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TECHNICAL REPORT 86-25

Experiments on Container Materials for Swiss High-Level Waste Disposal Projects Part III

J.P. Simpson
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December 1986

Sulzer Brothers Ltd, Winterthur

Parkstrasse 23 5401 Baden/Schweiz Telephon 056/20 55 11

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

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

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

SUMMARY

The present 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 is required to function as a high integrity barrier for at least 1000 years.

This report is the third in a 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. It was concluded that further corrosion testing was needed to confirm these materials as candidate container materials. In the second of these reports it was shown that cast steel possessed sufficient corrosion resistance under repository conditions for it to be considered as the primary candidate material for a high-level waste container. The long term corrosion rate was estimated to be 20 µm/a.

The chemical analyses of groundwaters carried out in the course of the Nagra geological programme suggested that the standard water composition used in the first series of corrosion tests with a total dissolved solids content of 3200 mg/l and 0.1 µg/g oxygen was considerably less saline and more oxidising than those to be expected in a Swiss high-level repository (total dissolved solids typically 15000 mg/l and virtually oxygen free).

Immersion tests were carried out in both waters at 80 and 140°C with two levels of oxygen, zero and 0.1 µg/g. The corrosion of cast steel as well as nodular cast iron under all conditions tested was uniform. It was observed that the corrosion rate was greater in the higher salinity water and at the higher oxygen level. The effect of temperature was not so marked. 6000 hour exposure corrosion rates observed were as high as 60 µm/a for cast steel in Böttstein water with 0.1 µg/g oxygen at 80°C and 31 µm/a at 140°C. The oxygen will be quickly consumed (e.g. by the corrosion reaction itself) and anaerobic conditions will predominate shortly after closure. The relevant long term data are therefore the zero oxygen results which range from 4 µm/a in Säckingen water at 140°C to 18 µm/a in Böttstein water at 140°C.

Long term corrosion tests were also carried out in water saturated highly compacted sodium bentonite at 80 and 140°C; under conditions which approximate the conditions in the proposed repository. The corrosion rates for cast steel at 6000 h exposure time were in the range 4-13 µm/a.

Pitting was not observed on the corrosion coupons in the immersion or bentonite tests. Nevertheless, it could be that variations in the groundwater chemistry would lead to severe pitting in particular in the early stages when sufficient oxygen

is present. The effects of variations on the main components of the groundwater, i.e. chloride and sulphate, and the role of carbonate, were investigated. Pitting requires a degree of passivity of the rest of the surface for deep pits to grow. Electrochemical measurements showed that passivity was possible at the temperatures tested (50 and 80°C). The most important factors are chloride, carbonate and pH. Carbonate and high pH values promote passivity but high chloride levels although they promote pitting also decrease the passive range so their effect can be to increase or decrease the tendency for pitting depending on the levels of the other two parameters. The electrochemical investigation confirmed the observation that pitting should not occur in the two reference waters.

The 6000 hour corrosion rates from both the immersion testing and in bentonite were below the long term estimate of 20 µm/a assumed for cast steel in the repository for oxygen free conditions. This is the relevant condition for the bulk of the life of the container. There is thus no reason to doubt that this estimate of the overall long term corrosion rate is conservative.

ZUSAMMENFASSUNG

Das gegenwärtige Konzept zur Beseitigung hochaktiver Abfälle in der Schweiz besteht aus einem Endlager in einer Tiefe von 1'000 bis 1'500 m im kristallinen Untergrund der Nordschweiz. Die Abfälle werden in einem Behälter eingelagert, der während mindestens 1'000 Jahren als technische Barriere mit hoher Integrität funktionieren soll.

Dieser Bericht ist der dritte in einer Serie, die sich mit der Evaluation potentieller Werkstoffe für solche Behälter befasst. Vier Materialien wurden im ersten Bericht für eine weitere Auswertung identifiziert: Stahlguss, Kugelgraphit-Gusseisen, Kupfer und Ti-Code 12. Es wurde daraus geschlossen, dass weitere Korrosionsversuche nötig sind, um die Eignung dieser Werkstoffe als mögliche Behältermaterialien zu bestätigen. Im zweiten Bericht wurde gezeigt, dass Stahlguss eine genügende Korrosionsbeständigkeit unter Endlagerbedingungen besitzt, um als primärer Werkstoff für einen Behälter für hochaktive Abfälle betrachtet zu werden. Die Langzeit-Korrosionsgeschwindigkeit wurde auf 20 µm/a geschätzt.

Die im Laufe des geologischen Untersuchungsprogramms der Nagra durchgeführten chemischen Grundwasseranalysen deuteten darauf hin, dass die Zusammensetzung des Standardwassers, mit einer Gesamtmenge an gelösten Stoffen von 3'200 mg/l und 0.1 µg/g Sauerstoff, welches in der ersten Serie von Korrosionsversuchen benützt wurde, bedeutend weniger salzhaltig und oxidierender war als die in einem schweizerischen Endlager für hochaktive Abfälle zu erwartenden Grundwässer (Gesamtmenge an gelösten Stoffen typischerweise 15'000 mg/l und praktisch sauerstoffrei).

Immersionsversuche wurden in beiden Wässern bei 80 und 140°C mit zwei Sauerstoffgehalten (Null und 0.1 µg/g) durchgeführt. Die Korrosion von Stahlguss sowie von Kugelgraphit-Gusseisen war unter allen getesteten Bedingungen einheitlich. Es wurde beobachtet, dass die Korrosionsgeschwindigkeit im Wasser höherer Salinität und mit höherem Sauerstoffgehalt grösser war. Der Einfluss der Temperatur war nicht so ausgeprägt. Nach 6'000 Stunden Immersion wurden Korrosionsgeschwindigkeiten bis zu 60 µm/a für Stahlguss in Böttstein-Wasser mit 0.1 µg/g Sauerstoff bei 80°C und bis zu 31 µm/a bei 140°C gemessen. Der Sauerstoff wird schnell verbraucht (z.B. durch die Korrosionsreaktion selbst), daher herrschen kurz nach Verschluss anaerobische Bedingungen. Die betreffenden Langzeitdaten sind also die Resultate für Null-Sauerstoff, die sich von 4 µm/a in Säckinger-Wasser bei 140°C bis 18 µm/a in Böttstein-Wasser bei 140°C erstrecken.

Langzeit-Korrosionsversuche wurden auch in wassergesättigtem hochkompaktiertem Na-Bentonit bei 80 und 140°C unter endlagernahen Bedingungen durchgeführt. Die Korrosionsgeschwindigkeiten für Stahlguss nach 6'000 Stunden Aussetzung lagen im Bereich von 4 - 13 µm/a.

Auf den Korrosionsproben der Immersions- und Bentonitversuche wurde kein Lochfrass beobachtet. Trotzdem könnte es sein, dass Aenderungen in der Grundwasserchemie zu starkem Lochfrass führen könnten, vor allem in den frühen Phasen mit genügendem Sauerstoff. Die Einflüsse von Aenderungen der Hauptbestandteile des Grundwassers (d.h. Chlorid und Sulfat) und der Einfluss des Carbonats wurden untersucht. Lochfrass braucht eine bestimmte Passivität der restlichen Oberfläche, um zu tieferen Löchern zu führen. Elektrochemische Messungen haben gezeigt, dass Passivität bei den untersuchten Temperaturen (50 und 80°C) möglicht ist. Die wichtigsten Faktoren sind Chlorid, Carbonat und pH. Während Carbonat und hohe pH-Werte die Passivität steigern, können hohe Chlorid-Gehalte sowohl Lochfrass fördern als auch den passiven Bereich vermindern; sie können also den Ansatz zum Lochfrass entweder erhöhen oder vermindern, abhängig von den Werten der anderen zwei Parameter. Die elektrochemische Untersuchung bestätigte die Beobachtung, dass Lochfrass in den zwei Referenzwässern nicht vorkommen sollte.

Die 6'000 Stunden-Korrosionsgeschwindigkeiten, abgeleitet aus den Immersionstests und jenen im Bentonit, lagen uner der Langzeitabschätzung von 20 µm/a für Stahlguss im Endlager unter anaerobischen Bedingungen. Diese Bedingung ist relevant für den Grossteil des Behälterlebens. Es besteht also kein Grund zur Revision der Abschätzung der gesamten Langzeit-Korrosionsgeschwindigkeit.

RESUME

La conception actuelle de l'élimination des déchets hautement radioactifs en Suisse repose sur un dépôt final aménagé entre 1'000 et 1'500 mètres de profondeur à l'intérieur du socle cristallin du nord de la Suisse. Les déchets sont emmagasinés dans un conteneur devant assumer la fonction de barrière ouvragée avec une intégrité élevée, pendant au moins 1'000 ans.

Ce rapport est le troisième d'une série traitant de l'évaluation des matériaux entrant en question pour la fabrication de tels conteneurs. Le premier rapport a identifié quatre matériaux pour une nouvelle évaluation: l'acier moulé, la fonte à graphite sphéroïdal, le cuivre et le Ti-Code 12. Il a été conclu que d'autres essais de corrosion étaient nécessaires pour confirmer si ces matériaux se prêtaient à la construction de conteneurs. Le deuxième rapport montre que, dans des conditions de dépôt final, l'acier moulé possède une résistance à la corrosion suffisante pour qu'on le considère comme un matériau approprié à la fabrication de conteneurs pour déchets hautement radioactifs. La vitesse de corrosion à long terme a été estimée à 20 µm/a.

Réalisées au cours du programme de recherches géologiques de la Cédra, les analyses chimiques des eaux souterraines ont montré que la composition de l'eau standard - avec une quantité totale de substances dissoutes de 3'200 mg/l et 0.1 µg/a d'oxygène -, utilisée lors de la première série d'essais sur la corrosion, était nettement moins saline et oxydante que les eaux souterraines escomptées dans un dépôt final pour déchets de haute radioactivité (quantité totale de substances dissoutes typiquement de 15'000 mg/l et pratiquement exempte d'oxygène).

Des essais d'immersion ont été réalisés dans les deux eaux, à des températures de 80 et de 140°C et avec deux teneurs en oxygène (zéro et 0.1 µg/g). La corrosion de l'acier moulé et celle de la fonte à graphite sphéroïdal est restée homogène dans toutes les conditions testées. On a observé que la vitesse de corrosion était plus grande avec l'eau de salinité plus élevée et avec une teneur en oxygène plus importante. L'influence de la température n'était pas aussi marquée. Après une immersion de l'acier moulé de 6'000 heures dans l'eau de Böttstein (0.1 µg/g d'oxygène), on a mesuré des vitesses de corrosion allant jusqu'à 60 µm/a à 80°C et de 31 µm/a à 140°C. L'oxygène s'épuise rapidement (par example par la réaction à la corrosion elle-même), raison pour laquelle des conditions anaérobies prévalent peu après la fermeture. Les données à long terme en question sont donc les résultats pour zéro oxygène; ils vont de 4 µm/a dans l'eau de Säckingen à 140°C à 18 µm/a dans l'eau de Böttstein à 140°C.

Des essais de corrosion à long terme ont également été réalisés dans de la bentonite Na saturée en eau et fortement compactée, à 80 et 140°C, dans des conditions proches de celles prévalant dans un dépôt final. Les vitesses de corrosion pour l'acier moulé, après une exposition de 6'000 heures, étaient de l'ordre de 4 à 13 µm/a.

