RESULTS

Stress corrosion cracking can be thought of as a three-stage process: initiation or formation of a mechanical crack, an incubation or transient stage during which the chemical and electrochemical conditions at the crack tip stabilize, and finally the crack propagation stage.

Pre-cracked DCB specimens bypass the first stage, but one of the difficulties remains the time scale for the second phase. Incubation times of up to 37,000 hours have been reported for carbon steel in pure water at 280°C /20/. The fact that an incubation period may exist will always pose a problem interpreting data from stress corrosion specimens, the problem in this case is further complicated by the fact that no crack propagation phase was observed. It is, thus, not possible to distinguish an incubation phase from a steady state crack propagation phase. Nevertheless, the data show that the incubation, if any, in anaerobic conditions at 80 and 140°C is probably greater than 17,000 hours, and in aerated solutions at both temperatures probably greater than 11,500 hours.

In this report, the incubation period is treated as a phase in which crack growth is so slow that it does not grow sufficiently to be detected, i.e. assuming slow crack from time zero crack growth rather than a true incubation period. This is conservative only if the incubation period approaches or exceeds the service life. Nevertheless, long incubation times are the exception rather than the rule, and this method of calculating a maximum crack growth rate will be used for the remainder of the discussion.

The maximum crack growth rates (SEM values) under anaerobic conditions are almost low enough for them to be uncritical for the container with its 50 mm corrosion allowance. Considering the relatively short aerated phase expected, and the fact that the higher values for the aerated phase are based on an arbitrary (but conservative) higher maximum crack growth figure, the values in aerated solutions give no cause for immediate concern.

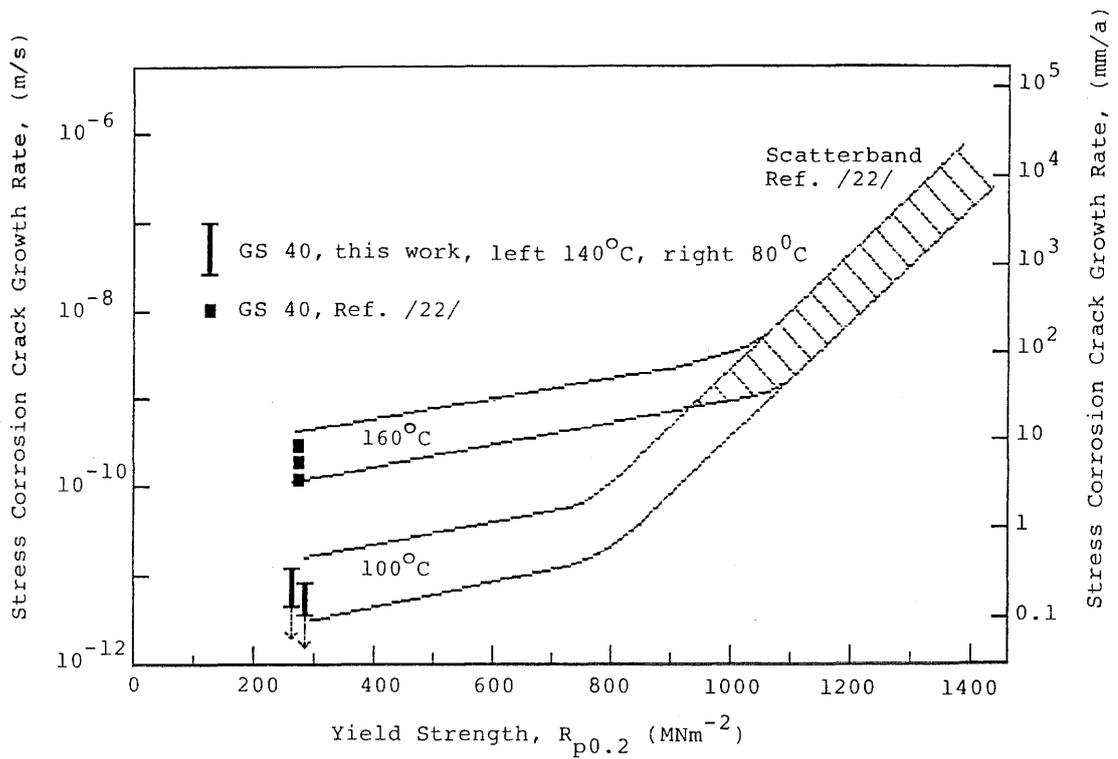
An increase in the measurement time by a factor of 2 (i.e. to 4 years) would be sufficient to confirm whether or not the crack growth in 1000 years would exceed the corrosion allowance of 50 mm on the assumption that the system is not subject to an exceptionally long incubation period.

Practically no stress corrosion crack propagation rate data is available for cast steels similar to GS 40. Pre-cracked fracture mechanics specimens of wrought mild steel plate under constant load were included in the US Basalt Waste Isolation Programme, they found no crack growth after 2000 hours at 150°C under essentially anaerobic conditions in a groundwater with ca. 300 mg/l chloride, and could not detect crack growth based on compliance measurements (similar to the lift-off technique used in this study). The sensitivity was about 0.5 mm minimum crack extension for detection. Microscopic examination was inconclusive /21/. The maximum crack growth rate of 2.2 mm/a is too high because of the short observation period to be of great significance, but is at least in agreement with the results from this programme.

