

Nagra

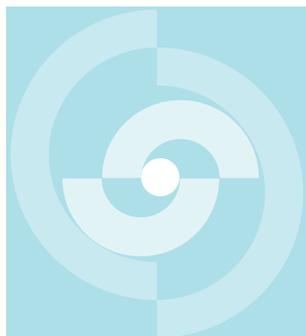
Nationale
Genossenschaft
für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
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pour l'entreposage
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Società cooperativa
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TECHNICAL REPORT 84-32

AN ASSESSMENT OF THE CORROSION
RESISTANCE OF THE HIGH-LEVEL WASTE
CONTAINERS PROPOSED BY NAGRA

December 1984

The Nagra Working Group on Container Technology

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FOREWORD OF NAGRA

From 1980 onwards Nagra has been carrying out a programme to identify potential materials for high-level radioactive waste (HLW) containers, study their corrosion behaviour under repository conditions and design appropriate reference containers within the framework of the proof of feasibility of safe nuclear disposal required by the Swiss authorities. Several Nagra Technical Reports have been issued on the subject of container materials and their corrosion behaviour / NTB 82-08, NTB 83-05, NTB 84-01, NTB 84-04, NTB 84-19 /, their creep behaviour / NTB 84-35 /, the design of containers / NTB 84-05, NTB 84-31 / and concepts for the encapsulation of the waste into the container / NTB 84-23 /.

Throughout the programme the various projects have been discussed and accompanied by a Working Group consisting of five acknowledged experts on materials science, particularly corrosion science: Professor H. Böhni, Professor D. Landolt, Dr. W. Rieger, Dr. F. Theiler and Dr. J. Weber. The present report presents their assessment of the materials proposed by Nagra for waste containers from the point of view of corrosion. The coordination of drafting and editorial work has been carried out by Nagra with the collaboration of Dr. J. Simpson.

SUMMARY

The Nagra concept for the final disposal of high-level radioactive waste includes a container ensuring isolation of the waste from the groundwater for a period of time of at least 1'000 years. Two types of containers are proposed by Nagra in current feasibility projects: the first type, for reprocessed vitrified waste is designed as a self-supporting shell; the material is cast steel GS-40. The second type, for spent fuel, is an adaptation of Swedish designs in which the spent fuel elements are cast in lead inside a thick-walled copper container.

The assessment of the corrosion resistance of these containers is based on the conditions expected in a repository in the crystalline bedrock of northern Switzerland. The groundwater is reducing, with salinity up to seawater level and a high sulphate content.

Under these conditions the only significant contributions to the corrosion of copper come from residual oxygen trapped in the bentonite used as backfill material and from sulphate, if it is assumed that the latter can be reduced to sulphide by microbial activity. This is certainly a very conservative assumption, since it implies that sufficient populations of appropriate bacteria can be supported under repository conditions, but it cannot be ruled out on present-day evidence. The use of this together with other conservative assumptions leads to the conclusion that the maximum penetration by corrosion will not exceed 40 mm in 1'000 years.

For iron the same mechanisms must be considered; the stoichiometry, however, is more favourable and the attack is expected to be less uneven than in copper. This results in a maximum depth of attack of 9 mm in 1'000 years. To this must be added a contribution from the direct reduction of water; the relatively few relevant literature data combined with the results of the Nagra corrosion programme indicate that the maximum penetration from this mechanism will not exceed 20 mm in 1'000 years. If the conservatively assessed contributions of the residual oxygen and the sulphate are added to this, a maximum penetration of less than 30 mm in 1'000 years is obtained.

The conclusions are reached using conservative assumptions. The evidence is well documented in the case of copper; it is slightly less complete in the case of iron, but confirming evidence should result from a sustained qualification programme.

ZUSAMMENFASSUNG

Das Konzept der Nagra für die Endlagerung hochaktiver Abfälle sieht einen Behälter vor, der die Abfälle vom Grundwasser während einer Zeit von mindestens 1000 Jahren isoliert. Zwei Behältertypen werden von der Nagra im Rahmen der gegenwärtigen Projekte zur grundsätzlichen Machbarkeit der Endlagerung vorgeschlagen; der eine, der für verglasten, wiederaufbereiteten Abfall vorgesehen ist, ist als selbsttragende Schale konzipiert; das Material ist Stahlguss GS-40; der andere, für die direkte Endlagerung abgebrannter Brennelemente, ist eine Anpassung schwedischer Entwürfe; dabei werden die Brennelemente in Blei innerhalb eines dickwandigen Kupferbehälters eingegossen.

Die Beurteilung des Korrosionswiderstandes dieser Behälter, die Gegenstand dieses Berichtes ist, basiert auf den in einem Endlager im kristallinen Grundgebirge der Nordschweiz zu erwartenden Bedingungen. Das Grundwasser ist reduzierend mit Salzgehalten bis auf Meerwasserniveau und hoher Sulfatkonzentration. Unter diesen Bedingungen stammen die einzigen bedeutenden Beiträge zur Korrosion aus dem Restsauerstoff im als Verfüllmaterial verwendeten Bentonit und aus dem Sulfat, unter der Annahme, dass dieser durch mikrobielle Aktivität zu Sulfid reduziert werden kann. Diese Annahme ist zweifellos sehr konservativ: sie setzt voraus, dass sich ausreichende Kolonien bestimmter Bakterien unter Endlagerbedingungen entwickeln können. Eine solche Entwicklung kann aber aufgrund der gegenwärtigen Kenntnisse nicht ausgeschlossen werden. Unter dieser sowie weiteren konservativen Annahmen kann der Schluss gezogen werden, dass die maximal zu erwartende Angriffstiefe kleiner ist als 40 mm in 1'000 Jahren.

Bei Eisen müssen dieselben Reaktionen berücksichtigt werden; gegenüber Kupfer ist einerseits die Stöchiometrie günstiger und andererseits ein gleichmässigerer Angriff zu erwarten. Daraus ergibt sich eine maximale Angriffstiefe von weniger als 9 mm in 1000 Jahren. Dazu kommt ein Beitrag aus der direkten Reduktion von Wasser; es gibt diesbezüglich verhältnismässig wenige relevante Daten, die aber alle darauf hinweisen, dass die maximale Angriffstiefe nicht über 20 mm in 1000 Jahren betragen wird. Wenn dazu die konservativ ermittelten Beiträge des Sauerstoffs und des Sulfats gezählt werden, so ergibt sich eine gesamte Angriffstiefe von weniger als 30 mm in 1000 Jahren.

Diese Schlussfolgerungen wurden aufgrund konservativer Annahmen abgeleitet. Der Nachweis ist im Falle von Kupfer gut dokumentiert. Für Eisen ist er etwas weniger vollständig, doch ist zu erwarten, dass ein entsprechendes Qualifikationsprogramm die Schlussfolgerungen des Berichtes bestätigen wird.

RESUME

L'une des barrières prévues par la Cédra pour le dépôt final des déchets hautement radioactifs est un conteneur assurant l'isolement des déchets vis-à-vis des eaux souterraines pour une période d'au moins mille ans. La Cédra propose deux types de conteneurs dans le cadre des projets de faisabilité actuellement en cours: l'un d'eux est une coquille creuse en acier coulé GS-40 et est destinée aux déchets vitrifiés; l'autre, pour le dépôt direct de combustible irradié, a été adapté à partir des concepts suédois: les éléments de combustible sont coulés dans du plomb liquide à l'intérieur d'un conteneur en cuivre à parois épaisses.

L'évaluation de la résistance à la corrosion de ces conteneurs présentée dans le rapport est basée sur les conditions présumées dans un dépôt situé dans le sous-sol cristallin de la Suisse septentrionale. L'eau de formation est réductrice avec une salinité pouvant aller jusqu'au niveau de l'eau de mer et une concentration en sulfate élevée.

Dans ces conditions les seules contributions importantes pour la corrosion du cuivre sont dues d'une part à l'oxygène résiduel présent dans la bentonite utilisée comme matériau tampon, d'autre part au sulfate, à supposer que ce dernier puisse être réduit en sulfure par activité microbologique. Il s'agit là d'une hypothèse sans aucun doute très prudente, puisqu'elle implique que des populations suffisantes de bactéries idoines peuvent se développer dans les conditions régnant dans le dépôt; l'on ne peut cependant pas éliminer un tel développement sur la base des connaissances présentes. En partant de cette hypothèse ainsi que d'autres hypothèses prudentes on conclut que la pénétration maximale n'excédera pas 40 mm en 1'000 ans.

Pour le fer les mêmes mécanismes doivent être considérés; la stoechiométrie est plus favorable et l'irrégularité de l'attaque est moindre que pour le cuivre; il en résulte une pénétration maximale de 9 mm en 1000 ans, à laquelle il sied d'ajouter la contribution provenant de la réduction directe de l'eau; les indications offertes par l'étude de la littérature pour les conditions considérées sont peu nombreuses, mais permettent de conclure que la pénétration maximale due à ce mécanisme n'excédera pas 20 mm en 1000 ans.