On n'a pas relevé de piqûre de corrosion sur les échantillons de corrosion des essais d'immersion et des tests réalisés dans la bentonite. Des modifications de la chimie des eaux souterraines pourraient cependant entraîner une forte corrosion localisée, surtout dans les premières phases où il y a suffisamment d'oxygène. On a analysé les influences de changements des éléments principaux de l'eau souterraine (c'est-à-dire chlorure et sulfate) et l'influence du carbonate. Les piqûres de corrosion ont besoin d'une certaine passivité du reste de la surface pour qu'il y ait des trous plus profonds. Des mesures électro-chimiques ont montré que la passivité est possible aux températures analysées (50 et 80°C). Les facteurs les plus importants sont le chlorure, le carbonate et le pH. Tandis que le carbonate et des valeurs élevées de pH augmentent la passivité, des teneurs élevées en chlorure peuvent aussi bien favoriser les piqûres de corrosion que réduire le domaine passif; elles peuvent donc augmenter ou réduire la tendance à la corrosion, en fonction des valeurs des deux autres paramètres. L'étude électro-chimique a confirmé l'observation selon laquelle il ne devrait pas y avoir de corrosion localisée dans les deux eaux de référence.

Les vitesses de corrosion de 6'000 heures, déduites des essais d'immersion et de ceux réalisés dans la bentonite, étaient inférieures à l'estimation à long terme de 20 µm/a pour l'acier moulé dans le dépôt final, dans des conditions anaérobies. Cette condition est importante pour une grande partie de la vie du conteneur. Il n'y a donc pas de raison de réviser l'estimation de la vitesse de corrosion à long terme totale.

CONTENTS

1. INTRODUCTION

The present 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. Technical 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.

This report is the third of a series dealing with the choice and evaluation of materials for the containers. The design criteria for the containers are discussed in Part I /1/. 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 identified as candidate materials for high level waste containers were:

i) iron or steel (unalloyed or low alloy)
ii) copper
iii) titanium or titanium alloy
iv) a nickel-chrome-molybdenum alloy
v) 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 /2/ 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 /3/.

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", no site has yet been chosen. This in turn means that a definitive groundwater chemistry for the repository is not available although investigation of the 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 will be described in section 2 of this report.

The immersion tests on cast steel and nodular cast iron were continued as were the corrosion tests in bentonite. The test methods were described in detail in Part II /2/. The results of the immersion tests will be presented in section 3 and the bentonite tests in section 4.

2. INVESTIGATION OF THE EFFECTS OF CHLORIDE AND SULPHATE IONS, AND pH ON THE PITTING BEHAVIOUR OF CAST STEEL AT 50 AND 80°C.

2.1 Introduction

Cast steel is a candidate material for containers for the final disposal of high level waste. Corrosion is the life limiting factor for cast steel containers in the proposed repository. Grauer in his review of the corrosion behaviour of iron and low-alloy steel under repository conditions concluded that the average corrosion rate on this class of materials would be acceptably low, probably below 50 µm/a. This was confirmed within the NAGRA corrosion programme /1,2/ where values under 10 µm/a were found for cast steel in a model synthetic groundwater. The working party in its report for "Projekt Gewähr" considered a corrosion allowance of 50 mm sufficient for a 1000 year lifespan /4/. The reference container has a corrosion allowance of 50 mm /5/.

These corrosion allowances are based on long term experimental evidence /1,2,6,7/ which suggests that localized corrosion in the form of pitting becomes indistinguishable from the average corrosion rate at long exposure times.

In his review of pitting on iron in 1970, Foley /8/ was unable to identify a universally accepted mechanism for the pitting behaviour of iron; the situation had not changed when Janik-Czachor and Kaszczyszyn /9/ again reviewed the subject in 1979. It is thus not possible to predict the effects of different ions on the pitting behaviour of iron.

Pitting occurs when the passive film is ruptured by the presence of an aggressive ion, passivation is thus a prerequisite for pitting. The ions which are known to promote pitting on iron are, in decreasing order of aggressivity:

$SO_4^{=} > Cl^- > Br^- > I^-$ /10,11/,

and the ions which promote passivity are:

$CO_3^{=}, HCO_3^-, NO_3^-, PO_4^{3-}$ and Fe(CN), /12,13/.

The pitting potential E_{pit} is dependent upon the concentration of the aggressive species C_{x-}, and the passivators C_{pass}; the following relationship is generally found:

$$E_{pit} = a + b\log(C_{x-}/C_{pass}) \quad /9/$$

The effect of chloride is strong, b can have values of 100 mV/decade or more /12,14/. It should be noted that as the concentration of the aggressive species is increased the pitting potential and the passivation potential will converge and as passivation must occur before pitting, pitting will no longer be possible.

It has also been observed that an increase in the concentration of the aggressive species increases the passive current density /11/, increases the number of pits /12/ and decreases the initiation time for pitting /15/.

Marsh et al /16/ have demonstrated that low carbon steels similar to GS 40 will passivate in carbonate solutions, the passive region on kinetic pH-potential diagrams extending to lower pH values the higher the bicarbonate -carbonate concentration. The presence of the chloride ion can cause local breakdown of passivity i.e. pitting. At 1000 µg/g Cl^-, the passive region started at pH 9.8 with carbonate-bicarbonate at 0.001 m and at pH 9 at 0.01 m carbonate-bicarbonate. Deep pitting can only be expected on passive surfaces; carbon steel should thus only suffer from general corrosion at pH values lower than the passive region in these chloride-carbonate-bicarbonate media.

The model groundwater (Böttstein water - composition given in table 1) contains both carbonate-bicarbonate and chloride ions. Passivity and hence pitting could, therefore, be expected if the pH were sufficiently high. The pH of the groundwater in granite in the repository is expected to be pH 6.8, below the reported passivation range.

It is proposed to backfill with bentonite, and it is known that bentonite will raise the pH of the groundwater reaching the container; pH values above 9 may have to be considered. In this case it cannot be assumed that the data analysed for local attack where the local penetration and the overall corrosion rate converge with time are still applicable as this data is for seawater with a pH around 8 i.e in the general corrosion range according to Marsh et al /16/.

This study is intended to investigate the effects of temperature, chloride, sulphate and bicarbonate/carbonate on the active, passive and pitting behaviour of cast steel. Chloride and sulphate represent the bulk of the anions in granitic groundwaters and the pH is predominantly controlled by the carbonate sytem.

Cations:	µg/g	Anions:	µg/g
Na^+	4038	Cl^-	6620
K^+	45	F^-	2.8
Mg^{++}	2.6	$SO_4^=$	1560
Ca^{++}	870	Silicates (as SiO_2)	17
Sr^{++}	21		
Mn (tot)	3.1		
Fe (tot)	0.5	Dissolved carbonates (tot)	1.91 mmol/l
U (tot)	10^{-4}	Alkalinity	1.58 meq/l

Dissolved gases:		pH, Eh:
log ($p(O_2)$/1 atm)	-59	pH = 6.8
log ($p(CO_2)$/1 atm)	-1.73	Eh = -60 mV to -230 mV

Table 1. NAGRA Gewähr reference water (Böttstein water)

2.2 Method.

A convenient way of presenting the effects of temperature, chloride, sulphate and bicarbonate/carbonate on the active, passive and pitting behaviour is to produce kinetic pH-potential diagrams such as those produced by Marsh et al /16/.

Two experimental techniques were used to produce these diagrams:

A) Potentiostatic,
B) Potentiodynamic.

2.2.1 A) Potentiostatic technique.

With the potentiostatic technique, the specimen is first polarized cathodically to reduce surface oxide films and then potentiostatically held at a set potential and the current recorded. Three distinct types of behaviour are observed. The corresponding current-time curves are shown in figure 2.1.

Type 1. Active corrosion.
The current either increases with time or starts at a high level and remains there (figure 2.1a). The surface of the specimen is evenly corroded.

Type 2. Passive.
The current decreases with time to a value below 1 $\mu A/cm^2$ and remains low for the duration of the experiment, figure 2.1b. (In this case the current was monitored for a minimum of 50 h.) The surface of the specimen is not corroded, grinding marks are clearly visible although the surface may be slightly discoloured by a translucent surface film.

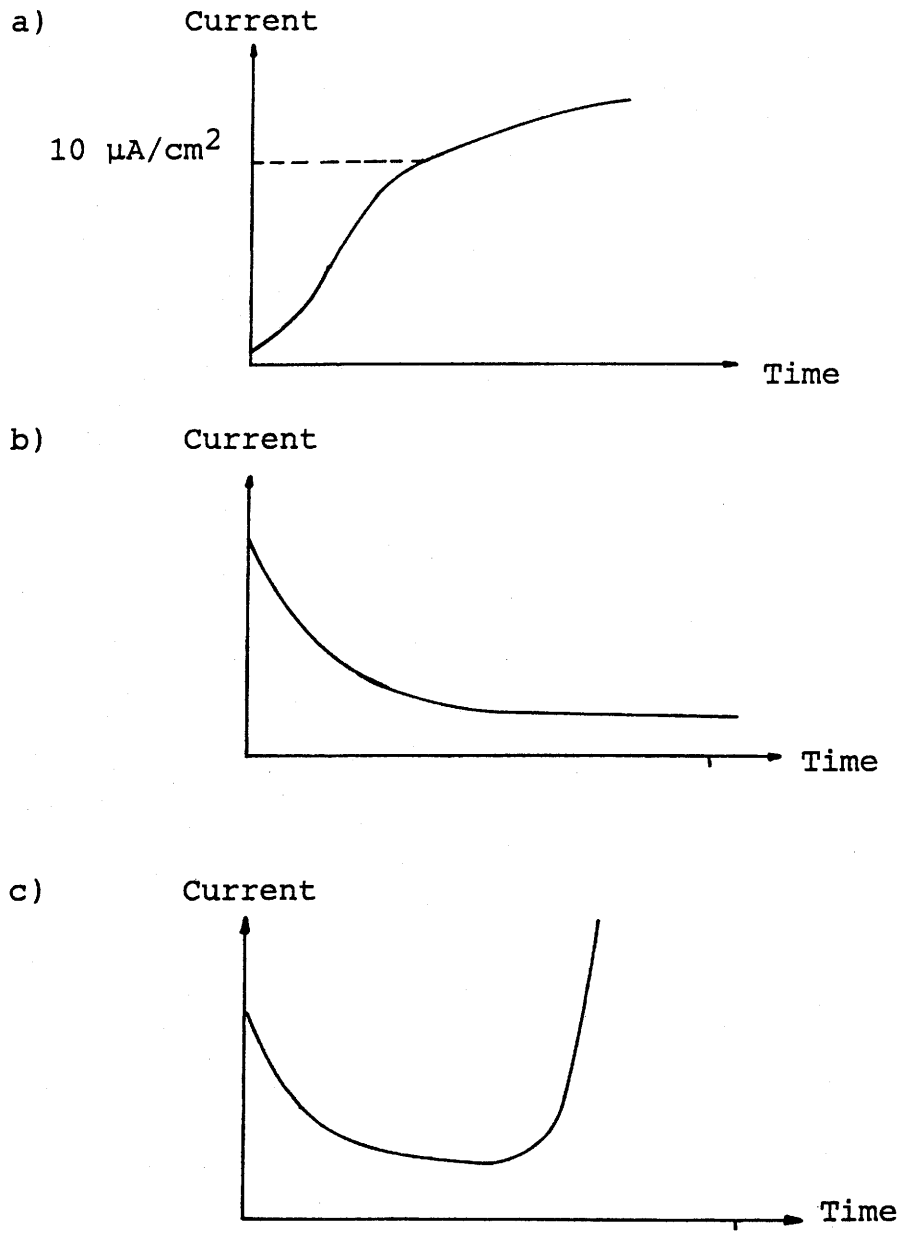

Figure 2.1 Current-time characteristics on potentiostatic polarization.
a) Active corrosion
b) Passive behaviour
c) Pitting

Type 3. Pitting.
The current decreases initially as for type two but increases in less than 50 h. The surface of the specimen is pitted, figure 2.1c.

