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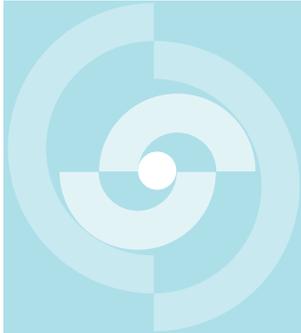
Nationale
Genossenschaft
für die Lagerung
radioaktiver Abfälle

Cédra

Société coopérative
nationale
pour l'entreposage
de déchets radioactifs

Cisra

Società cooperativa
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TECHNISCHER BERICHT 83-05

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

J. P. Simpson

October 1983

Sulzer Brothers Ltd, Winterthur

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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 1'000 to 1'500 m in the granitic bedrock of northern Switzerland. The waste will be placed in a container which is required to function as a high integrity barrier for a number of years following the closure of the repository. The present report is the first of a set of two dealing with the evaluation of potential materials for such containers. The properties which determine the selection of appropriate materials are: the resistance to elevated temperatures and high levels of radiation, mechanical resistance and resistance to corrosion. A review of the available literature leads to the conclusions that polymeric materials are unsuitable primarily because of their inadequate thermal performance and that ceramic materials, in particular alumina, can present problems because of their poor or unproven fracture toughness characteristics. Metals, in view of their mechanical properties and ease of fabrication and use, are considered most likely to provide a satisfactory solution at the present time. The main difficulty lies in proving the integrity of the container for the required life (up to approx. 1'000 years) when subjected to corrosion in groundwater under repository conditions. Nodular iron, cast steel, copper, inconel 625 and Ti-Code 12 are judged to be the most promising candidates for further consideration within the Swiss programme.

A more detailed appraisal of the materials retained, in particular with respect to corrosion, identifies a number of issues insufficiently covered by the available literature. The experimental programme initiated to provide a better data base includes

- (1) constant strain rate testing of Ti-Code 12 and copper at 80°C in solutions up to 2 mg/l O₂ and up to 15 g/l Cl⁻ at strain rates between 10⁻⁵ and 2 x 10⁻⁷ s⁻¹;
- (2) the effect of bentonite on the corrosion of Ti-Code 12, copper, nodular cast iron and cast steel;
- (3) general immersion corrosion tests of welded specimens of the above four materials at temperatures up to 140°C;
- (4) the behaviour of copper, Ti-Code 12 and Zircalloy-2 when immersed in liquid lead for times up to 500 hours under a tension equal to 80 % of their yield stress at room temperature;
- (5) corrosion potential and galvanic current measurements on electrodes of several material pairs (Cu/cast steel, Cu/cast nodular iron, Ti-Code 12/cast steel, Ti-Code 12/cast nodular iron, Cu/Pb, Ti-Code 12/Pb) at room temperature and 140°C up to 1'000 h.

In all the experiments the corrosive medium is chosen to represent expected groundwaters at repository depths in Switzerland.

An appendix to the present report presents the first experimental results obtained. Full experimental details, results and conclusions of the work will be given in a subsequent Nagra Technical Report.

ZUSAMMENFASSUNG

Im derzeitigen Entsorgungskonzept für hochaktive nukleare Abfälle ist vorgesehen, ein Endlager auf 1'000 m bis 1'500 m Tiefe untertag im granitischen Grundgebirge der Nordschweiz zu errichten. Der Abfall soll in Behälter eingebracht werden, die nach dem Verschluss des Endlagers die Rolle einer Barriere hoher Integrität übernehmen sollen. Das vorliegende Dokument ist der erste von zwei Berichten über die Evaluation möglicher Behältermaterialien. Folgende Eigenschaften bestimmten die Auswahl der Werkstoffe: Mechanische Festigkeit, Korrosionsbeständigkeit sowie deren Beeinflussung durch erhöhte Temperatur und Strahlung. Aus der Literatur lässt sich die Schlussfolgerung ziehen, dass Polymere oder keramische Materialien (z.B. Aluminiumoxyd) ungünstig sind; die ersteren vor allem wegen schlechter Eigenschaften bei erhöhter Temperatur, die zweiten aufgrund ihrer schlechten oder z.T. noch zu wenig bekannten Bruchfestigkeiten. In Anbetracht ihrer mechanischen Eigenschaften und ihrer guten Herstellbarkeit und Anwendbarkeit sind Metalle zum heutigen Zeitpunkt am besten dazu geeignet, eine zufriedenstellende Lösung darzustellen. Die hauptsächliche Schwierigkeit liegt darin, die langfristige Integrität der Behälter zu beweisen, dies unter den korrosiven Umgebungsbedingungen in Gesteinswässern während der erforderlichen Zeiten (ungefähr 1000 Jahre). Die für weitere Untersuchungen im Rahmen des schweizerischen Entsorgungsprogramms ausgewählten Metalle sind: Sphäroguss, Stahlguss, Kupfer, Inconel 625 und Ti-Code 12.