En ajoutant à ce résultat les contributions de l'oxygène et du sulfate, calculées sous des hypothèses prudentes, l'on obtient une pénétration de moins de 30 mm en 1000 ans.

On est parvenu à ces conclusions en se basant sur des hypothèses prudentes. Pour le cuivre, les moyens de preuve sont bien établis et documentés. Pour le fer, ceux-ci sont moins complets, mais l'on peut s'attendre à ce qu'un programme de qualification soutenu confirme les conclusions du rapport.

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1. INTRODUCTION

The Swiss Nuclear Waste Disposal Concept (see e.g. Ref. /1/) is based on a permanent storage of the waste in repositories, in conformity to the legal requirements. The repository must be so designed and built that after sealing no further measures are required to ensure the safety of the public. In order to achieve this aim reliance is put on the principle of multiple barriers, partly redundant and partly complementary to each other. In the Nagra repository concept for highly active waste the man-made, engineered safety barriers are the waste form (borosilicate glass from reprocessing or spent fuel), the container and the backfill. The container ensures that no groundwater contacts the waste form for a significant period of time and the backfill is designed to slow down groundwater and ion transport rates to low values during and after the lifetime of the container.

The life of the container is primarily limited by corrosion by groundwater. The purpose of the present report is to determine the minimum expected lifetime of the Nagra container concepts (for reprocessed waste and for spent fuel, respectively) for the so-called central scenario /2/, which has been determined on the basis of present day knowledge of the expected conditions in deep crystalline formations in the bedrock of northern Switzerland /3/ and of the proposed repository design as presented in /4/. The boundary conditions for container corrosion, which have been derived from the central scenario, are presented in section 2 of the report. In section 3 the container designs proposed by Nagra are presented and their most important characteristics discussed. The design for reprocessed waste in borosilicate glass form is a stressed shell design based on the use of cast steel, while the design for spent fuel chosen is derived from that proposed in Sweden /5/, i.e. the spent fuel elements are cast in lead inside a copper container with a wall thickness of 100 mm.

The possible corrosion mechanisms for the materials considered are then discussed, and the maximum expected corrosion rates are derived from the available evidence in sections 4 and 5 in turn. Section 6 concludes the report summarising those issues which cannot yet be considered as fully resolved and suggests the ways in which they should be tackled.

2. THE CENTRAL SCENARIO FOR THE SAFETY ANALYSES

In order to describe the behaviour of the safety barriers (engineered as well as natural barriers) and the transport of radionuclides from the waste form to the biosphere, it is necessary to define one or more so-called scenarios: these consist of sequences of postulated events, the consequences of which are then analysed through appropriate modelling with the aim of determining the resulting dose to individuals in the biosphere. The procedure is described e.g. in /2/, /5/. In the framework of nuclear waste management a particular importance is attached to the central scenario, or normal scenario: This is the sequence of events that is expected with the highest probability (very close to 1). Other scenarios can be generated from the normal scenario by postulating one or more events that are in principle judged to be possible but associated with a very low probability during the lifetime of the repository (typical examples for such scenarios would be human intrusion into the repository, or the sudden appearance of a geological fault in or in the immediate neighbourhood of the repository).

The present report deals exclusively with the behaviour of the containers with respect to corrosion in the central scenario; in this central scenario the lifetime of the containers is required to be at least 1'000 years for the boundary conditions and sequence of events presented below /2/; in other words, the nuclides are, for the purpose of the safety analyses, assumed to remain fully isolated from the groundwater during the first 1'000 years of the life of the repository; this period of 1'000 years ensures that the major part of the activity inventory of the waste, namely that associated with the fission products, decays to negligible levels, and therefore also that the heat generation associated with these fission products reaches such low levels that the temperature distribution at the repository site is essentially the same as that prior to the building of the repository and the storage of the waste.

The boundary conditions for the assessment of the container behaviour in the central scenario are determined by:

- the repository design /4/
- the repository site and its geological, tectonic and hydrogeologic characteristics /3/
- the characteristics of the waste form, especially its heat generation /6/

- the characteristics of the backfill material (highly compacted bentonite) /3/
- the storage procedure /4/

The relevant information pertaining to container behaviour is summarized in the following sections 2.1, 2.2, and 2.3.

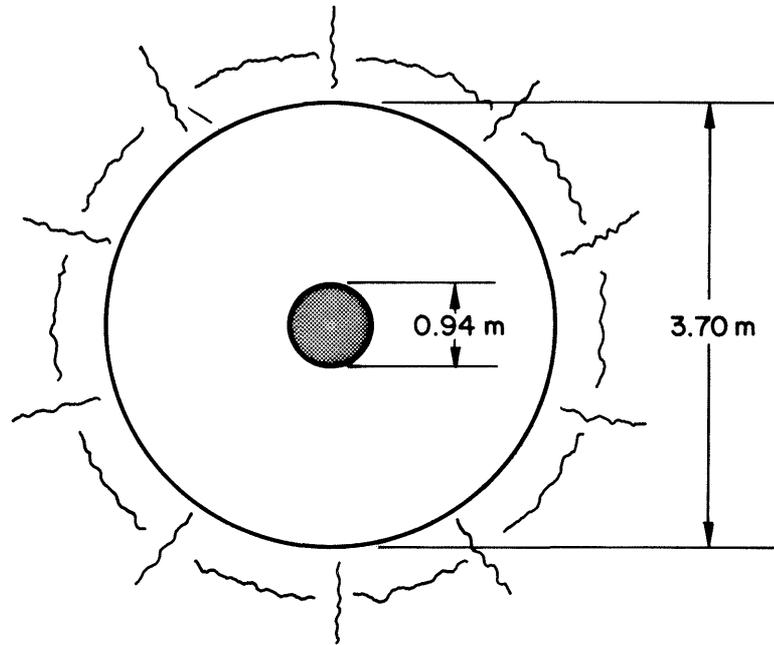
2.1 Repository design

The main features are as follows: The repository is sited in the crystalline bedrock of northern Switzerland, at a depth of approx. 1'200 m. The temperature at this depth prior to the construction of the repository is 55°C /3/.

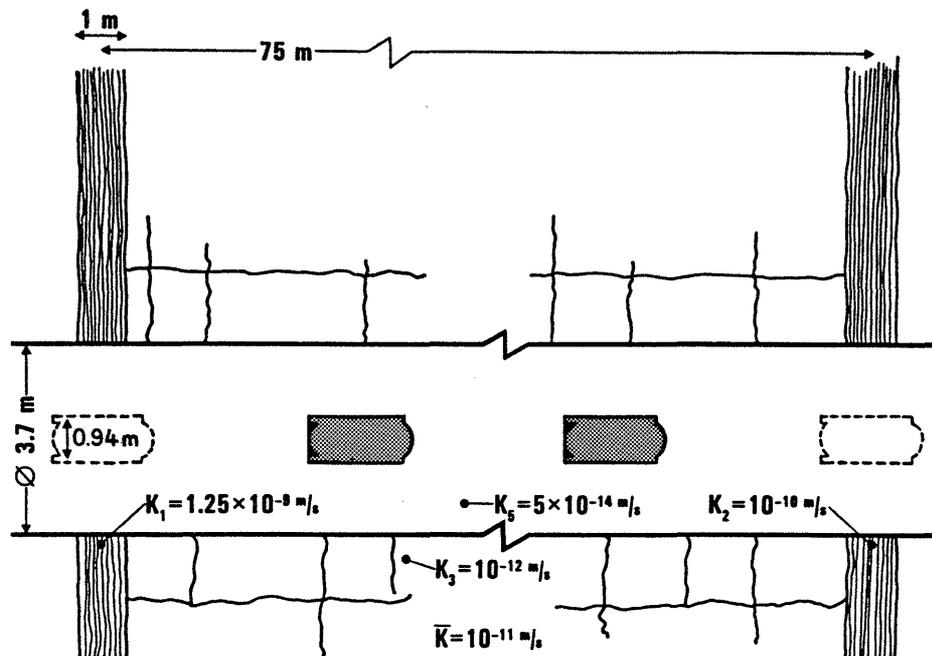
The containers filled with the waste form are stored horizontally in tunnels several hundred metre long, each tunnel separated from the neighbouring tunnel by a distance of 40 m. The diameter of the tunnels is 3.7 m and highly compacted bentonite is used as a backfill material between the container and the bedrock. The containers lie in the centre of the tunnel cross-section, as shown in Fig. 2.1(i), so that the thickness of the bentonite layer is constant over the whole circumference of the tunnel (cylindrical geometry). The distance between the centres of two neighbouring containers is 5 m in the case of reprocessed waste and 10 m in the case of spent fuel. Waste is stored only where the rock hydraulic conductivity is 10^{-11} m/s or less. No containers are stored opposite fractured zones of rock, which are assumed to be 1 m wide and of two types: "bad zones" (hydraulic conductivity $1.25 \cdot 10^{-9}$ m/s), and "medium zones" (hydraulic conductivity 10^{-10} m/s), and to occur at regular intervals, the distance between two "bad zones" being 150 m and that between a "bad zone" and a "medium zone" being 75 m, as shown in Fig. 2.1(ii).