2.2.2 B) Potentiodynamic technique.
The specimen is first polarized cathodically to reduce surface oxides and then the potential scanned from this initial value in the positive direction until the current density exceeds 1 mA/cm^2. Typical current potential curves are shown in figure 2.2. The same three basic types of behaviour can be recognised.

Type 1. Active corrosion.
The anodic current increases with potential and exceeds 1 mA/cm^2 without showing a decrease. The specimen is evenly corroded.

Type 2. Passive.
The current increases initially with increasing potential but then decreases and attains an approximately constant value. If the test is interrupted with the current in the passive range, the specimen surface is barely corroded.

Type 3. Pitting.
After an active/passive transition on further increasing the potential the current increases sharply. The specimen is pitted.

Kinetic pH-potential diagrams with domains for active corrosion, pitting and passivity can be constructed using both these techniques. The potentiodynamic technique is less time consuming at the potential scan rate used (20 mV/min) and was thus the method chosen for the parameter study. It is also possible to derive some useful kinetic parameters such as the active peak current density on passivation, a measure of the ease of passivation.

2.3 Test solutions.

Two waters were used, Böttstein(2) water, a synthetic water somewhat more saline than the Gewähr reference water but within the range variation expected for this water, and Säckingen water, a natural source water.

The major part of this study consisted of a parameter study of the effect of pH, chloride and sulphate concentration, temperature and the carbonate buffer system.

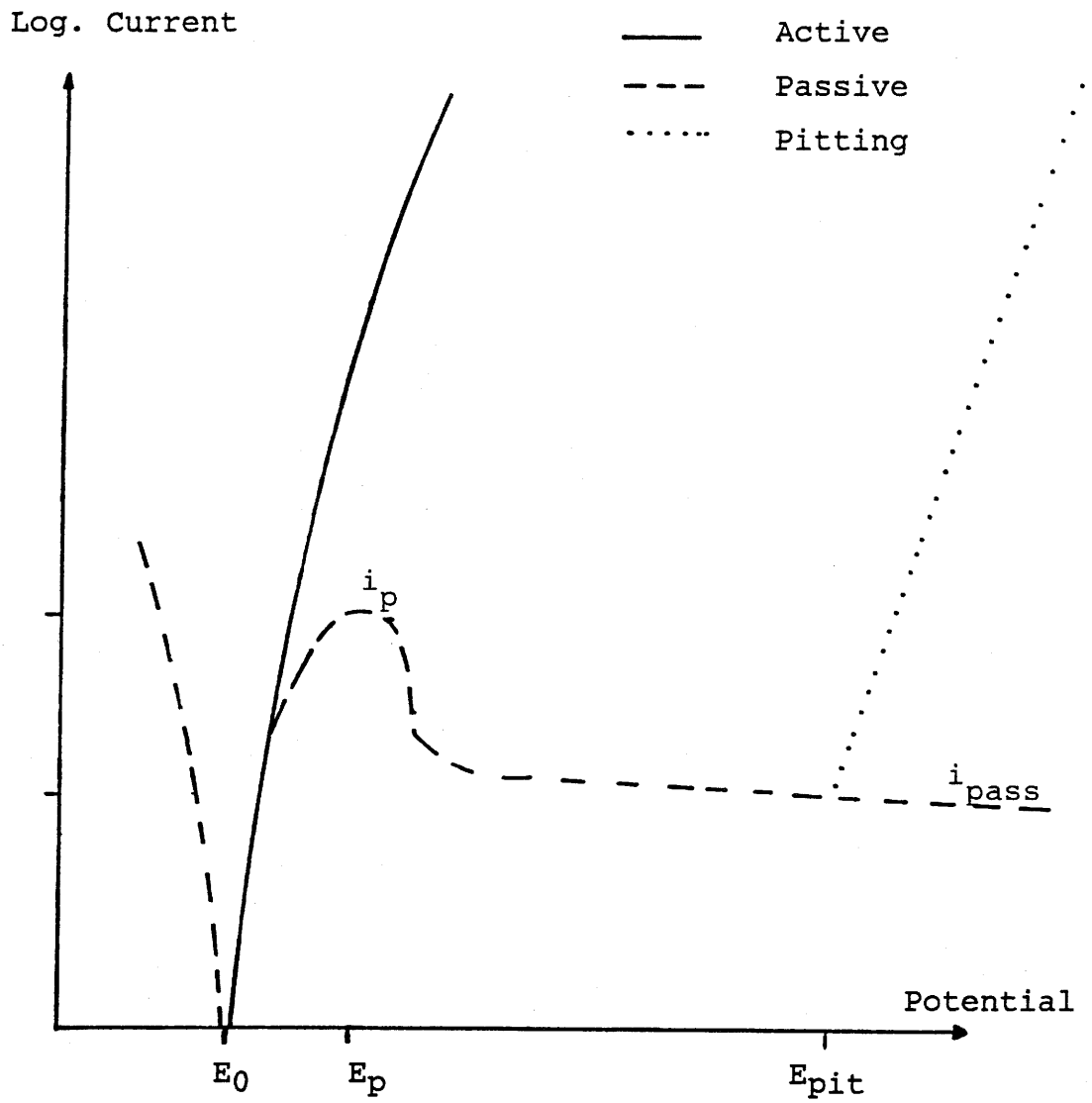

Figure 2.2 Typical potentiodynamic current-potential polarization curves.

Peak current	i_p
Passive current	i_{pass}
Zero current potential	E_0
Peak current potential	E_p
Pitting potential	E_{pit}

	Säckingen water µg/g	Böttstein(2) water µg/g
Na^+	900 - 1070	4800
K^+	75 - 86	54
Mg^{++}	12 - 15	3
Ca^{++}	124 - 158	1100
Cl^-	1480 - 1820	8100
F^-	2.3 - 2.8	3.8
$SO_4^=$	112 - 125	1820

Table 2. Compositions of Säckingen source water and the synthetic Böttstein(2) water used for corrosion experiments.

Three chloride concentration levels were used:
0 (i.e. <1) , 800 and 8000 µg/g: added as NaCl.

Three sulphate concentration levels were used:
0 (i.e. <1) , 900 and 2000 µg/g: added as Na_2SO_4.

Measurements were made at 50 and 80°C.

The pH range of interest was 7 to 10.5.

These values were chosen as they cover the range of the two reference groundwaters.

The pH in natural groundwaters is regulated primarily by the $CO_2/HCO_3^-/CO_3^=$ system. For this set of experiments, total carbonate (carbonate + bicarbonate) was 2000 µg/g as carbonate. pH values between 8.5 and 11 are attainable with carbonate + bicarbonate, below pH 8.5 CO_2 as 1, 5 or 10% mixtures in nitrogen + bicarbonate was used.

It was clear from the first few experiments that the carbonate system as well as acting as a pH buffer interacts with chloride and sulphate thus affecting the formation and breakdown of the passive film on iron. Calcium hydroxide was used as an alternative means of adjusting the pH to allow the effect of carbonate as an ion and carbonate as a pH buffer to be differentiated. pH values between 8 and 10 could be set with calcium hydroxide. Calcium sulphate is insoluble and addition of calcium hydroxide should remove sulphate from solution. In fact the rate of calcium sulphate precipitation is so slow that a change in dissolved sulphate concentration or pH could not be detected after 100 h at 80°C.

2.4 Material.

All experiments were carried out on material from one cast of the cast steel GS 40. The chemical composition of this material is given in table 3.

C	P	S	Si	Mn	Al	Fe
0.19	0.014	0.006	0.37	0.74	0.06	bal.

Table 3. Chemical composition of cast steel GS 40.

2.5 Experimental programme.

A) Potentiostatic.
Kinetic pH-potential diagrams were generated for cast steel GS 40 in Böttstein(2) and Säckingen reference waters at 80°C.

B) Potentiodynamic.
Kinetic pH-potential diagrams were generated for the solution compositions given in table 4 from the data in table 5.

µg/g	Cl^- = 0	Cl^- = 800	Cl^- = 8000
H_2O deionized*		50°C	50°C
Carbonate buffer	50°C	50°C	50°C
Carbonate buffer + $SO_4^=$ = 900 µg/g	50°C	50 & 80°C	
Calcium hydroxide	50°C	50°C	80°C
Calcium hydroxide + $SO_4^=$ = 900 µg/g	50°C	50 & 80°C	50°C
Calcium hydroxide + $SO_4^=$ = 2000 µg/g		50°C	

* single pH value.

Table 4. Test solutions for potentiodynamic polarization.

2.6 Results.

2.6.1 A) Potentiostatic empirical pH-potential diagrams for cast steel in Bottstein and Säckingen water.

The kinetic pH-potential diagram for cast steel GS 40 in Böttstein(2) water is shown in figure 2.3. The diagram has four regions, specimens polarized within these four regions corrode in a manner characteristic for that region.

1)
At potentials and pH values below the dotted line hydrogen is evolved (below this line net cathodic currents are observed, above it net anodic currents), this is the cathodic protection region.

2)
Above the dotted line to the left of the diagram i.e. at low pH values, the current is anodic and increases rapidly with increasing potential and the corrosion rate increases accordingly. The specimen is evenly attacked.

3)
At high pH values and potentials above the zero net current line the current is independent of potential and remains low. The specimen surface is passive, often displaying a thin but visible oxide film but no severe corrosion.

4)
On further increasing potential in the pH range where passivity is observed the current will eventually suddenly increase. The surface becomes pitted; the pits are large and hemispherical in section. The boundary active corrosion / pitting is not pH independent. At potentials greatly exceeding the pitting potential (the pitting potentials are described by the passive / pitting region boundary) the pits coalesce and pitting becomes indistinguishable from general (active) corrosion.

The diagram for Säckingen water is shown in Figure 2.4. No passive region and hence no pitting were observed over the pH range studied.

2.6.2 B) Potentiodynamic empirical pH-potential diagrams for cast steel in chloride, sulphate, and carbonate solutions.

Typical potentiodynamic polarization curves are shown in figure 2.2. To construct the pH potential diagrams the boundary for hydrogen evolution was drawn at the zero current potential; the lower limit for passivity at the active-passive transition peak potential $E_{a/p}$; and the passive pitting boundary at the pitting potential E_{pit}.