In contrast Magdowski and Speidel /22/ detected crack growth in GS 40 DCB specimens immersed in aerated pure water at 160°C, reporting crack growth rates of  $1-3 \times 10^{-10} \text{ m/sec}^{-1}$  (3-10 mm/a). Crack growth rates generally fall as the strength of the material decreases, i.e. in the limit low strength materials are immune to stress corrosion cracking. Magdowski and Speidel showed that the decrease in crack growth rate with decrease in strength is less marked in low strength materials than in high strength materials in oxygenated pure water, see figure 11. Results from this work suggest that oxygenated pure water may be a more severe environment than the high chloride groundwater; maximum growth rates from this study plotted show lower rates than would be expected for pure oxygenated water (figure 11), particularly as values calculated from observed crack growths are compared with maximum crack growth rates based on crack growth detection limits and exposure times.

Figure 11

Crack growth propagation rate of carbon and low alloy steels in oxygenated pure water at 100 and 160°C as a function of yield strength /22/. The results from this test programme are the range bars at the bottom left of the diagram marked 80 and 140°C. These are for aerated specimens; the lower bound of the range bar is according to the SEM estimation, the upper bound from the lift-off/visual examination. The arrow below the bar indicates that these are maximal possible rates, i.e. no crack growth was detected in contrast to the rest of the points.



#### 4. GENERAL DISCUSSION

This report marks the conclusion of the first NAGRA programme on the evaluation of container materials for disposal of high level waste in a crystalline formation. The bulk of the effort has concentrated upon investigating the suitability of cast low carbon steel as a container material.

Since other potential host rocks for a Swiss high level repository are being currently considered, the service conditions, in particular the corrosion environment, are not definitive, the programme has concentrated on general behaviour and suitability rather than site specific qualification of the material.

Nevertheless, it has been shown that carbon steel along with pure copper remains a candidate material for high level waste containers in model Swiss conditions.

General corrosion of low carbon steels would appear to be no cause for concern over a wide range of groundwater compositions, except possibly for the accompanying production of hydrogen.

The most probable causes of eventual failure of cast carbon steel containers are pitting and stress corrosion cracking. Although this programme has indicated that failure through these mechanisms is unlikely during the design life of 1000 years, they are two issues which will have to be treated in more depth when a final repository site is identified, as both of these phenomena are more sensitive to differences in conditions, particularly groundwater composition, than general corrosion.

Resistance to pitting and stress corrosion is also more difficult to demonstrate. Within this programme an attempt has been made to demonstrate that these two corrosion forms do not occur (see Part III /6/ for pitting corrosion, where it was demonstrated that corrosion conditions are unsuitable for pit initiation and growth, and this report, where stress corrosion was not observed). It should, however, be recognised that it is difficult to

demonstrate, from experiments on a time scale much shorter than the design life, that corrosion forms which can exhibit long incubation times will in fact not occur.

In this context it may be useful to briefly mention alternative approaches to these two issues; two in particular, one for pitting and one for stress corrosion from other waste disposal programmes may form an appropriate basis for future corrosion programmes when site specific testing is required. Both seek to circumvent the lack of a possibility of modelling or extrapolating in time inherent in experiments which attempt to demonstrate the negative, by producing data which can be used in a predictive model.

#### 4.1 PITTING CORROSION

The most detailed treatment of pitting in carbon steels under repository conditions similar to the Swiss conditions is that of Marsh and co-workers /23, 24/. They used a combination of mathematical modelling and experimental studies to evaluate the rate of general corrosion and pitting over the container life. The model showed /23/ that pits will not propagate under anaerobic conditions; however an initial aerobic period must be expected for any type of repository. Marsh et al. assumed that this aerobic period would last 125 years. From an extreme value statistics evaluation of pit depth determinations under aerobic conditions they estimated that 10 percent of all containers would be pitted to a depth of 143 mm in the 125 year period. This work /23,24/ provides a sound basis for evaluating pitting, provided that data under relevant conditions are available. However, Marsh et al. had to resort to a test solution more favourable to pitting than would be present in a repository to produce reliable data for extreme value analysis in the time available. Thus their conclusions may well be over-conservative. Their work nevertheless illustrates the importance of the time during which the repository is aerobic for the life of a carbon steel container.

#### 4.2 STRESS CORROSION

As was discussed in section 3.6, one of the problems in proving that stress corrosion is not a potential cause of premature failure of a container is the possibility of very long incubation periods which even for constant loaded fracture mechanics specimens cannot be ruled out.

An alternative, as described by James /25/, is to resort to fatigue testing pre-cracked fracture mechanics specimens. Cyclic loads are not expected under repository conditions, but they are the most satisfactory means of accelerating the environmental cracking process, as no change of environment or temperature are necessary.

With this method crack growth was observed at stress intensities and for testing times where static testing in the Basalt Waste Isolation Programme /21/) under identical exposure conditions produced no measurable crack growth.

James was able to identify a threshold stress intensity for fatigue crack propagation which was independent of frequency. However, he observed that the crack growth rate decreased with decreasing cyclic stress frequency. His experiments suggest that one way of avoiding potential problems with incubation effects would be to start DCB tests under cyclic fatigue loading and, once crack growth has been established, to return to a static load and measure the crack growth velocity under this static load.

#### 4.3 CONCLUDING REMARKS

Copper and cast steel have been confirmed as suitable container materials. It should, however, be borne in mind that both pitting corrosion and stress corrosion are sensitive to the groundwater chemistry and in particular the duration of the aerobic phase in the immediate post closure period of the repository: further work should concentrate on these topics.

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