The waste is stored 40 years after discharge from the reactor at the earliest and the heat generated by each container is at most 580 W in the case of reprocessed waste and 1'260 W in the case of spent fuel /6/.

The sodium bentonite used as backfill material (Type MX-80, Volclay Company, USA) is precompressed into blocks with masses of approx. 0.5 t to 2.0 t. Smectite clays such as bentonites swell when they come into contact with water. This swelling leads to a sealing of any voids caused by imperfect matching of the block dimensions in the tunnel. The swelling of the bentonite in a confined space such as the repository tunnels will also cause a pressure to be applied by the clay to the container and to the tunnel wall; this pressure is essentially isostatic



(i): viewed along the tunnels axis.



(ii): viewed across the tunnel axis.

Fig. 2.1: The storage geometry in the tunnels for disposal of reprocessed waste

The average rock hydraulic conductivity is $\bar{K} = 10^{-11} \text{ m/s}$; so-called "bad zones" ($K_1 = 1.25 \cdot 10^{-9} \text{ m/s}$) occur at 150 m intervals; half-way between "bad zones", so-called "medium zones" ($K_2 = 10^{-10} \text{ m/s}$) are assumed; containers are only stored in "good zones" ($K_3 = 10^{-12} \text{ m/s}$, fulfilling the criterion $K < 10^{-11} \text{ m/s}$); the hydraulic conductivity of the bentonite is $K_5 = 5 \cdot 10^{-14} \text{ m/s}$.

and depends on the density of the bentonite, i.e. on its degree of precompaction during the block fabrication and also on the (small) volume available for expansion when groundwater contacts the waste. These parameters are adjusted so that the final dry density of the bentonite is not less than 1.65 Mg/m^3 (corresponding to a porosity of max. 41 %) and not more than 1.75 Mg/m^3 . The bentonite contains approx. 7% water when storage takes place. Once complete saturation has taken place the water content is between 20% and 25% and the swelling pressure is not less than 15 MPa and not more than 30 MPa. Under those conditions the hydraulic conductivity of the bentonite is less than 10^{-13} m/s and therefore transport in the bentonite is controlled by diffusive phenomena.

As described in /3/ an appropriate, conservative value for the anion diffusivity in bentonite is $5 \cdot 10^{-10} \text{ m}^2/\text{s}$.

The thermal conductivity of bentonite has been determined for various dry densities and various water contents /3/. Using the heat generation values given above the temperature profiles in and around the container can be calculated at different times after emplacement. Such calculations have been performed /3/, /7/ and they show:

- that for a container made of metallic material with good thermal conductivity the temperature difference between any two points in the container does not exceed 5°C
- that the temperature history at the container surface can be conservatively approximated as follows:
 - . 50 years at 155°C
 - . 100 years at 100°C
 - . 300 years at 80°C
 - . 550 years at 60°C

Of importance for container corrosion is also the fact that the bentonite material considered can contain as supplied a certain amount of sulphate and sulphide. A typical value of 0.3% of dry weight can be expected /8/ although this may vary from batch to batch; a maximum value of 0.8% of dry weight will be used.

2.2 Groundwater composition, flow rate and velocity in the bedrock

The Nagra programme on hydrogeology and water chemistry in northern Switzerland has shown /3/ that a representative water composition at the depth of 1'200m selected for a typical repository in crystalline rock is as follows:

Cations (in mg/litre)

Na ⁺	4'038
K ⁺	45
Mg ²⁺	2.6
Ca ⁺⁺	870
Sr ²⁺	21
Fe (tot)	0.45
Mn (tot)	3.1
U (tot)	10 ⁻⁴

Anions (in mg/litre)

Cl ⁻	6'620
F ⁻	3.6
SO ₄ ²⁻	1'560
Silicates (as SiO ₂)	17
Alkalinity	1.58 meq/litre
Dissolved carbonates (tot)	1.91 mmol/litre

Dissolved gases

log (p (O ₂)/1 atm)	-59
log (p (CO ₂)/1 atm)	-1.73

pH, Eh

pH =	6.8
Eh between	-60 mV and -230 mV

The bentonite will buffer the water to pH values between 8 and 9, but does not influence the reducing character of the water. Oxidising conditions will be present in bentonite only in the first few years after closure of the repository, due to the air trapped in the bentonite.

The water flow from the bedrock into the bentonite will be determined by the hydrological characteristics of the bedrock as well as those of the bentonite. The Nagra investigations /3/ have shown that a flow rate of approx. 0.5 litre/m²a and a water velocity of approx. 50 m/a are representative of the flow regime expected in the fractured zones of rock, where no waste will be stored; in the storage zones, where the permeability is 10⁻¹¹ m/s or less, the corresponding figures are 0.04 litre/m²a and 4 m/a, respectively. The rock porosity, and the fissure distribution in the bedrock are given in /3/. These data are sufficient to describe the flow regime in the near field after the bentonite has been saturated.

2.3 Wetting history of the bentonite

The precompacted bentonite blocks brought into place in the repository have a water content of 7% to 9%, which ensures the most favourable compaction behaviour /4/, /9/. The design value for the bentonite water content at complete saturation is 20% to 25%. A small part of this water will be supplied by the ambient air humidity, but the larger part will be supplied by groundwater. With a tunnel diameter of 3.7 m the volume of bentonite per m of tunnel is about 11 m³; the dry density of bentonite in the NAGRA design is (on average) 1.7 Mg/m³, therefore per m of tunnel about 19 Mg (metric tonnes) of dry bentonite is necessary. The amount of water required for saturation is about (20% - 7%) of this mass, i.e. approx. 2.5 Mg of water. With the rock and flow characteristics expected in the Swiss bedrock /3/ at least several decades would be expected to pass before this amount flows into the bentonite even at the high hydraulic gradient that will be present until the hydrostatic pressure in the tunnel rises from atmospheric pressure to the 12 MPa corresponding to the repository depth of 1200 m. Due to the heat production of the waste, the water that is present initially will be displaced from those parts of the bentonite that are closest to the container towards the tunnel wall. Because the heat conductivity of the bentonite decreases with decreasing water content, the temperature at the container wall rises, and this has been taken into account in the calculations of the temperature distribution that show that the maximum temperature of the container does not exceed 155°C /3/. In those parts of the bentonite at temperatures above 100°C, H₂O is present in the vapour phase. With time the heat generation of the waste decreases, the hydrostatic head rises and the groundwater flows into the bentonite; it is therefore expected that the liquid front moves monotonically towards the container, and this has indeed been found to be the case in the Stripa mine experiments in Sweden /10/. Corrosion by a steam/air mixture is not expected to be more significant than corrosion by water with dissolved air, provided no wetting and drying cycles are present; therefore the assumption of instantaneous wetting of the bentonite is a conservative assumption with respect to corrosion for the conditions outlined above.

3. DESCRIPTION OF THE NAGRA REFERENCE CONTAINERS

3.1 Cast steel container for high-level waste

For vitrified high-level waste delivered from the reprocessing plant /6/ the Nagra reference design is a self-supporting shell design. The material chosen is cast steel GS-40 /11/, although other unalloyed cast or wrought steels or irons with similar mechanical properties would be just as suitable. The mechanical design criteria and stress analysis as well as the main aspects of the manufacture, sealing and quality assurance are presented in /12/ and only those aspects that are relevant to the assessment of the corrosion resistance will be summarized in the framework of the present report.

The container is designed against a uniform external pressure of 30 MPa; in order to ensure a favourable stress distribution it is in the form of a thick-walled cylinder with hemispherical ends (Fig. 3.1) After emplacement of the vitrified waste the lid is welded. The weld is located in a region of low stress and good heat dissipation capabilities.

The stress analysis carried out show that the requirements of the ASME Boiler and Pressure Vessel Code /13/ are fulfilled with an appreciable safety margin if the wall thickness is 200 mm in the cylindrical part of the container and 100 mm in the hemispherical ends. To these wall thicknesses a design corrosion allowance of 50 mm has been added, yielding an overall wall thickness of 250 mm for the cylindrical part of the container and 150 mm for the hemispherical ends. The depth of the weld is somewhat higher than the general corrosion allowance: if required, depths of up to 100 mm could be achieved.