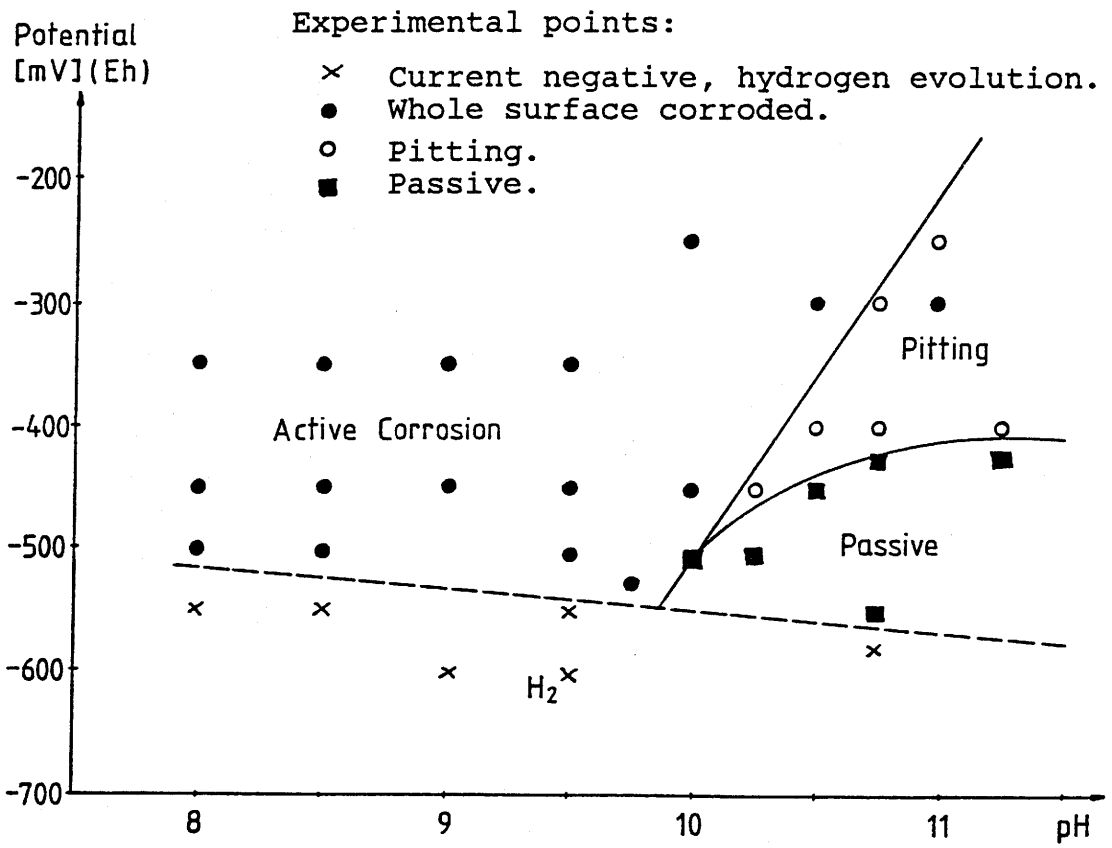

Figure 2.3 Kinetic pH-potential diagram for cast steel GS 40 in Böttstein(2) water at 80°C.

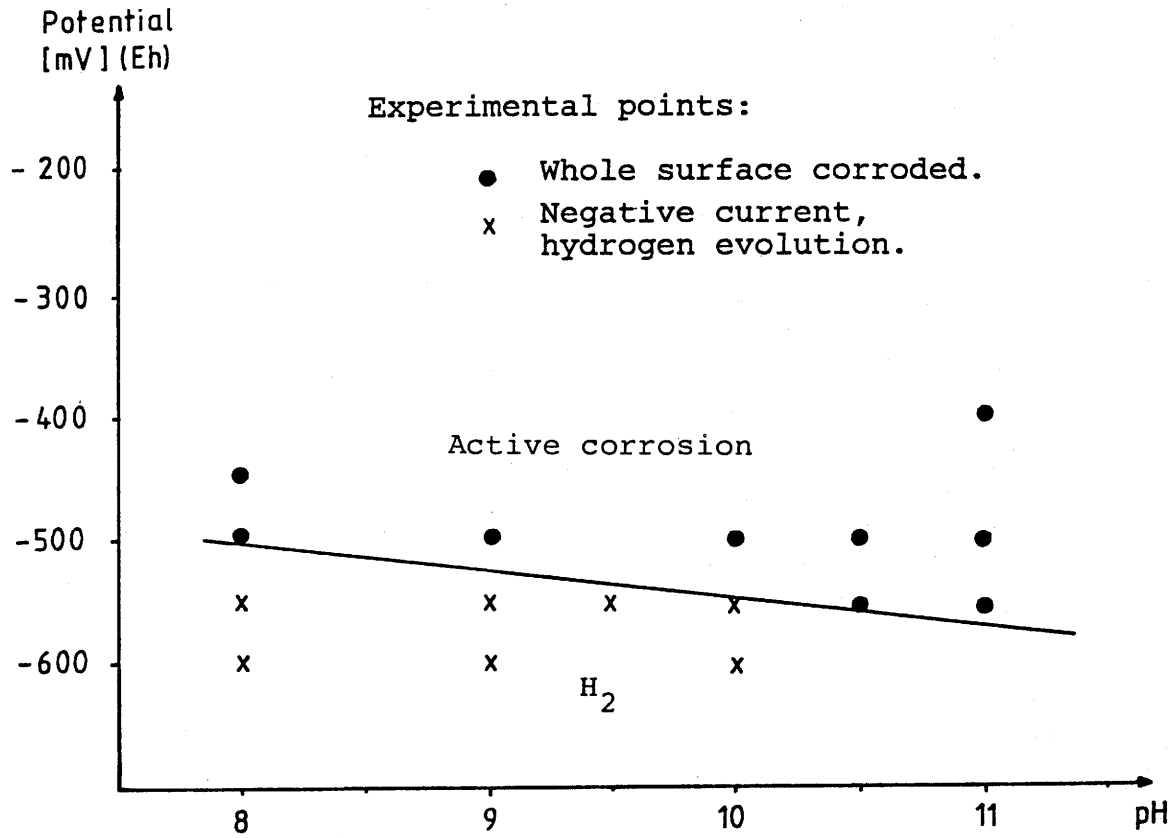

Figure 2.4 Kinetic pH-potential diagram for cast steel GS 40 in Säckingen water at 80°C.

The importance of carbonate for passivation is illustrated by the results shown in figure 2.5. The steel passivated in carbonate buffer solutions with and without chloride; when calcium hydroxide was used to set the pH the steel did not passivate.

Figure 2.6 shows the effect of chloride on the passive range in carbonate buffered solutions. With zero chloride there is no breakdown of passivity (at least below 0 mV n.h.e). Local attack (pitting) was observed in the solution containing 800 µg/g Cl^-, the passive region on the kinetic pH-potential diagram was restricted to higher pH values and lower potentials on increasing the chloride concentration to 8000 µg/g.

Sulphate can also induce passivity as shown in figure 2.7. Whereas no passivity was observed in $Ca(OH)_2$ + 800 µg/g Cl^-, the addition of sulphate (900 µg/g) gave a passive region on the kinetic pH-potential diagram. In contrast to carbonate passivity, steel in sulphate will also pit due to the action of the sulphate ion alone; chloride is neutral in sulphate solutions, it does not alter the passive range.

Figure 2.8 shows the effect of sulphate and chloride on carbonate passivity. The differences between the results for chloride only, chloride + sulphate and sulphate only are small. Chloride and sulphate are equally effective at promoting pitting.

Two levels of sulphate were tested with $Ca(OH)_2$ and 800 µg/g Cl^-. There was no difference in behaviour when the sulphate was increased from 900 to 2000 µg/g (figure 2.9). This diagram also shows clearly how much more effective carbonate is than sulphate at promoting passivity.

Figures 2.10 and 2.11 show the effect of temperature on the behaviour in carbonate and calcium hydroxide systems respectively. In both cases the passive region is larger at the higher temperature, again carbonate is more effective than sulphate as a passivating agent.

The kinetic pH-potential diagrams based as they are on inflections in the polarization curves do not carry all the information available from the basic measurement. The active peak current, i_p and the minimum passive current, i_{pass} are important parameters reflecting the ease of passivation and the degree of passivation respectively. The i_p and i_{pass} current densities measured are given in table 5. The active peak current density increases markedly towards the low pH nose of the passive region, indicating an increasing reluctance to passivate as the pH

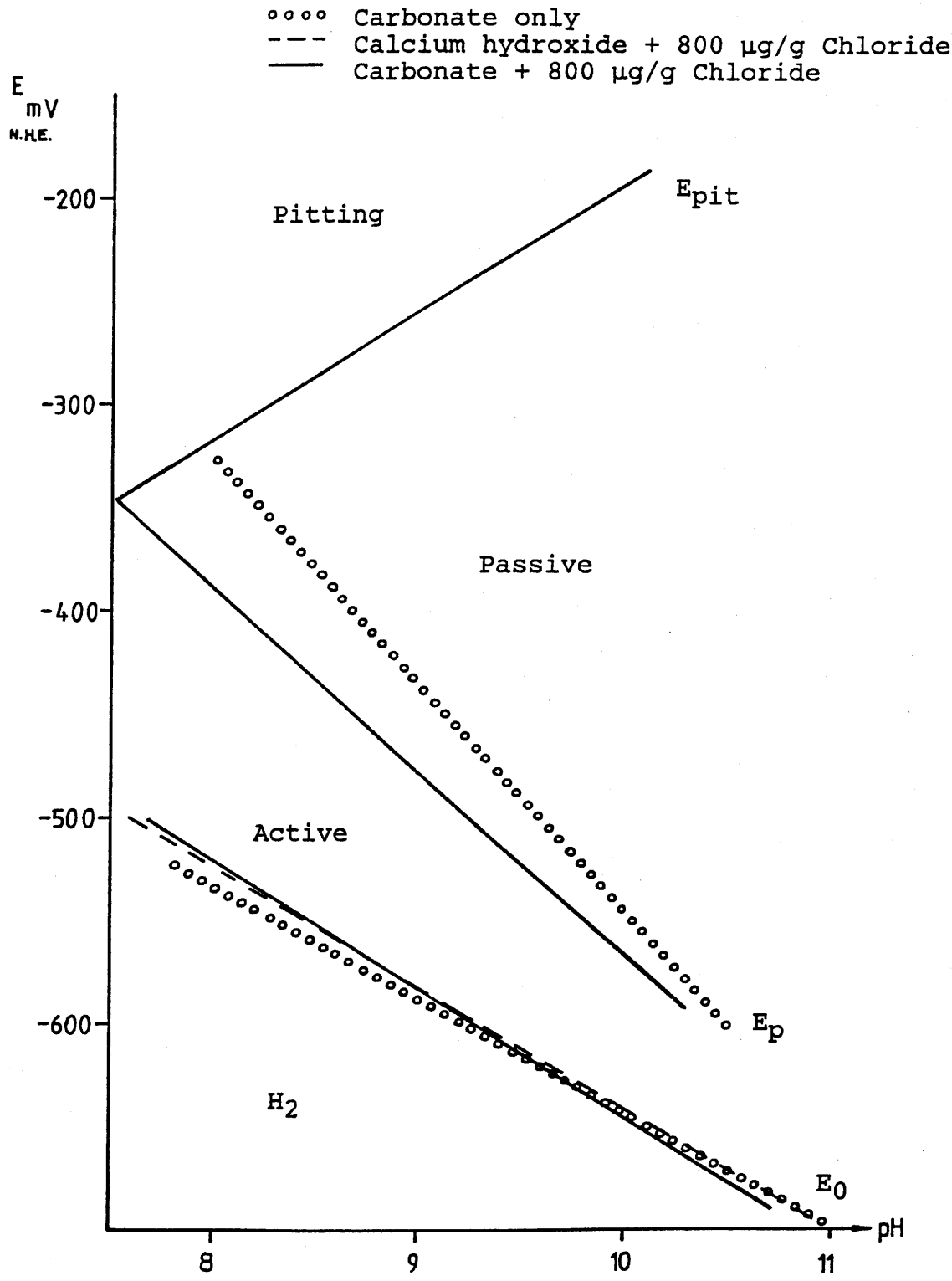

Figure 2.5 Effect of carbonate and calcium hydroxide on the passivation of cast steel GS 40 at 50°C. GS 40 does not passivate in calcium hydroxide + chloride. It passivates in carbonate alone but requires chloride to pit.