Während einer gründlicheren Bewertung der ausgewählten Metalle stellte sich heraus, dass vor allem auf dem Gebiet der Korrosion eine Anzahl Sachfragen nur unzureichend in der Literatur behandelt wurden. Das zur Verbesserung der Datenbasis in Angriff genommene Experimentalprogramm umfasst:

- 1) Prüfung von Ti-Code 12 und Kupfer unter konstanten Verformungsraten (zwischen 10^{-5} und $2 \times 10^{-7} \text{ s}^{-1}$) in wässriger Lösung (bis 2 mg O_2 pro Liter und bis 15 g Cl^- pro Liter) bei 80°C
- 2) Einfluss von Bentonit auf das Korrosionsverhalten von Ti-Code 12, Kupfer, Sphäroguss und Stahlguss
- 3) Langfristige Korrosionsprüfung von geschweissten Proben dieser vier Materialien zur Untersuchung der Korrosionsphänomene bei Temperaturen bis 140°C
- 4) Das Langzeitverhalten (bis 500 Stunden) von Ti-Code 12, Kupfer und Zircalloy-2 in flüssigem Blei unter einer Zugsspannung gleich 80 % der Streckgrenze bei Raumtemperatur
- 5) Messung von Korrosionspotentialen und galvanischen Strömen an Elektrodenpaaren einiger Metalle (Kupfer/Stahlguss, Kupfer/Sphäroguss, Ti-Code 12/Stahlguss, Ti-Code 12/Sphäroguss, Kupfer/Blei, Ti-Code 12/Blei) bei Raumtemperatur und 140°C für Zeiten bis zu 1000 Stunden.

Alle Versuche werden in einem korrosiven Milieu durchgeführt, welches den erwarteten Bedingungen im Grundwasser in der Tiefe des geplanten Endlagers entspricht.

Die ersten experimentellen Resultate sind in einem Anhang zum vorliegenden Bericht zusammengestellt. Der volle Umfang experimenteller Details, Resultate und Schlussfolgerungen wird in einem späteren Nagra Technischen Bericht (NTB) dokumentiert.

RESUME

Le présent concept pour l'entreposage définitif des déchets hautement radioactifs en Suisse consiste en un dépôt à une profondeur de 1'000 à 1'500 m dans le socle granitique de la Suisse septentrionale. Les déchets seront placés dans un conteneur devant former une barrière d'une efficacité considérable pour plusieurs années à la suite de la fermeture du dépôt. L'évaluation de matériaux appropriés pour ces conteneurs est l'objet du présent rapport, le premier d'un groupe de deux. Les propriétés qui déterminent le choix d'un matériau sont: résistance aux températures et aux doses de radiation élevées, résistance mécanique et résistance à la corrosion. L'étude de la littérature permet de conclure que les polymères sont inadéquats à cause de leur résistance thermique insuffisante et que les céramiques (en particulier l'alumine) présentent des difficultés du fait que leur résistance à la rupture est faible ou mal connue. Les propriétés mécaniques des métaux et leur propriété de pouvoir être travaillés aisément les désignent comme l'option la meilleure dans l'état actuel des connaissances. La principale difficulté associée à leur emploi est de prouver l'intégrité du conteneur pour la durée de vie requise (de l'ordre de 1000 ans) quand ce dernier est exposé à la corrosion par les eaux souterraines sous les conditions physico-chimiques régnant dans le dépôt. La fonte sphéroïdale, l'acier coulé, le cuivre, l'inconel 625 et le Ti-Code 12 sont jugés être les candidats les plus prometteurs dans le cadre du programme suisse et mériter une étude plus poussée.