The wall thickness of 250 mm in the cylindrical part of the container ensures that even at the time of disposal the radiation level at the surface does not exceed 200 mrem/h. Additional internal shielding materials without mechanical function are provided in the hemispherical ends to ensure that this radiation level is not exceeded at any point of the container surface. As a result, the influence of the radiation on the corrosion rate of the container, directly as well as indirectly via radiolysis of the water contained in the bentonite is negligible /12/, /14/, /15/.

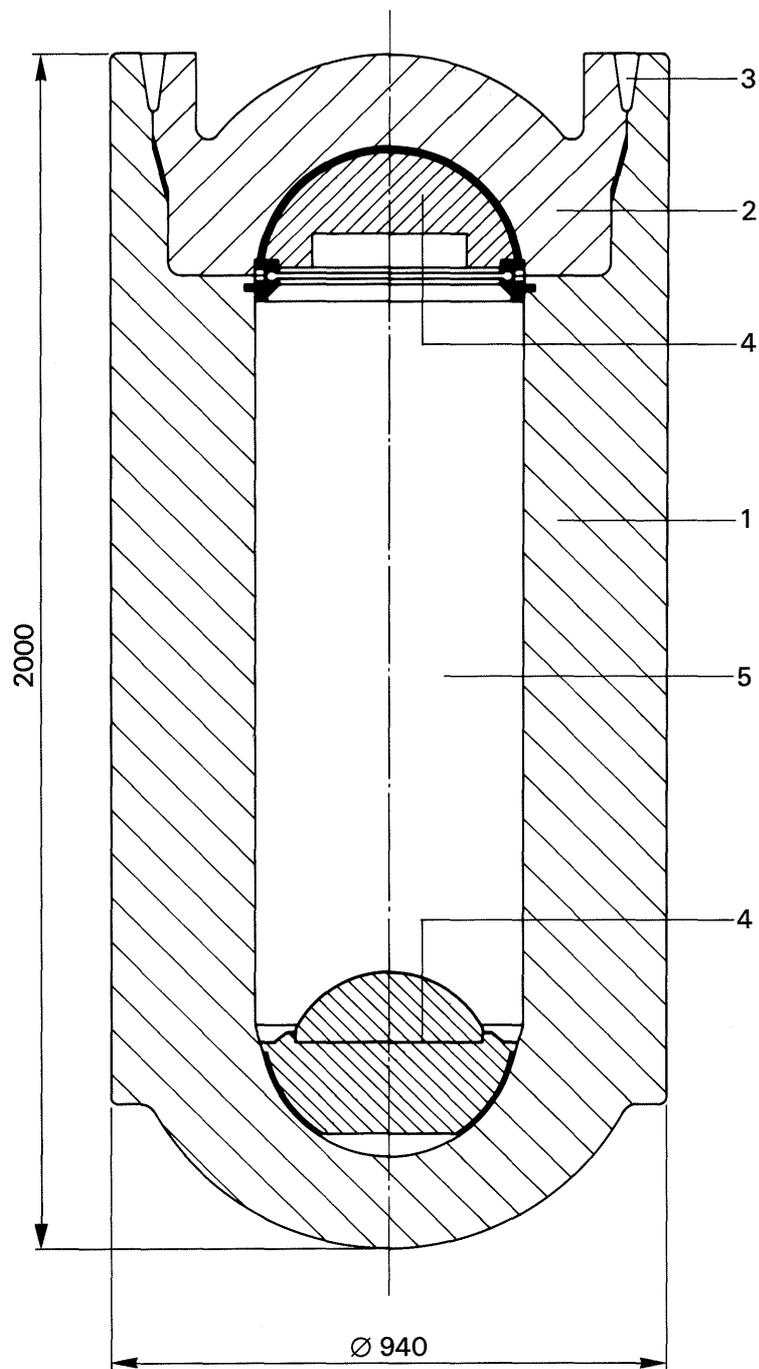


Fig. 3.1: The Nagra reference design for reprocessed high-level waste. Material: cast steel GS 40, wall thickness: cylindrical part 250 mm, hemispherical ends 150 mm

All dimensions are in mm.

- 1: container body;
- 2: lid;
- 3: sealing weld;
- 4: radiation screening material;
- 5: emplacement of vitrified high-level waste.

3.2 Copper container for spent fuel

As reference design for the encapsulation of spent fuel a welded, lead-filled copper container essentially the same as one of the reference designs proposed in Sweden has been chosen /5/, /16, /17/. The basic features of the design are shown in Figure 3.2. The wall thickness is 100 mm, and the copper does not fulfil any mechanical function during final disposal, since it is supported by the lead filling. Any small voids in the lead filling will be closed by slight deformations of the copper; because the voids represent a very small proportion of the inside volume of the container (typically 1 % to 2 %), the strains in the copper will remain considerably smaller than the ultimate strain. Any stresses associated with these strains will be relieved in time because of annealing and creep, so that essentially the whole copper wall thickness can be regarded as a corrosion allowance.

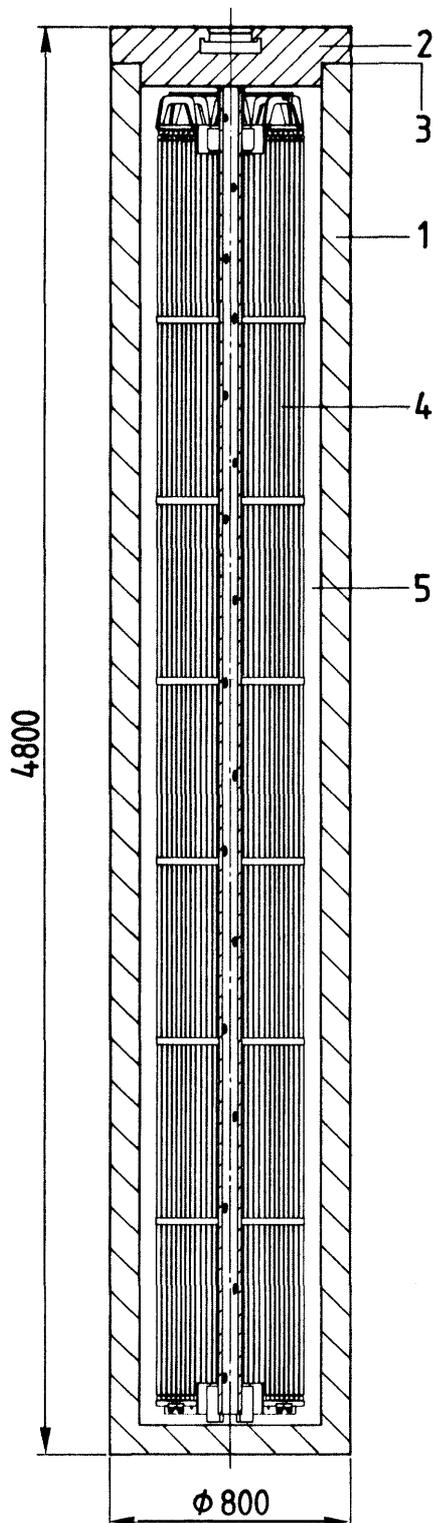


Fig. 3.2: The Nagra reference design for spent fuel.
Material: copper. Wall thickness: 100 mm

All dimensions are in mm.

1: container body; 2: lid; 3: sealing weld;
4: spent fuel elements, embedded in lead;
5: lead filling.

4. CORROSION OF COPPER CONTAINERS4.1 Corrosion mechanisms

Copper is defined as a noble metal since its standard electrode potential (E°) is positive. Some standard electrode potentials from /18/ are given in Table 4.1.

Reaction	E° (Volts) for unit activity at 25°C
$\text{Au} \longrightarrow \text{Au}^{3+} + 3e$	+ 1.50
$\text{Ag} \longrightarrow \text{Ag}^+ + e$	+ 0.799
$\text{Cu} \longrightarrow \text{Cu}^+ + e$	+ 0.521
$\text{Cu} \longrightarrow \text{Cu}^{++} + 2e$	+ 0.337
$\text{H} \longrightarrow \text{H}^+ + e$	0.000 (by definition)
$\text{Pb} \longrightarrow \text{Pb}^{++} + 2e$	- 0.126
$\text{Ni} \longrightarrow \text{Ni}^{++} + 2e$	- 0.250
$\text{Fe} \longrightarrow \text{Fe}^{++} + 2e$	- 0.44
$\text{Zn} \longrightarrow \text{Zn}^{++} + 2e$	- 0.763

Tab. 4.1: Selected standard electrode potentials E°

The standard electrode potentials are equilibrium thermodynamic values, a positive E° means that the metal will not displace hydrogen ions from solution; the metal is thermodynamically stable in the presence of the H^+ ion and hence in pure water.