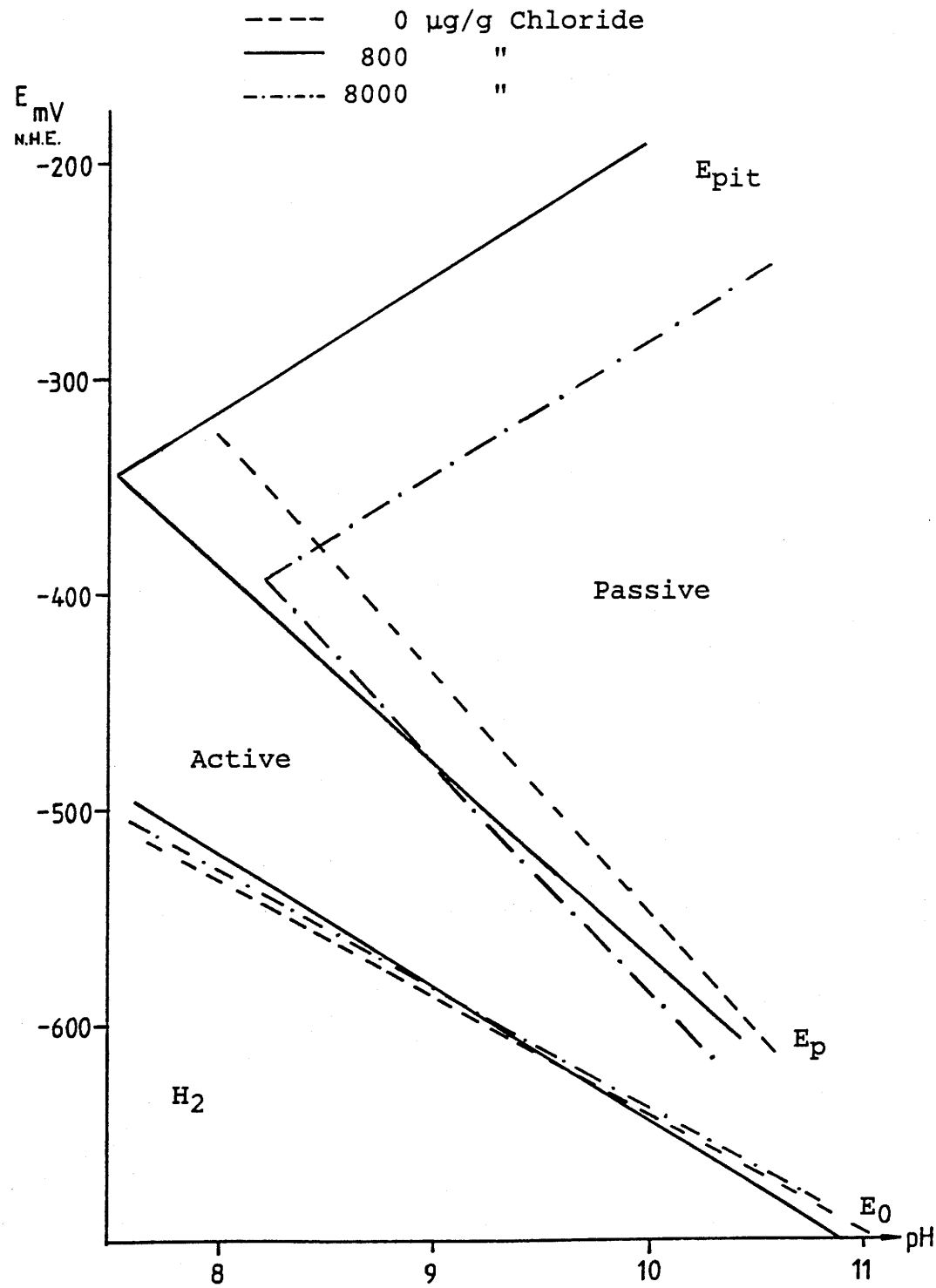

Figure 2.6 Effect of chloride on the passive range in carbonate buffer at 50°C. The passive range is restricted to higher potentials and the pitting potential decreases on increasing the chloride concentration.

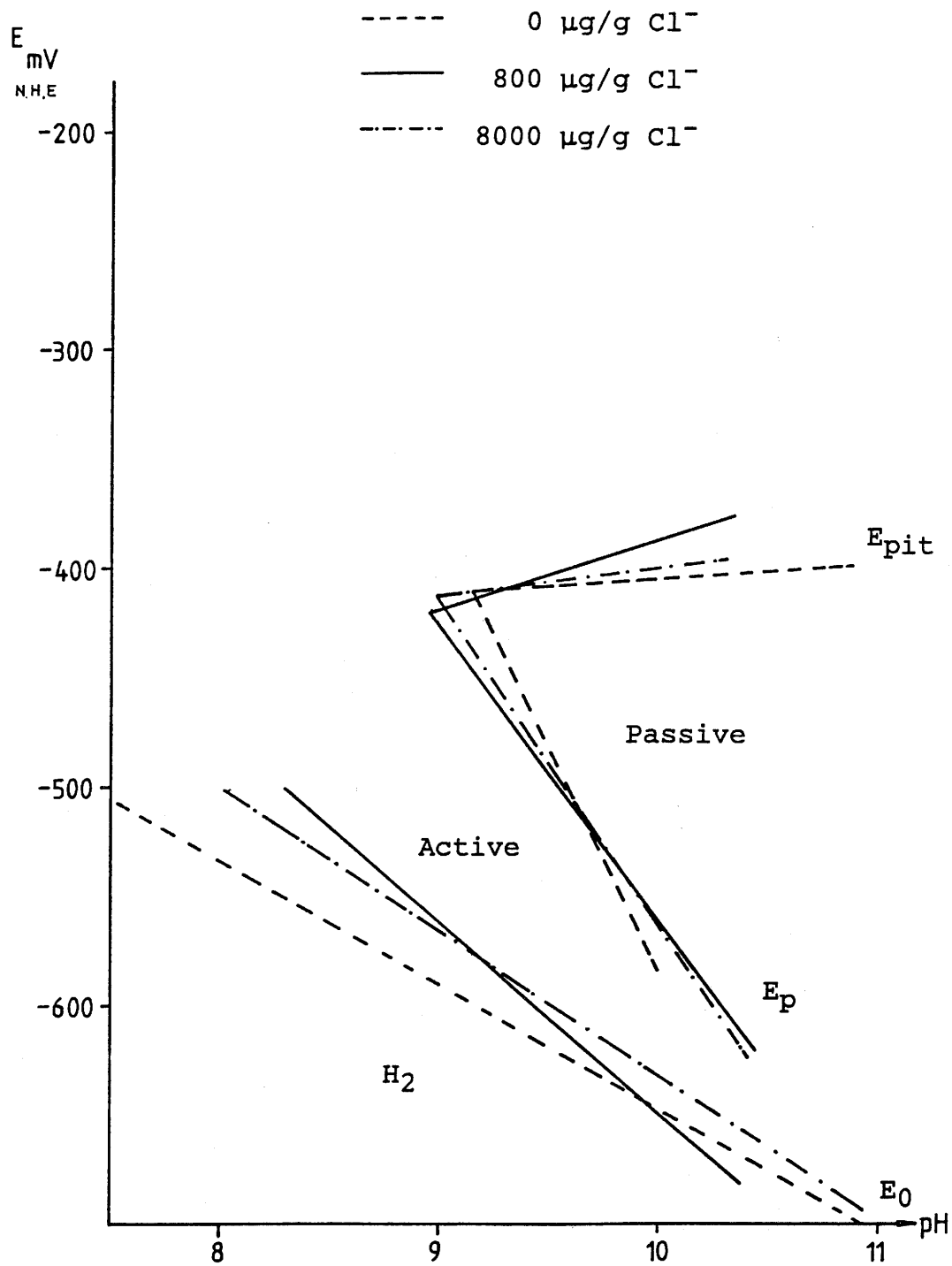

Figure 2.7 Effect of chloride on sulphate passivity in calcium hydroxide at 50°C. The passive region is unaffected by chloride.

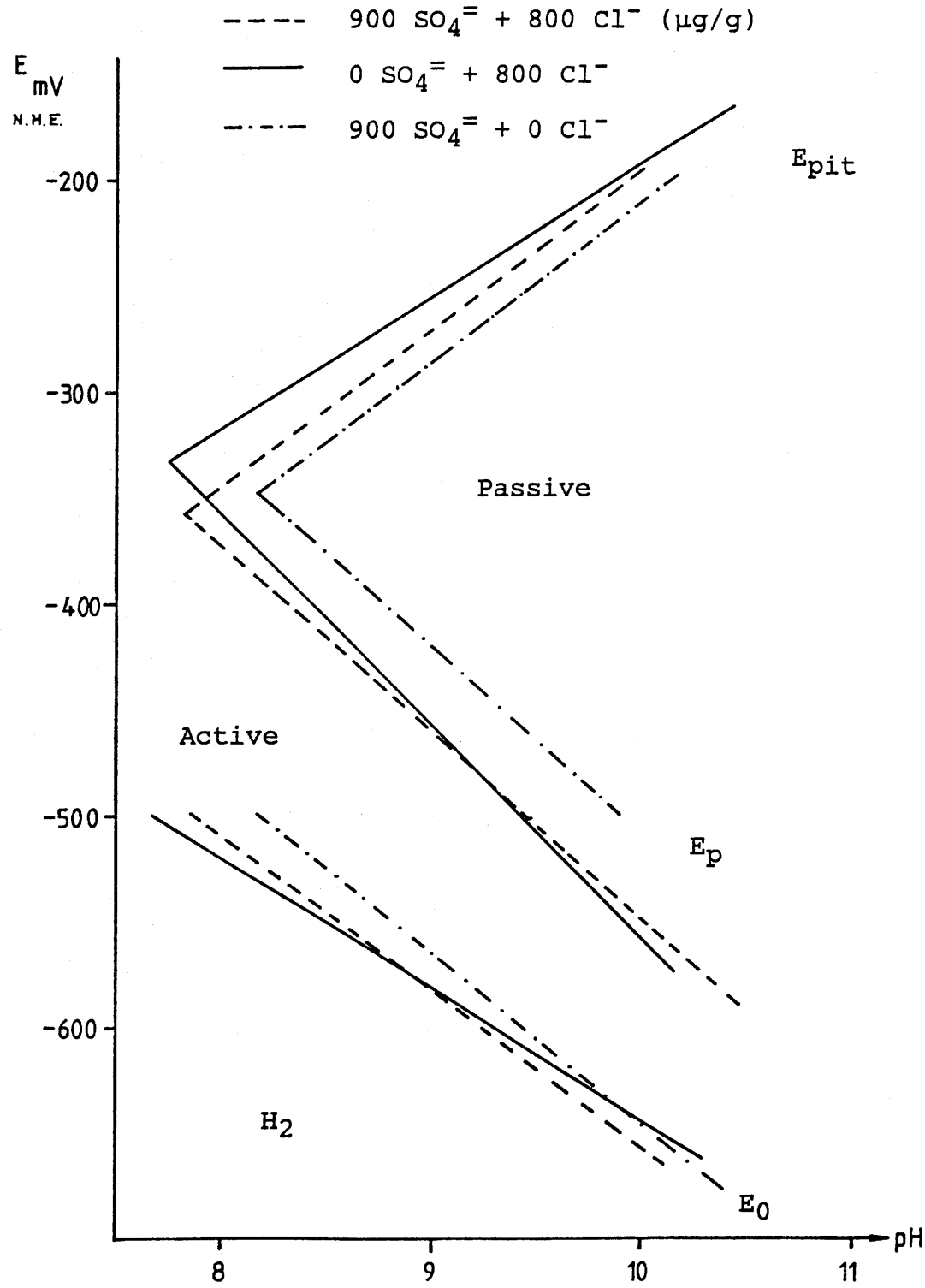

Figure 2.8 Effect of sulphate and chloride on passive range in carbonate buffer at 50°C.