Une évaluation détaillée des cinq matériaux retenus, en particulier du point de vue de la corrosion, met en évidence des aspects qui ne sont qu'insuffisamment couverts par la littérature existante. Le programme expérimental envisagé pour augmenter les données de base comprend:

- 1) des essais à taux de déformation constant sur le Ti-Code 12 et le cuivre à 80°C avec jusqu'à 2 mg/l O₂ et 15 g/l Cl⁻ en solution, ceci à des taux de déformation de 1×10^{-5} à 2×10^{-7} s⁻¹
- 2) l'étude de l'effet de la bentonite sur la corrosion du Ti-Code 12, du cuivre, de l'acier coulé et de la fonte sphéroïdale
- 3) des essais de corrosion par immersion de spécimens soudés utilisant chacun des quatre matériaux énumérés ci-dessus, pour des températures atteignant 140°C
- 4) l'étude du comportement du cuivre, du Ti-Code 12 et du Zircalloy-2 sous immersion dans le plomb liquide pendant des périodes allant jusqu'à 500 heures sous une tension de 80% de leur limite d'élasticité définie à température ambiante
- 5) des mesures du potentiel de corrosion et des courants galvaniques sur des couples d'électrodes (Cu/acier coulé, Cu/fonte sphéroïdale, Cu/Pb, Ti-Code 12/Pb) à température ambiante et à 140°C pour des périodes allant jusqu'à 1000 heures.

Pour tous les essais, le milieu corrosif est représentatif des eaux souterraines se trouvant à des profondeurs entre 1'000 à 1'500 m en Suisse.

Une annexe au rapport présente les premiers résultats expérimentaux obtenus. Les détails des techniques expérimentales, les résultats complets et les conclusions du programme seront donnés dans un rapport technique de la Cédra devant paraître ultérieurement.

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1. INTRODUCTION

1.1 The multibarrier concept

In general, toxic substances can be rendered harmless in two ways. Firstly "concentrate and confine" (CC), i.e. isolate the substances fully from man. Secondly "dilute and disperse" (DD), i.e. ensure that only insignificant concentrations can reach man's environment. In radioactive waste disposal, the latter approach is routinely used for low emissions to the atmosphere or to water bodies from operating nuclear installations. For the bulk of the wastes, however, underground disposal is planned and the concepts are oriented towards the containment approach. Absolute containment for very long times cannot, of course, be guaranteed and the justification of this method for nuclear wastes lies in their extremely useful property of decreasing in activity due to radioactive decay. But even at very long times small quantities can remain because of high initial activities or of long half lives. This has led to the generally accepted principle of meeting safety objectives by means of a series of safety barriers which together provide a "multibarrier system". The barriers are partly sequential in that one (for example a waste container) ensures isolation and safety for some time until another (e.g. leach resistance) comes into play. They are also partly independent or overlapping so that poorer than expected performance by one system component need not lead to unacceptable degradation of the whole system. An important attribute of multibarrier systems is that they allow "flexibility" in achievement of overall objectives in that weaknesses in particular components can to some extent be compensated by improved characteristics of others. The Nagra concept for the disposal of highly radioactive wastes (HLW) relies on a series of barriers as described below.

1.2 HLW Final Repository Concept for Switzerland and the Role of the Containers

The present concept of Nagra for final disposal of high-level waste in Switzerland consists of a repository at a depth of approx. 1000 - 1500 m in the granitic bedrock of northern Switzerland. The safety barriers consist of natural barriers, i.e. the rock formation, the overlying geological formation and consequently the pattern of groundwater flow, as well as technical manmade barriers: the waste form itself (vitrified waste from reprocessing or possibly spent fuel elements), the container and filling materials and sealants. The role of the container is primarily that of a high integrity barrier to the movement of radioactive species during the operational phase as well as during the first years of the final storage phase of the repository, when the fission products dominate the behaviour of the waste, generating a considerable amount of heat and radiation. The container must further, in conjunction where appropriate with a

transport vessel, withstand stresses imposed upon it during handling (including accident conditions) and protect operating personnel against the effects of radiation during the operational phase of the repository. After closure of the repository, groundwater ingress into the repository and external pressure build-up threaten the container, which must have sufficient corrosion resistance in an environment characterized by high levels of radiation and relatively high temperature as well as mechanical stresses imposed by the lithostatic pressure to retain its barrier properties until the waste has decayed to the point that the other barriers can take over with the required degree of safety.