A more complete picture of the thermodynamic equilibria for the copper-water system is given in the Pourbaix diagram, Figure 4.1 /19/. The two dotted lines represent the stability field for water in the Eh-pH domain, the lower the $\text{H}_2/\text{H}_2\text{O}$ and the upper the $\text{H}_2\text{O}/\text{O}_2$ boundary. The stability fields of the copper species are marked. The exact positions of the boundaries are dependent upon the activity of the soluble species Cu^{++} and CuO_2^{--} . For corrosion purposes the 10^{-6} mol/litre boundary is normally considered to be definitive. Even under these more stringent conditions, the lower boundary line for water remains entirely within the Cu (copper as metal) field. Copper will thus not react with water directly over the entire pH range at 25°C.

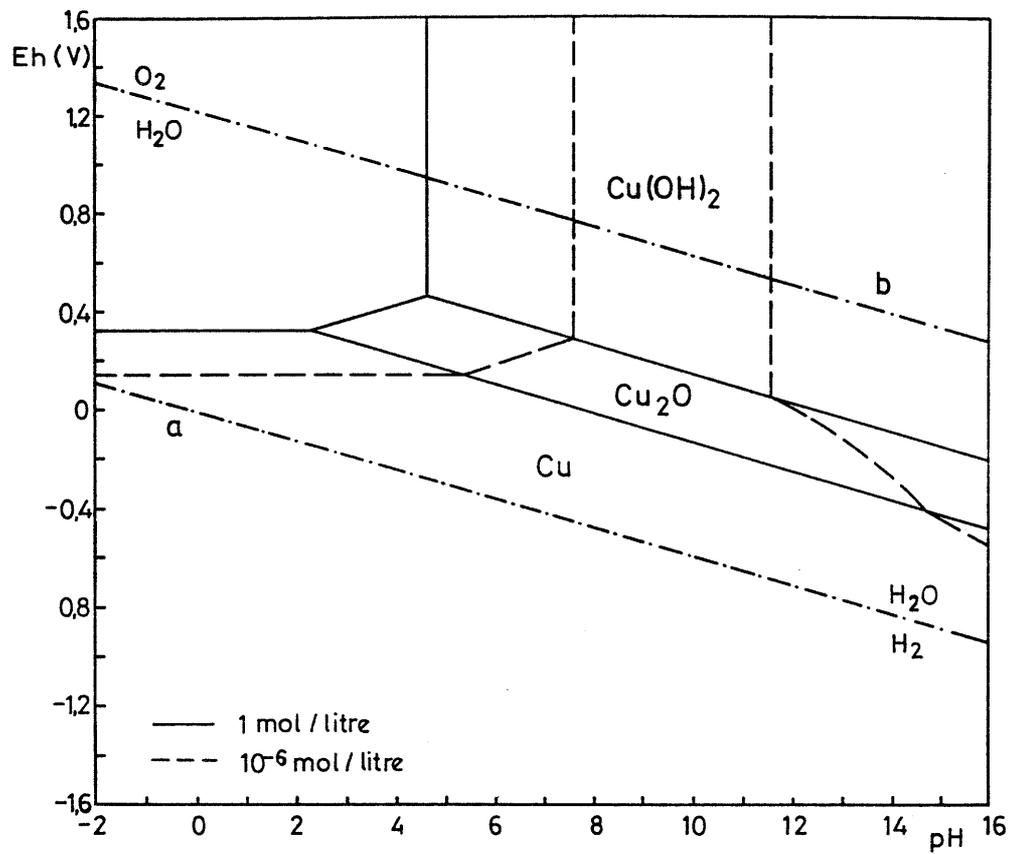


Fig. 4.1: The Pourbaix diagram for copper at 25°C and 0.1 MPa

Lines (a) and (b) limit the domain of stability of water; the concentration limits are shown for the species Cu^{++} , resp. CuO_2^{--} .

The thermodynamic basis for the immunity to corrosion of copper by water has been thoroughly documented in /20/. It was demonstrated that copper was thermodynamically stable up to at least 150°C.

The thermodynamic immunity of copper in water is the basis for the choice of copper as a container material. Copper is the most readily available metal which fulfills this criterion. Water is the only potential corrodant available in unlimited quantities in the repository, and therefore immunity of direct corrosion by water greatly simplifies the treatment of corrosion of copper under repository conditions. The corrosion rate due to any other corrodant may be conservatively assumed to be equal to the rate of supply of that corrodant.

The conditions within the repository were presented in Section 2. The potential corrodants present in the repository are oxygen, chloride, sulphate and sulphide.

The container will be packed in highly compacted bentonite. At the time of sealing the repository is dry, and the pores in the bentonite will be filled with air, a source of oxygen. The rate of reaction of copper with oxygen is fast on the time scales involved. Groundwater will seep into the repository and saturate the bentonite. The groundwater is practically oxygen free; therefore, once the pore oxygen is consumed no more oxygen will reach the container.

Sulphate and chloride are present in the reference groundwater (see section 2.2); they may directly or indirectly act as oxidants for copper. The bentonite backfill is a source of sulphate and sulphide.

The reference groundwater contains a considerable amount of chloride (6620 mg/litre). Chloride can promote the corrosion of copper by the hydrogen ion. The formation of copper chloride complexes can lead to solubilities of copper which exceed the 10^{-6} mol/litre normally required for thermodynamic immunity. The solubility of copper as chloride complexes is dependent upon temperature, chloride ion concentration, and the redox or corrosion potential Eh. Figure 4.2, derived from /17/, shows the effect of temperature and chloride concentration on the solubility of copper chloride complexes as a function of Eh. The copper chloride complexes are dominated by CuCl_2^- . The corrosion reaction may thus be written as:

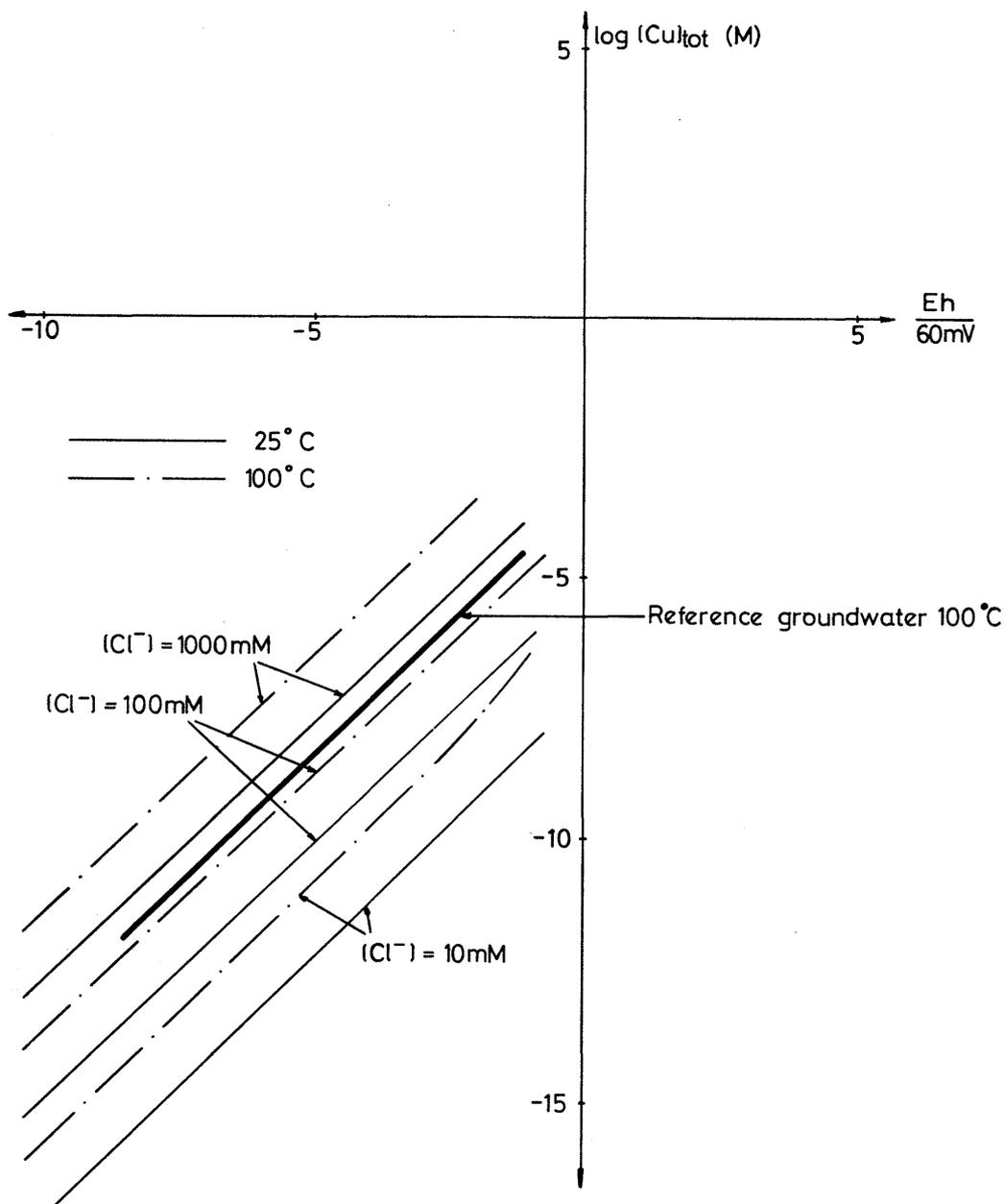
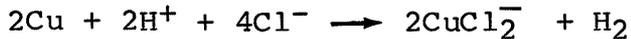


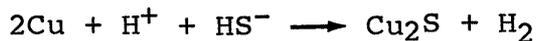
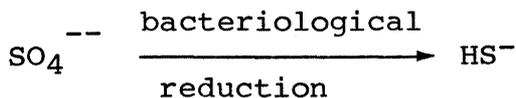
Fig. 4.2: Total copper concentration in thermodynamic equilibrium with metallic copper at various temperatures and chloride concentrations for pH between 6.5 and 8.5



At equilibrium the total concentration of copper in solution can be estimated from Figure 4.2.