—·—·— Calcium hydroxide + 2000 $SO_4^{=}$ + 800 Cl^- (µg/g)

– – – – Calcium hydroxide + 900 $SO_4^{=}$ + 800 Cl^-

——— Calcium carbonate + 900 $SO_4^{=}$ + 800 Cl^-

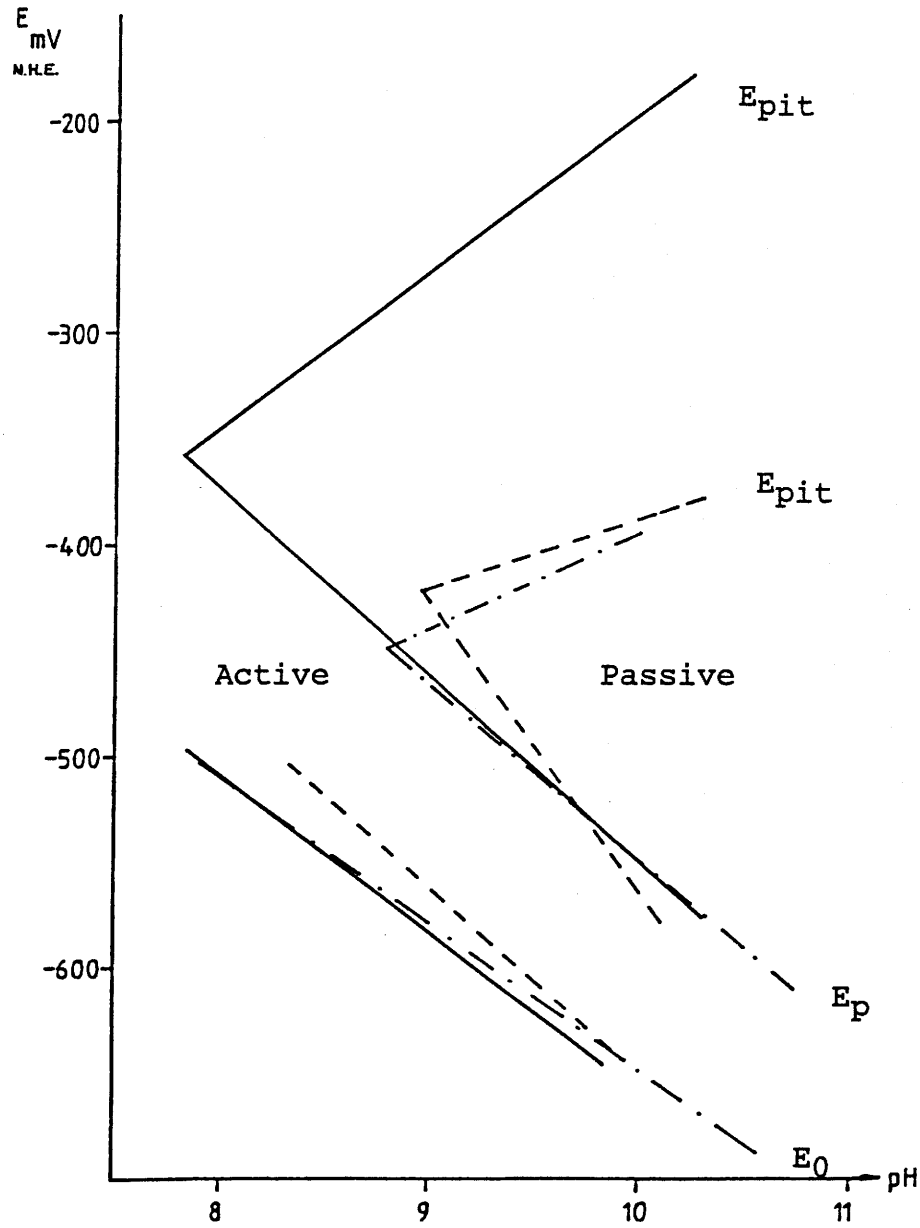

Figure 2.9 Effect of sulphate concentration on sulphate passivity and comparison between carbonate and sulphate passivity domains. Carbonate is more effective at promoting passivity than sulphate.

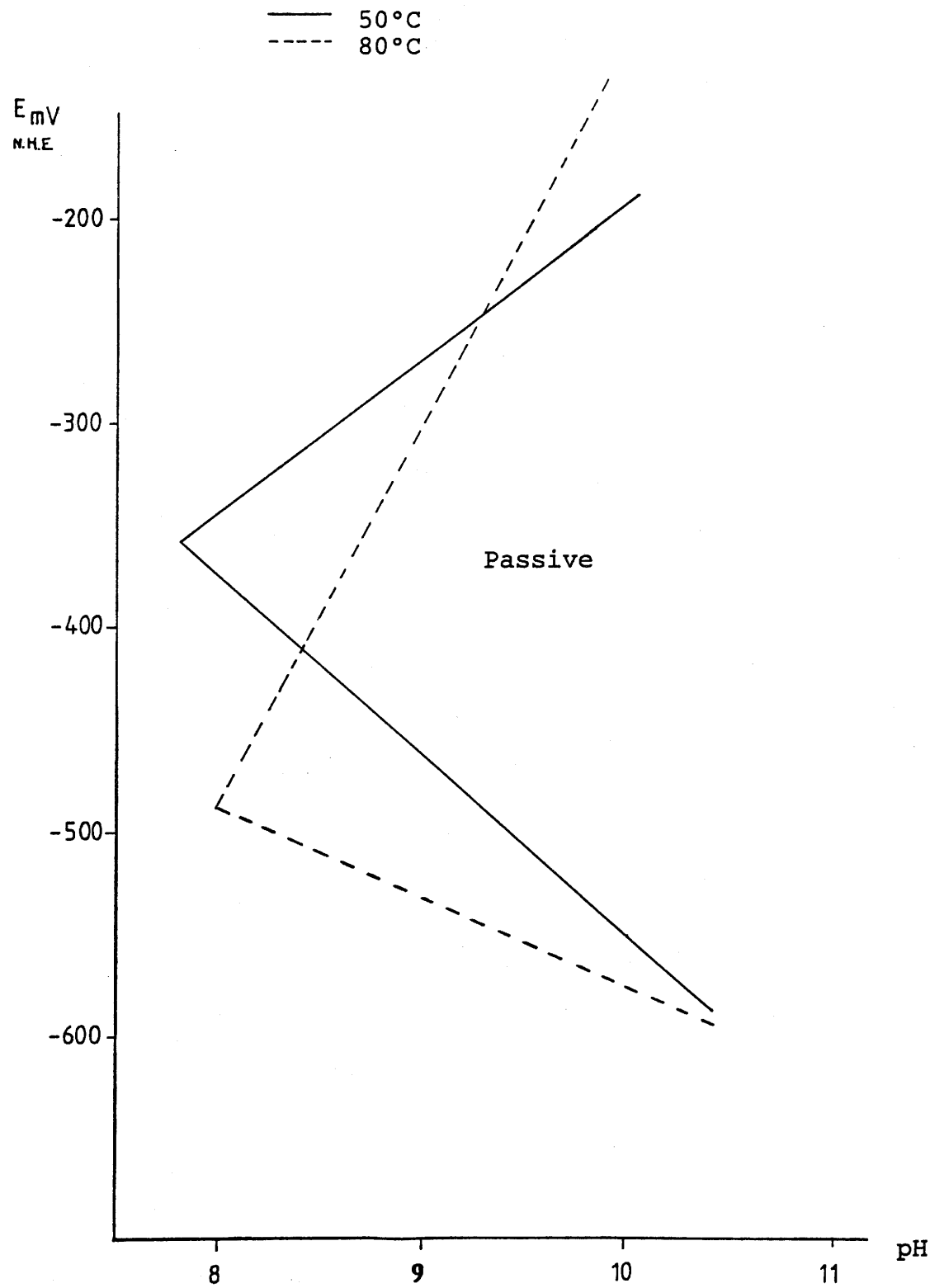

Figure 2.10 Effect of temperature on carbonate passivity. (900 µg/g $SO_4^{=}$ + 800 µg/g Cl^-)

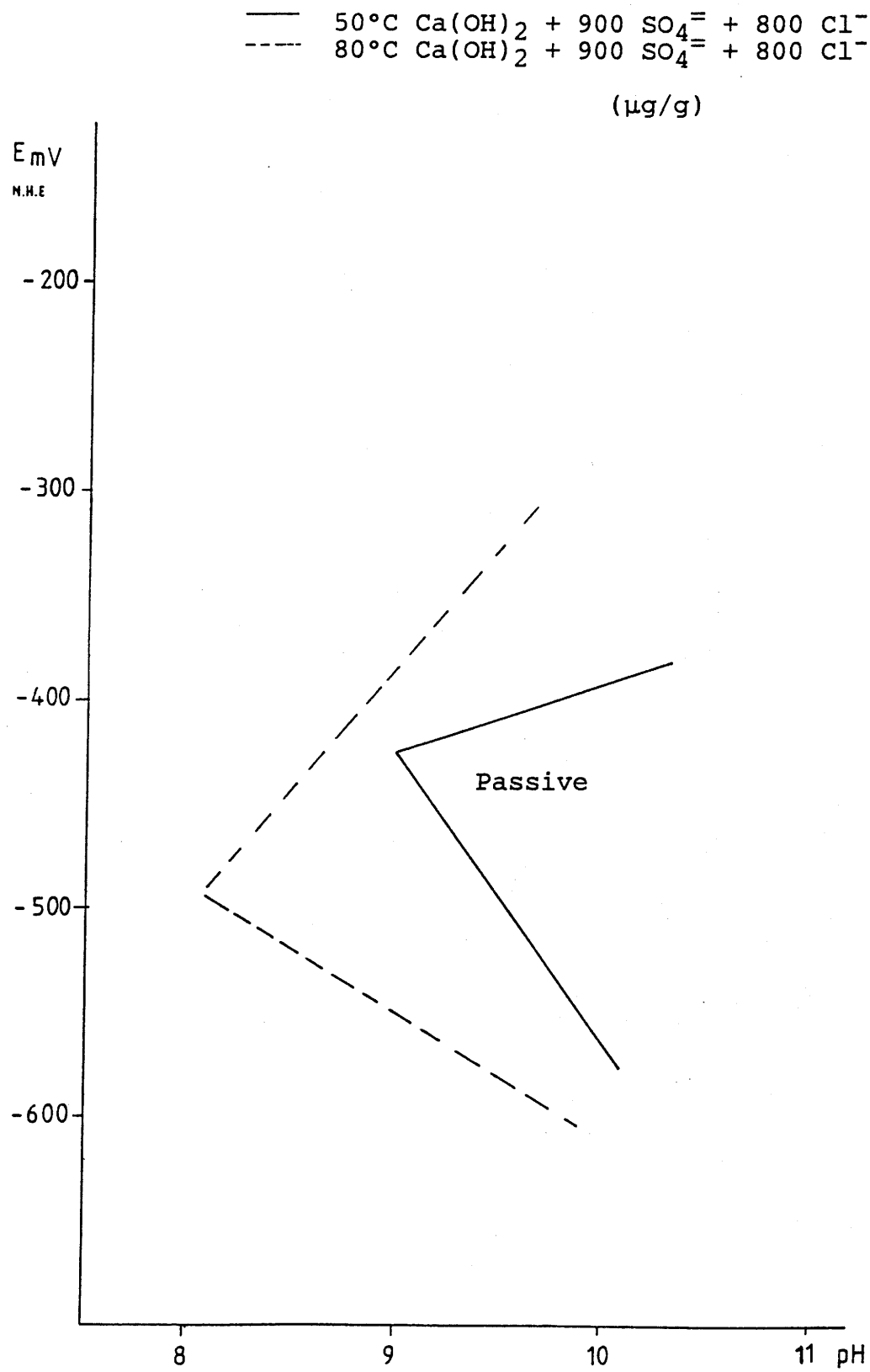

Figure 2.11 Effect of temperature on sulphate passivity.