1.3 Aims of the Swiss Containers Programme and of the Present Report

The legal requirements concerning the peaceful use of atomic energy in Switzerland are contained in the Federal Atomic Energy Act of 1959 and the Federal Decree of 1978 modifying the Act of 1959. The Decree makes further use of atomic energy dependant on the existence of projects that ensure the permanent and safe disposal of radioactive waste. In view of this requirement, the Federal Department of Transport and Energy has imposed as a condition for the renewal of the operating licenses of the Swiss nuclear power plants beyond 1985 the demonstration of the feasibility of the safe disposal of all types of radioactive wastes by the end of that same year. Nagra must therefore

- in the short and medium term set up projects and demonstrate the feasibility of safe disposal of radioactive waste
- in the long term prepare construction and operation of such final repositories as are needed.

These boundary conditions set the aims of the Nagra programmes in general and of a programme to define and develop containers for high level waste. In particular the demonstration of the feasibility of safe disposal include the following steps.

- i) Define design criteria for the containers and demonstrate that these criteria, combined with all other data and criteria for other barriers, ensure the required degree of safety.
- ii) Design containers to the degree of detail required to demonstrate that these criteria are fulfilled and that such containers as designed can be manufactured within the framework of present day technology with the required quality.

It is clear that the first step cannot and need not be finally decided before the results of all other programmes are known.

However, it is possible to delimitate ranges for the expected values of the parameters that will have a bearing on the design. By choosing conservative values within these ranges it is then possible to set up provisional design criteria and consequently to carry out the second step under conservative assumptions. Fulfillment of the conservative criteria will necessarily imply fulfillment of the final criteria that will be obtained from safety analyses performed in the framework of other Nagra programmes.

The approach taken to the design of containers for high level waste was

- to review the potential materials and evaluate with respect to the provisional design criteria in order to select one or more of them for further study
- and then to follow with a more critical appraisal of these selected materials, in order to identify potential problems
- and to initiate experimental or theoretical studies to cover those points where insufficient data is available.

This report covers the first two of the above steps and a first phase of experimental work. Section 2 contains a brief description of the design criteria and boundary conditions used for the selection and assessment of potential container materials. The approach to and the results of the selection process are discussed in Sections 3 to 5, Section 6 looks in more detail at the selected materials and Section 7 describes the experimental programme set up to test these materials. Publication of further results and conclusions of this programme and other relevant Nagra programmes is planned in the form of Nagra Technical Reports.

The amount of ground which has to be covered is immense, and in this short form presentation simplifying generalizations are the rule. Numbers are only given where necessary in order to give the reader some idea of the size, rate or time period, etc. involved. Furthermore, it seemed incorrect to apply the standard reference form to such a summary of accumulated knowledge and experience. However, the bibliography, Section 5, containing as it does several extended review articles should provide the means to a more detailed insight to the problem at hand.

There are several foreign programmes (see bibliography) with similar aims and similar container requirements to those presented here. The conclusions reached in these do not all concur, such that a further appraisal of the available material in particular with respect to the peculiarities of the Swiss concept was necessary.

2. DESIGN CRITERIA AND BOUNDARY CONDITIONS

2.1 Design Criteria

At the present stage, only general design criteria can and need be specified. As already mentioned in section 1, the approach has been to choose conservative requirements for these provisional design criteria:

- container integrity for a period of the order of 1000 years under the conditions outlined in section 2.2
- design and manufacture with quality assurance and control comparable to those in use in the nuclear industry.
- behaviour as an absolute barrier against migration of nuclides from the inside to the outside, i.e. construction that will prevent all leakages for the time mentioned above.

Further to these criteria the following assumptions were made:

- no retrievability is required.
- the design criteria apply to the final storage phase. It is considered that any requirements pertaining to the operational phase of the repository and in particular to the transport and manipulation of the container, if they cannot be met by the container alone, will be met by a suitable combination of the container and an additional temporary container that would be removed once the container is in its final storage location in the repository.

2.2 Boundary Conditions

The boundary conditions that had to be assumed for the material selection, assessment and experimental programme are highly conservative.

2.2.1 Waste Form

The preferred form is vitrified waste from reprocessing, but the option of direct disposal of spent fuel elements must also be considered.

The minimum internal dimensions of the container are much larger in the case of spent fuel elements (roughly $\varnothing 400$ mm x 5000 mm) than in the case of reprocessed waste (roughly $\varnothing 450$ mm x 1300 mm).

Further factors which must be considered are the radiation and heat production from the decay of the waste. The quantity of heat and radiation for both reprocessed waste and the fuel element

bundles themselves depend on the age after removal from the reactor. The present concept calls for an intermediate storage of 30 to 40 years. A quantitative treatment of these two parameters is not necessary at this stage. The heat production is responsible for a temperature rise over ambient and the radiation can through radiolysis modify the groundwater composition and hence corrosion rates. It is possible to control both by design should it prove necessary.