Sulphate can only act as a direct oxidant for copper in the presence of an Fe(II) species. Although the reaction is thermodynamically possible, there is firm geochemical evidence that the oxidation of native copper in the presence of sulphate and Fe(II) species is negligible over geological time spans (10^6 a and more) /17/.

Sulphide is capable of promoting the oxidation of copper by the hydrogen ion. Sulphide is present as an impurity in the bentonite backfill. Sulphate can be reduced to sulphide by the action of microorganisms. The bacteriological reduction of sulphate to sulphide is favoured by the low redox potential values to be expected within the repository. The bacteriological reduction of sulphate to sulphide provides an alternative reaction path for the oxidation of copper by the sulphate present in the repository.



Bacteriological activity within the bentonite cannot be excluded, although no reliable data is available. In the event of biological activity it is considered unlikely that more than a small fraction of the sulphate will be reduced as only a limited amount of organic material, which sulphate reducing bacteria require for growth, is available within the repository. Nevertheless, in order to ensure conservatism it will be assumed that all of the sulphate is reduced to sulphide and thus available as a corrodant for copper.

4.2 Estimation of corrosion allowance for copper

In the previous section oxygen, chloride, sulphate and sulphide were identified as direct or indirect corrodants for copper present in the repository. The amount of corrosion due to each of these will be estimated in turn and the corrosion allowance calculated from the sum of these individual components.

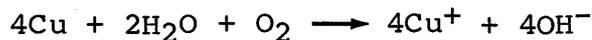
4.2.1 Corrosion due to oxygen

Oxygen is initially present in the vicinity of the canister as air trapped in the pores of the compacted bentonite. There is no other source of oxygen.

Oxygen will be consumed by the Fe(II) present in the bentonite as an impurity, and in the surrounding rock formation. Nevertheless, it will be conservatively assumed that all the trapped oxygen is available for corrosion of the copper containers. The amount of oxygen assigned to each container is that trapped within the bentonite between the tunnel walls and the container and over a distance equal to 1.5 times the spacing of adjacent containers. The reasons for this conservative assumption is given in /21/. The copper containers for spent fuel elements are 4.8 m long, 0.8 m in diameter and spaced 10 m apart along the tunnel (container centre to container centre).

This gives:	Volume of tunnel section	161.3 m ³
	Volume of container	2.4 m ³
	Volume of bentonite	158.9 m ³
	Volume of air trapped, 41 % porosity	65.2 m ³ NTP
	Volume of oxygen, 20 % in air	13.0 m ³ NTP
	Mass of oxygen	18.5 kg

It will be conservatively assumed that copper is oxidised to Cu⁺ via the reaction:



whereby 32 kg of oxygen oxidises 254 kg of copper.

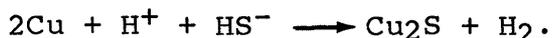
Therefore, at most 147 kg of copper can be corroded by the residual oxygen in the bentonite, corresponding to an average attack of less than 1.3 mm for a container surface area of 13 m².

4.2.2 Corrosion due to sulphate/sulphide

It will be conservatively assumed that all sulphate will be reduced to sulphide by bacteriological action and thus available for corrosion, and further that the reaction rate of sulphide with copper is extremely fast, i.e. that the rate limiting step is the transport of corrodant to the container. The details of the calculation of the corrosion by sulphate/sulphide are given in /21/.

It should be noted that the reference groundwater is sulphate saturated, so that all the sulphate and sulphide contained in the bentonite after wetting may conservatively be assumed to be available for corrosion, since they will not be able to diffuse away from the bentonite into the groundwater.

The reaction assumed for the calculation in /21/ is



It is conservative, since it assumes that all copper corrosion products contain monovalent copper. The results of the calculation, as presented in /21/, show that with conservative values of the diffusivity of HS^- in bentonite the total sulphate/sulphide content of the bentonite will be used by corrosion in slightly more than 10'000 years, and that in the first 1'000 years less than 25% of that total content, i.e. at most 6.1 kmol will react with 12.2 kmol of copper. Therefore, the maximum amount of copper corroded by sulphate/sulphide in the first 1'000 years is 775 kg, corresponding to an average attack of less than 6.7 mm for a container surface area of 13 m².

4.2.3 Corrosion due to chloride

The reference groundwater contains 6620 mg/litre (187 mmol/litre) chloride. Chlorides form complexes with copper raising the solubility of copper in the groundwater /20/. The total copper solubility in the model groundwater can be extracted from the data presented in Figure 4.2 /17/.

It will be conservatively assumed that after flooding the pore water at the container surface becomes instantaneously saturated with copper chloride complexes. The temperature will, as a conservative assumption, be assumed to be 100°C throughout the repository for the chloride corrosion estimate. The pH will be taken as that of the groundwater (pH 6.8) and the highest estimate for Eh (Eh = -60 mV) taken since this represents the most unfavourable condition.

For 187 mmol/litre Cl^- at pH 6.8 and Eh = -60mV at 100°C, the total dissolved copper is $32 \cdot 10^{-6}$ mol/litre, i.e. 2.05 mg/litre. The bentonite contains 65 m³ of pore water. Furthermore, as shown in /3/, the container will interact with the chloride contained in less than 2 m³ of groundwater in the first 1'000 years. The total amount of copper corroded by chloride will therefore be about 0.1 kg in 1'000 years.

At this chloride concentration, corrosion due to chloride may be neglected. This result also serves to illustrate that for the assumption of thermodynamic immunity, a metal solubility limit of 10^{-6} mol/litre is more than adequate.

4.2.4 Form of attack

The corrosion attack on the copper container has so far been assumed to be perfectly uniform, however, as this is rarely the case some allowance has to be made for non-uniform attack. Metals which do not rely for their corrosion resistance on a passive film are not in general prone to deep pitting, nevertheless some localization of the corrosion attack is to be expected. This problem has been discussed very carefully in the framework of the KBS project in Sweden /17/; the conclusion of the work was that pitting factors (defined as the ratio of maximum penetration to average penetration) of more than 5 are not to be expected. The conditions in the NAGRA repository design are such that no mechanism that would tend to promote pitting can be identified. The experimental results obtained so far in the Nagra programme /14/ confirm this: they do not show evidence of any tendency to pitting. Therefore a pitting factor of 5 is considered to be a very conservative estimate.

4.3 Corrosion allowance for copper

Only oxygen and sulphate/sulphide cause significant corrosion of copper under repository conditions. Thus the maximum expected average penetration is less than 8 mm for 1'000 years (1.3 mm due to oxygen and 6.7 mm from sulphate/sulphide). Even with the conservative assumption of a pitting factor of 5, the maximum penetration after 1'000 years would be 40 mm. The wall thickness of the Nagra reference design is 100 mm. The full 100 mm are a corrosion allowance, since the copper in that design does not fulfil any mechanical function. It is concluded that from the point of view of corrosion the Nagra reference design will have a lifetime of more than 1'000 years in the conditions expected for the central scenario.

5. CORROSION OF CAST STEEL GS-40 CONTAINERS5.1 Corrosion mechanisms

GS-40 is an unalloyed iron base material, the typical chemical composition is given in Table 5.1 /11/. The corrosion thermodynamics are those of iron.

	C	P	S	Si	Mn	Al	Fe
GS-40	0.19	0.014	0.006	0.37	0.74	0.06	bal.

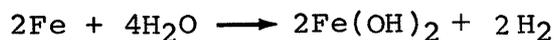
Tab. 5.1: Typical chemical composition of GS-40 (in weight %)

Iron is a base metal as its standard electrode potential is lower than that for hydrogen in the electrochemical series (Table 4.1).