Medium. µg/g	pH	E_o	E_p mV n.h.e.	E_{pit}	i_p µA/cm²	i_{pass}	Figure
Carbonate,	7.15	-504		no passivation			
Cl^- = 0	9.10	-594	-434	-	29	3 *	2.5
$SO_4^=$ = 0	9.45	-614	-479	-	18	3 *	2.6
	9.85	-629	-544	-	30	3 *	
50°C	10.54	-669	-569	-	23	3 *	
Carbonate,	8.03	-529	-359	-309	993	-	2.5
Cl^- = 800	8.20	-524	-434	-304	206	28	2.6
$SO_4^=$ = 0	8.60	-574	-459	-279	152	30	2.8
	8.84	-574	-504	-264	75	16	
50°C	9.24	-579	-494	-254	56	10	
	9.48	-614	-509	-259	89	11	
	9.75	-634	-529	-189	63	4	
	9.93	-614	-554	-129	17	4	
	10.30	-664	-589	-174	20	3	
Carbonate,	8.05	-544		no passivation			2.6
Cl^- = 8000	8.62	-574	-394	-369	551	408	
$SO_4^=$ = 0	8.88	-579	-489	-349	84	20	
	9.33	-604	-534	-299	47	4	
50°C	9.62	-614	-534	-339	73	6	
	9.79	-614	-574	-289	12	2	
	10.37	-664	-574	-264	30	3	
Carbonate,	9.33	-584	-479	-269	34	1	2.8
Cl^- = 0	9.64	-614	-454	-229	77	5	
$SO_4^=$ = 900	9.93	-649	-489	-204	79	7	
	10.23	-674	-529	-224	110	1	
50°C	10.55	-689	-549	-179	120	1	
Carbonate,	8.00	-509	-379	-334	680	620	2.8
Cl^- = 800	8.85	-594	-489	-289	88	22	2.9
$SO_4^=$ = 900	9.20	-609	-489	-224	90	20	2.10
	9.66	-594	-504	-264	152	14	
50°C	9.84	-649	-484	-229	94	9	
	10.06	-659	-554	-184	22	6	
	10.47	-674	-589	-124	42	3	
Carbonate,	8.83	-599	-524	-319	38	13	2.10
Cl^- = 800	9.20	-629	-534	-309	50	1	
$SO_4^=$ = 900	9.45	-634	-549	-164	1	0.2	
	9.77	-614	-574	-189	2	<0.1	
80°C	10.00	-594	-574	-154	<0.1	<0.1	

* = no pitting.

Table 5a. Potentials, i_p and i_{pass} in carbonate solutions.

Medium. µg/g	pH	E_o	E_p mV n.h.e.	E_{pit}	i_p µA/cm²	i_{pass}	Figure
$Ca(OH)_2$ 50°C	9.80	-654	-549	-	10	2 *	
$Ca(OH)_2$	8.00	-539	no passivation				2.5
Cl^- = 800	8.30	-554					
$SO_4^=$ = 0,	8.56	-539	at all				
50°C	8.75	-564					
	9.15	-574	pH values				
	9.75	-634					
$Ca(OH)_2$	8.03	-559	no passivation				2.7
Cl^- = 0	8.56	-564	no passivation				
$SO_4^=$ = 900	9.11	-589	no passivation				
	9.35	-599	-459	-404	48	44	
50°C	9.50	-619	-519	-399	28	12	
	9.70	-589	-519	-419	14	9	
	9.95	-644	-534	-399	12	6	
$Ca(OH)_2$	9.05	-564	no passivation				2.7
Cl^- = 800	9.10	-579	-444	-	51	50	2.9
$SO_4^=$ = 900	9.20	-589	-454	-409	41	37	2.10
	9.50	-619	-504	-399	16	10	
50°C	9.85	-619	-519	-389	14	7	
	10.00	-634	-549	-394	18	8	
$Ca(OH)_2$	8.28	-524	no passivation				2.10
Cl^- = 800	8.45	-619	-524	-424	0.8	0.5	
$SO_4^=$ = 900	8.70	-634	-524	-409	0.8	0.7	
	9.00	-629	-544	-379	0.2	0.1	
80°C	9.30	-664	-579	-329	1.2	0.4	
	9.60	-644	-579	-	7.9	1.7	
$Ca(OH)_2$	9.05	-569	-	-	no passivation		2.7
Cl^- = 8000	9.20	-534	-459	-404	33	29	
$SO_4^=$ = 900	9.52	-604	-494	-404	26	20	
	9.85	-619	-534	-404	23	14	
50°C	10.00	-644	-534	-394	15	11	
$Ca(OH)_2$	8.03	-506	-	-	no passivation		2.9
Cl^- = 800	8.80	-574	-	-	no passivation		
$SO_4^=$ = 2000	9.20	-589	-484	-419	34	30	
	9.50	-609	-519	-424	20	14	
50°C	9.83	-639	-524	-404	8	7	
	10.00	-629	-549	-399	10	5	

* = no pitting.

Table 5b. Potentials, i_p and i_{pass} in $Ca(OH)_2$ solutions.

is decreased. The transition from active-passive to active behaviour is thus not abrupt, the kinetic pH-potential diagrams do not reflect this aspect of the material's behaviour.

2.7 Discussion

The results obtained in carbonate-bicarbonate buffer are in general agreement with the literature. The presence of carbonate causes the carbon steel to passivate, hydroxide alone is not sufficient at least at pH values up to 9.75 (OH^- = 0.95 µg/g) to cause passivation in the presence of 800 µg/g chloride. An increase in pH does however stabilize a carbonate passive film as the pitting potential in carbonate solutions increases with increasing pH.

An increase in the chloride concentration from 800 to 8000 µg/g decreased the pitting potential by 70 - 100 mV in agreement with the 100 mV/decade quoted in the literature. The passive range also decreases on increasing the chloride concentration, from 7.8 at 800 µg/g chloride to 8.6 at 8000 µg/g. This increase was also found by Marsh et al /16/.

The fact that a passive region was found for sulphate in the absence of carbonates and that this passivity is not affected by the normally aggressive chloride ion could not be predicted from the literature sources studied. This effect is however of little relevance to an end repository in crystalline repositories as carbonates are always present and both sulphate and chloride cause loss of passivity in the presence of carbonates. The effect of chloride and sulphate on the pitting potential was not additive at the concentration levels tested, 800 µg/g chloride and 900 µg/g sulphate.

The passive and the peak current increase as the pH decreases such that approaching the low pH limit of the passive region in figures 2.5 - 2.11 it is doubtful whether the steel truly passivates giving a conservative estimate of the lower pH limit of the passive range.

Passivity on iron has been attributed to a hydrous $Fe(OH)_2$ layer which forms in the -400 to -600 mV nhe potential range onto which in the presence of carbonate a layer of $FeCO_3$ forms /17/. According to Valentini et al i_p increases with temperature in the range 0 - 75 °C /17/. In contrast, the most notable differences between the results in this study at 50°C and those at 80°C are the lower i_p and i_{pass} current densities in the passive region which suggests a change in mechanism. The formation of a

different surface film such as magnetite which is also thermodynamically stable in this potential range /18/ is a possibility.

The aim of this work was to assess the possibility of a passive film forming on the steel under repository conditions and to look at the factors involved. The two forms of corrosion which should be avoided are pitting and stress corrosion cracking. Pitting requires a degree of passivity on the rest of the surface for deep pits to form, and an active - passive transition is also a characteristic of systems known to cause anodically controlled stress corrosion cracking in mild steels /19/.

The results show that passivity could occur at 50 and 80°C in the types of groundwaters expected. The most important factors are chloride, carbonate and the pH. High pH values should probably be avoided if possible, on the other hand high chloride levels may not always be detrimental as although chloride promotes pitting of passive iron it can also prevent passivation if present at sufficiently high concentrations.

For pitting to occur at all the potential must be raised above the pitting potential. In the absence of an oxidant other than water, the potential of the steel will remain around the hydrogen line on the potential pH diagrams, i.e. pitting is unlikely even if the steel passivates. The only time another oxidant is present is immediately after closure when oxygen is trapped in the repository. In the active region this oxygen will cause accelerated general attack but in the passive region may raise the potential sufficiently for pitting to occur. As the repository temperature is expected to be higher than 80°C when oxygen is present information on the active - passive transition on mild steels in groundwaters should be obtained at higher temperatures.

3. IMMERSION CORROSION TESTING

3.1 Introduction

A series of immersion corrosion tests have been carried out within the NAGRA programme on cast steel GS 40, nodular cast iron GGG 40, copper and the titanium alloy Ti-Code 12. The results from the first series of tests were presented in Part II /2/. It was clear from these tests and values reported in the literature that an extension of the immersion testing on copper and Ti-Code 12 would yield little further useful information, testing of GS 40 and GGG 40 however was continued, along with a single test on copper in oxygen free Böttstein(2) water.

3.2 Experimental

3.2.1 Method

Details of the experimental method are given in Part II /2/. For ease of reading the most important details are repeated here.

Both the 80 and 140°C test systems were of the refreshing type. The solution was circulated from a reservoir held at room temperature to the test vessel installed in a heated cabinet. The total volumes were 30 and 50 l at 80 and 140°C respectively. The refreshing rate was set in the range 0.7 - 0.8 l/h to both the 80 and 140°C test vessels. The oxygen level was set by bubbling a gas through the test solution in the reservoir. A 0.27 vol.% O_2 oxygen nitrogen mixture was used for the 0.1 µg/g oxygen level and commercial high purity nitrogen gas for the oxygen free condition, i.e. ca. 0.002 µg/g O_2.

The specimen material was identical to that used in the earlier tests. The copper is a high purity phosphorus de-oxidised grade with 0.007% phosphorus. The chemical analyses for GS 40 and GGG 40 are given in table 6. The materials are described in more detail in the appendices to parts I and II /1,2/.

Material	C	P	S	Si	Mn	Al	Fe
GS 40	0.19	0.014	0.006	0.37	0.74	0.06	bal.
GGG 40	3.58	0.032	0.007	2.26	0.24	0.043	bal.

Table 6. Chemical composition of GS 40 and GGG 40.

Six corrosion coupons 30 x 20 x 2 mm^3 were exposed to each test condition and time. The weight loss was determined on four of these coupons and the mean taken to determine the reported corrosion rate. Variations from the mean greater than ± 20% were only observed when the corrosion rate exceeded 50 µm/a on the GS 40 or GGG 40 specimens. A metallographic section was prepared from the fifth specimen and the sixth was a reserve.

With this specimen set enough oxygen is supplied in the case of the 0.1 µg/g O_2 oxygen level to support a corrosion rate for cast steel or nodular cast iron of about 40 µm/a assuming the oxygen supplied is completely consumed by the corrosion reaction:

$$Fe \rightarrow Fe^{++} + 2e$$

The residual oxygen in the "oxygen free" test of about 0.002 µg/g will thus support less than 1 µm/a corrosion. (N.B. Different autoclaves were used for the first tests at 140°C reported in part 2. In these tests 3 specimen sets were started simultaneously and removed one by one to achieve the total test time. This method was used for Säckingen water + 0.1 µg/g O_2 at 140°C. In this case sufficient oxygen was supplied to support a corrosion rate of only 14 µm/a for the first 700 h, 20 µm/a for 700 - 3200 h and 40 µm/a for 3200 - 6020 h for GS 40. The corresponding times for GGG 40 are 0 - 700 h, 700 - 2900 h and 2900 - 6500 h.

The compositions of the two reference waters, Böttstein(2) and Säckingen water are given in table 2.

3.2.2 Results

The results of the immersion test programme on GS 40 and GGG 40 are given in tables 7 a and b, and for copper in table 8..