The Pourbaix diagrams for iron, Figure 5.1 /19/, show that the stability domain for iron lies completely below the lower stability line for water (line a), i.e. iron is thermodynamically unstable in water. At low pH values, iron will go into solution as Fe^{++} :



At higher pH values, as the Pourbaix diagrams indicate, various solid phases are thermodynamically stable; the domains for Fe_3O_4 in Figure 5.1(i) and for $Fe(OH)_2$ in Figure 5.1(ii) largely overlap, as do those for the higher oxidation states Fe_2O_3 and $Fe(OH)_3$. Other phases which may be formed but have not been considered in the construction of the two Pourbaix diagrams are FeO and $FeO(OH)$. All of these phases may be formed by direct reaction with water, e.g.:



The actual phase or phases which form depend upon pH, temperature, Eh, and solution composition, and is not necessarily that which thermodynamics indicate to be the most stable under the prevailing conditions.

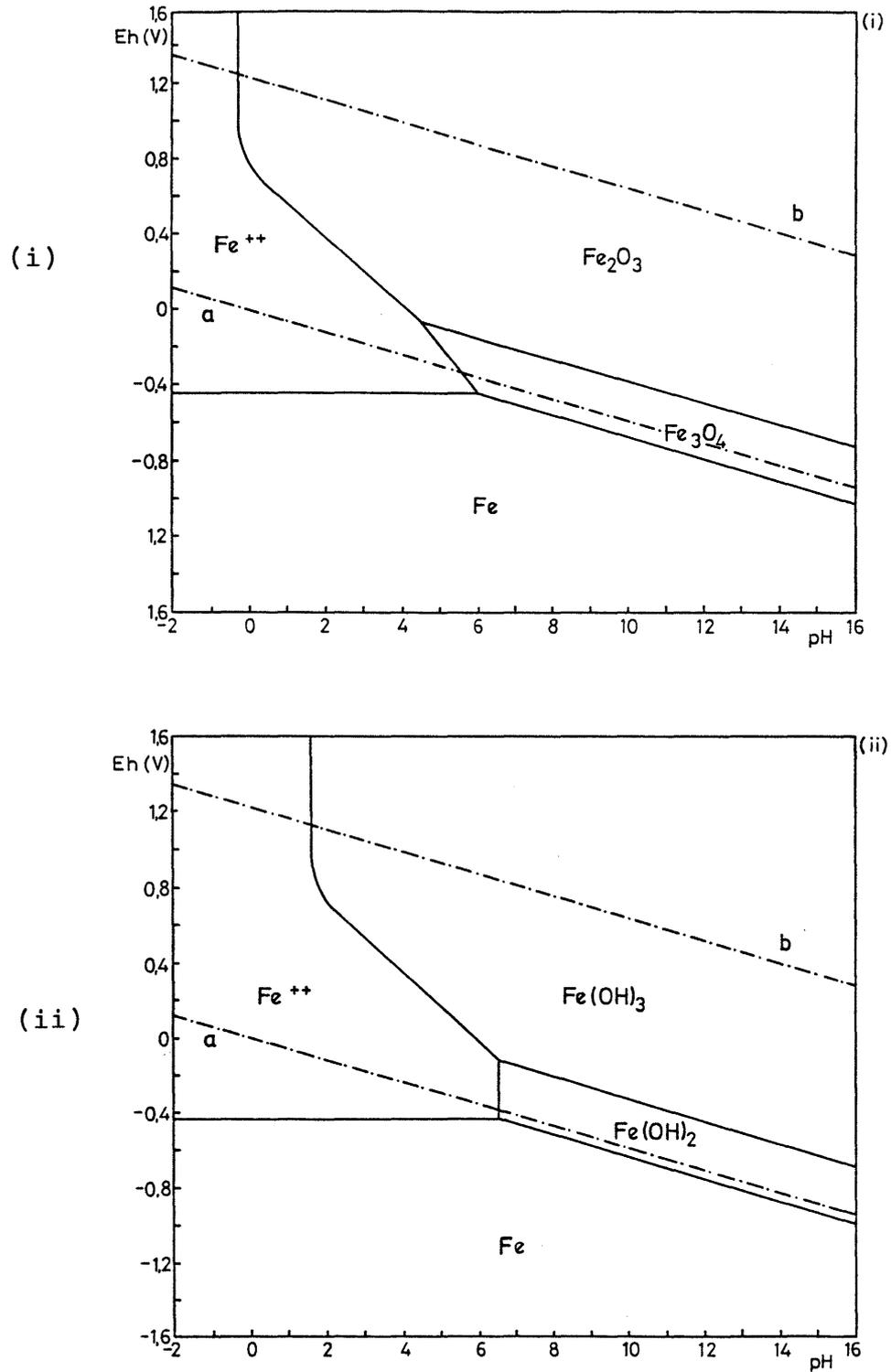
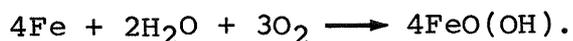


Fig. 5.1: The Pourbaix diagrams for iron at 25°C and 0.1 MPa: (i) considering oxides and (ii) considering hydroxides

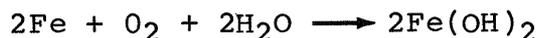
The Pourbaix diagrams have been derived for a temperature of 25°C and a pressure of 0.1 MPa. In principle, pressure could suppress the corrosion of iron, but thermodynamic data /22/ indicate that the formation of the thermodynamically most stable phase, Fe₃O₄, is not likely to be suppressed by the pressures of up to 30 MN/m² expected in the repository. It must be assumed that water will react with iron at all temperatures and pressures to be found within a repository.

The container will be packed in highly compacted bentonite. At the time of sealing the repository is dry, and the pores in the bentonite will be filled with air, a source of oxygen. Iron may be oxidised by oxygen. The rate of reaction of iron with oxygen is fast on the time scales involved. Groundwater will seep into the repository and saturate the bentonite. The groundwater is practically oxygen-free; therefore, once the pore oxygen is consumed no more oxygen will reach the container.

Iron may be corroded by oxygen via:

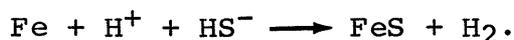


For the purpose of the calculations, iron will be conservatively assumed to react via:



since this results in the maximum iron consumption for a given quantity of oxygen.

As discussed for copper, sulphate and sulphide can be supplied by the groundwater and are present in the bentonite as impurities. Sulphide can be produced from sulphate reduction by bacterial action. Sulphide may corrode iron by forming an alternative path for oxidation by the hydrogen ion:



5.2 Estimation of corrosion allowance for cast steel GS-40

The case for iron differs from that for copper in that the direct reaction with water must be considered, whereby there is no limitation to the supply or rate of supply of water to the metal as is the case with the other oxidants.

The fact that iron is thermodynamically unstable does not mean that the corrosion rate on iron in water is fast; this is definitely not the case at solution pH values of 6 and above. The reaction rate of iron with water is kinetically controlled, the rate determining step is thought to be within the surface film which forms. The mechanism

is not completely understood and is for the purposes of this discussion of secondary importance. The use of iron as an engineering material is largely based upon the empirical observation that the corrosion rate of iron is acceptably low over a wide range of water composition and temperature. The choice of GS-40 in /23/ was based upon this fact. Both Heitz and Zur Megede, /24/ and Grauer /25/ in their evaluations of suitable materials for Nagra containers came to the conclusion that there was sufficient existing evidence to justify the choice of iron as cast steel.

In order to determine the total corrosion allowance for cast steel the following approach is used: the corrosion allowances for the sulphate/sulphide and the oxygen reactions are estimated in the same way as for copper; an upper limit for the corrosion attack from all other corrosants, including in particular chloride and water itself, is estimated from the available evidence pertaining to anaerobic, sulphide-free conditions; this upper limit is then added to the oxygen and sulphate/sulphide allowances to obtain the total corrosion allowance.

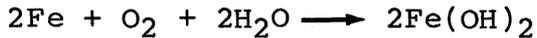
5.2.1 Corrosion due to oxygen

Oxygen is initially present in the vicinity of the container as air trapped in the pores of the compacted bentonite. There is no other source of oxygen.

Oxygen will be consumed by the Fe(II) present in the bentonite as an impurity, and in the surrounding rock formation. Nevertheless, it will be conservatively assumed that all the trapped oxygen is available for corrosion of the steel containers. The amount of oxygen assigned to each container is that trapped within the bentonite between the tunnel walls and the container and over a distance equal to 1.5 times the spacing of adjacent containers. The reasons for this conservative assumption is given in /21/. The steel containers for high level waste are 2.0 m long, 0.94 m in diameter and spaced 5 m apart along the tunnel (container centre to container centre).

This gives:	Volume of tunnel section	80.6 m ³
	Volume of container	1.3 m ³
	Volume of bentonite	79.9 m ³
	Volume of air trapped, 41 % porosity	32.8 m ³ NTP
	Volume of oxygen, 20 % in air	6.5 m ³ NTP
	Mass of oxygen	9.3 kg

It will be conservatively assumed that steel is oxidised to Fe^{++} via the reaction:



whereby 32 kg of oxygen oxidises 112 kg of iron.

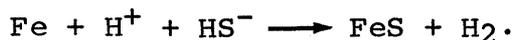
Therefore, at most 32 kg of iron as cast steel can be corroded by the residual oxygen in the bentonite, corresponding to an average attack of less than 0.7 mm for a container surface area of 6 m².

5.2.2 Corrosion due to sulphate/sulphide

It will be conservatively assumed that all sulphate will be reduced to sulphide by bacteriological action and thus available for corrosion, and further that the reaction rate of sulphide is extremely fast, i.e. that the rate limiting step is the transport of corrodant to the container. The details of the calculation of the corrosion by sulphate/sulphide are given in /21/.

It should be noted that the reference groundwater is sulphate saturated, so that all the sulphate and sulphide contained in the bentonite after wetting may conservatively be assumed to be available for corrosion, since they will not be able to diffuse away from the bentonite into the groundwater.

The reaction assumed for the calculation in /21/ is



It is conservative, since it assumes that all iron corrosion products contain divalent iron. The results of the calculation, as presented in /21/ show that with conservative values of the diffusivity of HS^- in bentonite the total sulphate/sulphide content of the bentonite will be used by corrosion in 8'800 years, and that in the first 1'000 years less than 25 % of that total content, i.e. 3.1 kmol, will react with 3.1 kmol of steel. Therefore, the maximum amount of steel corroded by sulphate/sulphide in the first 1'000 years is 173 kg, corresponding to an average attack of less than 3.8 mm for a container surface area of 6 m².

5.2.3 Corrosion of cast steel GS-40 in saline groundwater

As already discussed, the purpose of this section is to estimate the long-term corrosion rate of iron in anaerobic, sulphide-free saline waters representative of repository conditions. An accurate value cannot be derived from the available data, but the setting of a likely upper limit for the corrosion attack over 1'000 years is possible.

The discussion will therefore concentrate on the data available most closely relevant to repository conditions. These are an evaluation of long-term corrosion tests in sea water /26/, the results of the UK corrosion programme for a repository in a crystalline formation /27/, and the results from Nagra's own corrosion programme /14/, /23/. Finally mention is made of the observations on archeological finds /25/.

The analysis in /26/ uses data from the 16 year corrosion tests of Southwell et al. /28/ as a basis. The argumentation is based on short-term measurements which show that the temperature dependence of the corrosion rate follows an Arrhenius-type law under conditions where no magnetite layer forms. The activation energy is independent of whether the conditions are oxidising or reducing. The temperature dependence of the short-term experiments were then combined with an analysis of the time dependence of the long-term results of Southwell et al. /28/ to obtain the time-temperature dependence of the corrosion rate. This relationship should be valid for both aerobic and anaerobic conditions, the only difference being a scaling factor which was derived from short-term experiments. The following equation was derived for corrosion in anaerobic sea water,

$$P = 267 t^{0.76} \exp. (-2'850/T)$$

where P is the maximum depth of attack in mm, t the time in years and T the temperature in K. For the temperature history assumed for the container (Section 2.1), i.e.: 155°C for 50 years, 100°C for 100 years, 80°C for 300 years and 60°C for 550 years, this equation gives a depth of attack of less than 19.5 mm.

A study by Heusler /22/ of the thermodynamics and kinetics of the corrosion of iron at temperatures between 100°C and 150°C with magnetite as the corrosion product suggests a much lower corrosion rate than that predicted from the Southwell data. Since magnetite forms in the model groundwater at 140°C /14/, the use of the above equation is conservative.

The work of Marsh and co-workers in the UK /27/ is concerned with the direct measurement of corrosion rates of carbon steels in deaerated sea water at 90°C, and are therefore directly relevant to Nagra conditions. They show that the corrosion rate settles after a short transient to a value of less than 10 $\mu\text{m/a}$. They also investigated the influence of radiation on the corrosion of iron and only found an effect at levels of 2'000 rad/h or more, i.e. 10'000 times higher than has been determined for the Nagra reference design.

These results are in good agreement with those from the Nagra programme. This programme is in two phases, the first phase includes immersion testing in slightly aerated Säckinger water at 80°C and 140°C, and in bentonite saturated with Säckinger water at 140°C /14/, /23/. Säckinger water has a lower total dissolved solids content than the Nagra reference water. In the second phase similar tests are in progress in a deaerated water with a slightly higher salinity than that of reference water (Section 2.2).

The results from both phases at 80°C show that after an initial fairly high corrosion rate in the first month (30-70 $\mu\text{m/a}$), the corrosion rate slows down to approximately 5 $\mu\text{m/a}$. The corrosion rates measured in bentonite are very similar to those for the plain immersion tests. The corrosion rates at 140°C in Säckinger water are lower than at 80°C since a compact magnetite layer formed, in agreement with the prediction of Heusler /22/.

The archaeological evidence evaluated by Grauer /25/ and Johnson and Francis /29/ shows that iron materials can survive for considerable periods of time in the presence of water. Grauer came to the conclusion that under anaerobic conditions many buried iron objects corrode at rates of less than 10 mm in 1'000 years, including a case where the object was in sea bottom sediment. The archaeological evidence in itself is not sufficient to conclude that such low rates will apply to a repository, but is on the other hand extremely valuable as it included the factor time to an extent impossible otherwise, and shows that once low corrosion rates are established they are retained indefinitely. The corrosion rates observed on a laboratory timescale should thus provide an upper limit valid over the life of the repository.

The conditions within the repository are favourable for iron. All the evidence is that the major pre-requisite for very low corrosion rates is the absence of oxygen; if this condition is fulfilled the corrosion rate for iron is insensitive to temperature and groundwater composition over the range of interest. It was concluded in /14/ that a corrosion allowance of 20 $\mu\text{m/a}$ was a conservative upper limit for the corrosion rate under repository conditions; it should be noted that in all three experimental studies quoted as well as for the archaeological evidence the corrosion rates given are for the maximum, as opposed to average, penetration, i.e. no further allowance for the unevenness of the attack is required over and above the 20 $\mu\text{m/a}$ forecast.

5.2.4 Form of attack

The corrosion rate forecast for the attack by saline groundwaters, as discussed above, includes an allowance for the unevenness of attack. As far as the oxygen and sulphate/sulphide reactions discussed in sections 5.2.1 and 5.2.2 are concerned, no significant localized attack is expected, so that the maximum penetration is unlikely to be more than twice the average penetration.

5.3 Corrosion allowance for cast steel GS-40

Oxygen and sulphate/sulphide corrode 32 kg and 173 kg of iron, respectively. The container has a surface area of 6.0 m², thus oxygen and sulphate/sulphide corrode less than 4.5 mm of iron on average. This, as discussed in section 5.2.4, is judged to be equivalent to a maximum penetration of 9 mm; to this must be added the 20 mm from the saline water corrosion. Therefore the maximum corrosion penetration in 1'000 years forecast for GS-40 is less than 30 mm. The Nagra reference design has a corrosion allowance of 50 mm. It is therefore concluded that from the point of view of corrosion this design will have a lifetime of more than 1'000 years in the conditions expected for the central scenario.

6. CONCLUSIONS AND RECOMMENDATIONS

The corrosion allowances estimated in this report have been obtained using conservative assumptions, the most important of which are:

- that all the residual oxygen will contribute to the corrosion of the container material
- that all the available sulphate in the bentonite is reduced to sulphide by microbiological activity
- that all the copper corrosion products are monovalent and all the iron corrosion products are divalent
- that the highest measured values of anion diffusivity in bentonite are applicable to the conditions in the repository.

The evidence for the use of copper as a container material is at the present time very strong, so that no aspects need to be further investigated in the framework of the feasibility of safe disposal from the point of view of corrosion.

Iron is expected to behave as well as copper under repository conditions; however, the evidence is at the present slightly less complete than for copper. This situation can be improved by a sustained qualification programme, which should include long-term tests of up to 10 years duration under repository conditions. Alongside these tests more fundamental research should be undertaken in order to improve the understanding of the processes involved; for instance the direct measurement of the corrosion kinetics via the amount of hydrogen evolved /30/, and electrochemical experiments and corrosion morphology determinations such as those carried out by Marsh and co-workers /27/.

Investigations of this sort should make it possible to further confirm the conservatism afforded by the estimate of a penetration of less than 30 mm in 1'000 years or even allow a lower limit to be set.

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