The following exposure conditions were used:

Böttstein(2) water - oxygen free - 80°C.
Böttstein(2) water - 0.1 µg/g O_2 - 80°C
Säckingen water - oxygen free - 80°C
Säckingen water - 0.1 µg/g O_2 - 80°C

Böttstein(2) water - oxygen free - 140°C.
Böttstein(2) water - 0.1 µg/g O_2 - 140°C
Säckingen water - oxygen free - 140°C
Säckingen water - 0.1 µg/g O_2 - 140°C

Material	Medium	Temp. °C	Exposure time h	Rate µm/a
GS 40	Böttstein(2), oxygen free	80	0 - 643	42
			0 - 2160	14
			0 - 6170	10
GGG 40	Böttstein(2), oxygen free	80	0 - 812	11
			0 - 2280	24
			0 - 6170	5
GS 40	Säckingen, oxygen free	80	0 - 767	30
			0 - 2163	16
			0 - 6170	5
GGG 40	Säckingen, oxygen free	80	0 - 812	16
			0 - 2280	8
			0 - 6170	6
GS 40	Böttstein(2), 0.1 µg/g O_2	80	0 - 812	24
			0 - 2160	52
			0 - 6744	60
GGG 40	Böttstein(2), 0.1 µg/g O_2	80	0 - 812	25
			0 - 2160	67
			0 - 6744	68
GS 40	Säckingen, 0.1 µg/g O_2	80	0 - 504	86
			0 - 1440	34
			0 - 2280	7
GGG 40	Säckingen, 0.1 µg/g O_2	80	0 - 812	45
			0 - 2160	30
			0 - 6744	18

Table 7a. Results of immersion tests on GS 40 and GGG 40 in both reference waters at 80°C.

Material	Medium	Temp. °C	Exposure time h	Rate µm/a
GS 40	Böttstein(2), oxygen free	140	0 - 1008	50
			0 - 2520	26
			0 - 6170	18
GGG 40	Böttstein(2), oxygen free	140	0 - 1008	38
			0 - 2280	22
			0 - 6170	17
GS 40	Säckingen, oxygen free	140	0 - 770	14
			0 - 2670	7
			0 - 6170	4
GGG 40	Säckingen, oxygen free	140	0 - 1008	31
			0 - 2520	20
			0 - 6972	14
GS 40	Böttstein(2), 0.1 µg/g O_2	140	0 - 1008	55
			0 - 2520	34
			0 - 6170	31
GGG 40	Böttstein(2), 0.1 µg/g O_2	140	0 - 1008	33
			0 - 2520	33
			0 - 6972	34
GS 40	Säckingen, 0.1 µg/g O_2	140	0 - 700	11
			0 - 3200	6
			0 - 6020	2
GGG 40	Säckingen, 0.1 µg/g O_2	140	0 - 700	37
			0 - 2920	15
			0 - 6500	12

Table 7a. Results of immersion tests on GS 40 and GGG 40 in both reference waters at 140°C.

Medium	Temp. °C	Exposure time h	Rate µm/a
Böttstein(2),	80	812	7.0
oxygen free	80	1272	10.7

Table 8. Results of immersion tests on copper.

No macroscopic features which could be attributed to localized corrosion or pitting could be identified on any of the cast steel or nodular cast iron corrosion test coupons after exposure. Metallographic sections prepared from the exposed coupons revealed microscopical surface roughening, the appearance of the surfaces were similar to those shown in Part II /2/. An assessment of the surface morphology revealed that (except for the shortest testing times) the difference between the highest and lowest points on the surface was not greater than the mean corrosion loss as measured by the weight loss.

3.3 Discussion

The corrosion under all conditions tested may be considered to be uniform, the average corrosion rate from weight loss may thus be used as a representative value for the corrosion damage to the material.

The points of interest are the effects of material (GGG 40 or GS 40), salinity (Säckingen or Böttstein(2) water), temperature (80 or 140°C) and oxygen level (0.002 or 0.1 µg/g) on the corrosion rate. The more representative longest test period results will be used to look for the influence of these parameters on the corrosion rate. The results will be tabulated for each parameter pair to ascertain the effect of each variable individually.

Effect of material.

Table 9 shows the corrosion rates measured sorted by material. The corrosion rates for GS 40 tend to be lower than for GGG 40 when both corrosion rates are low (<20 µm/a). The differences between the materials are otherwise small and the values for the two materials will be averaged in the following tables. Table 10 shows the effect of oxygen level, table 11 the effect of salinity and table 12 that of temperature.

Medium	Temp. °C	O_2 µg/g	Corrosion rate (µm/a) GS 40	GGG 40
Säckingen	80	0.002	5	6
Böttstein(2)	80	0.002	10	5
Säckingen	80	0.1	7	18
Böttstein(2)	80	0.1	60	68
Säckingen	140	0.002	4	14
Böttstein(2)	140	0.002	18	17
Säckingen	140	0.1	2	12
Böttstein(2)	140	0.1	31	34

Table 9. Effect of material on corrosion rate.

Medium	Temp. °C	Corrosion rate (µm/a) 0.002	0.1 (µg/g O_2)
Säckingen	80	6	12
Böttstein(2)	80	8	64
Säckingen	140	9	7
Böttstein(2)	140	18	33

Table 10. Effect of oxygen level on the corrosion of iron base materials in the reference waters.

Temp. °C	Oxygen level µg/g	Corrosion rate (µm/a) Säckingen	Böttstein(2)
80	0.002	6	8
80	0.1	13	64
140	0.002	9	18
140	0.1	7	33

Table 11. Effect of groundwater salinity on the corrosion rate. Bottstein water has a 3 - 4 times higher salt content than Säckingen water.

Medium	Oxygen level µg/g	Corrosion rate (µm/a) 80	140 (°C)
Säckingen	0.002	6	9
Böttstein(2)	0.002	8	18
Säckingen	0.1	13	7
Böttstein(2)	0.1	64	34

Table 12. Effect of temperature on the corrosion rate.

The main conclusion from these results is that the corrosion rate on GS 40 and GGG 40 is adversely affected by an increase in salinity and oxygen content of the groundwater. Increasing the temperature has a minor effect, if anything an increase in temperature from 80 to 140°C reduces the corrosion rate at higher oxygen levels, but may slightly increase it in oxygen free solutions.

There is a marked difference in the corrosion rate between the two reference waters with 0.1 µg/g oxygen at both 80 and 140°C, the oxygen supply rate may be rate limiting in Böttstein(2) water but this is not true for the lower salinity Säckingen water. There is less difference between the two waters in the absence of oxygen; rates may be slightly higher in Böttstein(2) water.

The 6000 hour corrosion rate was below the long term average of 20 µm/a assumed when estimating the corrosion allowance /4/ at both 80 and 140°C in both reference waters. There is thus no reason to revise this estimate.

The supply of oxygen to the container is strictly limited to the amount of oxygen trapped in the repository on closure, the amount of oxygen generated by radiolysis even over 1000 years is negligable in comparison /5/. The corrosion rates measured in the 0.1 µg/g oxygen solutions are thus not directly relevant. More important, however, is the observation that the corrosion attack morphology remains uniform in the presence or absence of oxygen justifying the approach taken in the estimate /4/ of simply adding the potential oxidation of iron by the trapped oxygen to the estimate of the long term corrosion loss due to anaerobic corrosion.

4. CORROSION IN BENTONITE

4.1 Introduction

It is proposed to embed the containers in highly compacted bentonite. The purpose of this experimental programme was to investigate the effect of bentonite on the corrosion behaviour of cast steel or nodular cast iron in the model ground waters.

The method and apparatus are described in detail in Part II /2/; only a brief description of the experiment is included in this report.

4.2 Method and materials

The material GS 40 was identical to that used for immersion corrosion testing. The specimens for each test were three 10 x 10 x 2 mm^3 coupons which were embedded in 55 mm diameter, 30 mm high density sodium bentonite (MX 80, see /20/). Two densities of compressed bentonite were investigated, 1.55-1.6 and 1.95-2.05 $gx10^6.m^2$ which give total water contents in the saturated state of 30-32% and 20-22% respectively.

The experimental conditions were as described in part II /2/ except that the pressure drop across the bentonite cylinder was reduced fron 90 to 10 bars; the pressure over the test solution was 40 bars and on the exit side 30 bars.

4.3 Results

The corrosion rates measured for GS 40 embedded in bentonite saturated with Säckingen or Böttstein(2) water at 80 and 140°C are given in table 13.

Test period (h)	Water content (%)	Corrosion rate (µm/a) Säckingen 80°C	Säckingen 140°C	Böttstein(2) 80°C	Böttstein(2) 140°C
0 - 816	30-32	66	40	68	40
	20-22	26	20	24	24
0 - 2160	30-32	24	14	29	14
	20-22	13	8	14	12
0 - 6648	30-32	10	13	4	8
	20-22	6	5	8	5

Table 13. Results of corrosion tests on GS 40 embedded in bentonite.

4.4 Discussion

The corrosion rates in both reference waters and at both temperatures are generally higher for the bentonite with the higher water content. This is most probably due to the oxygen trapped in the bentonite on preparing the samples. The void volume of ca. 12 and 22 % in the as-pressed condition for the low and high saturated water contents respectively initially contains air. As was suggested in part II /2/, most of this air is swept out with the initial surge of water into the bentonite but some residual oxygen will remain to dissolve in the water and corrode the steel. This is probably the reason for the high initial corrosion rates and the observation that they are higher for the lower density bentonite. After the initial trapped oxygen is consumed no more oxygen is available and the longer the test is continued the less influence the initial high oxygen corrosion rate has on the measured corrosion rate. This test thus very closely simulates the conditions expected within the repository itself.

In table 14 the results of the corrosion tests in bentonite are compared with those from the immersion tests. The rates are in good agreement. It must be concluded that the bentonite has no adverse effect on the corrosion of cast steel.

Test period (h)	Test method	Corrosion rate (µm/a) Säckingen 80°C	Säckingen 140°C	Böttstein(2) 80°C	Böttstein(2) 140°C
0 - 6648	Bentonite 20-22% water	6	5	8	5
0 - 6648	Bentonite 30-32% water	10	13	4	8
0 - 6170	Immersion oxygen free	5	4	10	18

Table 14. Comparison between corrosion rates from immersion tests and coupons embedded in bentonite.

5. CONCLUSIONS.

The results of the immersion tests have confirmed the conclusions made in Part II /2/ and thus those made in the assessment of the corrosion resistance of the cast steel waste container /4/. There is no reason to doubt that 20 µm/a is a conservative upper limit for the uniform corrosion rate of cast steel under repository conditions.

There were no signs of pitting on the immersion test coupons or on those embedded in bentonite in either Böttstein or Säckingen water even if 0.1 µg/g oxygen was present. Pitting is only possible if the steel passivates; at 80 °C the cast steel only passivated at pH values above 9.7, and no active - passive transition was found in Säckingen water at the same temperature.

The kinetic pH-potential diagrams for the carbonate-chloride-sulphate system show that the active - passive behaviour is sensitive to the concentrations of these three components in the groundwater. pH values above ca. 10 should be avoided as passivity is fully developed in the carbonate-chloride-sulphate system at high pH levels; this is not in itself detrimental, but could result in pitting as opposed to general corrosion under adverse conditions such as the presence of a stronger oxidant than water.

Investigations into the active - passive behaviour of cast steel should be extended to the higher temperatures prevailing shortly after sealing the repository where the presence of oxygen could increase the potential sufficiently for passive film breakdown and hence pitting.

The NAGRA corrosion programme is being continued; the next phase of the programme already under way is investigating the susceptibility of GS 40 cast steel to stress corrosion cracking under repository conditions.

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