2.2.2 Backfill material

As backfill material separating the container from the rock, sodium or calcium bentonite is foreseen.

The choice of this material implies that temperatures above 140°C at the container/bentonite interface need not be assumed.

Bentonite has the ability to swell when it takes up water. Highly compacted bentonite, as it becomes saturated develops a considerable swelling pressure when restrained, which, combined with the low shear strength of the material, results in an even distribution of pressure within the rock formation; it also tends to flow and seal any cracks within the rock cavity. Water saturated bentonite has an extremely low permeability. Bentonite is also reported to alter the composition of the groundwater. It is expected to buffer the pH in the range of 7 - 9 and possesses ion exchange properties. Any possible beneficial effect of the bentonite from chemical interaction with the ground water has been ignored in this phase of the container programme.

2.2.3 Mechanical stresses

The mechanical stresses transmitted to the container by the filling material have been assumed to be those arising at the maximum depth foreseen for a repository, i.e. 1500 m. Detailed parameters can be found in the Nagra Technical Report 80-02 (project study for a HLW repository). Grimsel granite has been taken as representative of the host rock.

2.2.4 Groundwater

The definition of groundwater velocity and particularly composition are critical parameters as they determine the environment in which the container must survive.

As a conservative groundwater that of the thermal source of Bad-Säckingen in the Federal Republic of Germany, but very close to the Swiss border, has been selected. This source has a high mineral content and also a very much higher oxygen concentration than is currently expected of repository sites in Switzerland.

Typical analyses of Bad Säckingen water are given in table 2.1.

The groundwater flow is also an important parameter for container design. Expected values at repository depths in granite range from 0.1 to 1 $\text{kg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$. For the present study a conservative value of 10 $\text{kg}\cdot\text{m}^{-2}\cdot\text{a}^{-1}$ has been assumed.

Table 2.1

Water analysis - Bad Säckingen Source

Parameter	Unit	22/7/81	28/10/81	5/3/82	25/5/82	20/8/82
Li ⁺	mg/l	5.80	5.10	5.55	6.00	5.50
Na ⁺	mg/l	898	930	966	1045	1073
K ⁺	mg/l	75.1	78.6	78.4	85.2	86.6
NH ₄ ⁺	mg/l	1.80	n. d.	0.05	n. d.	n. d.
Mg ⁺⁺	mg/l	12.1	13.9	13.7	15.1	15.4
Ca ⁺⁺	mg/l	124.5	137.3	139.1	155.2	158.7
Fe ⁺⁺	mg/l	n. d.	n. d.	n. d.	n. d.	n. d.
Fe total	mg/l	n. d.	n. d.	n. d.	n. d.	n. d.
F ⁻	mg/l	2.7	2.3	3.2	3.2	2.8
Cl ⁻	mg/l	1487	1572	1619	1767	1817
Br ⁻	mg/l	4.2	4.0	4.6	5.4	5.1
NO ₃	mg/l	7.0	5.4	5.0	7.7	5.3
HCO ₃ ⁻	mg/l	290	289	289	295	298
SO ₄ ⁼	mg/l	112	117	117	125	125
O ₂ dissolved	mg/l	n. a.	3.8	n. a.	7.1	0.8
H ₂ S dissolved	mg/l	n. d.	n. d.	n. d.	n. d.	n. d.
H ₂ SiO ₃	mg/l	40.4	34.6	41.7	42.4	39.7
H ₃ BO ₃	mg/l	16.5	15.9	17.6	17.9	17.9
Total dissolved solids (110°C)	mg/l	3052	3083	3194	3469	3498
Conductivity 20°C	S/cm	3920	4263	4900	5210	4742
pH	-log(H ⁺)	5.68	6.53	6.47	6.48	6.50
Redox potential	mV	180	300	180	185	200

n. d. = not detected

n. a. = not analysed

3. MATERIALS SCREENING AND SELECTION

3.1 Introduction

The Swiss programme for high level nuclear waste disposal has not yet reached the detailed planning stage, and no specifications as such for a container exist. Nevertheless, it is necessary at this conceptual stage of the programme to look more closely at the container designs which fit into the overall concept as it stands at present. As the overall programme proceeds and more information with respect to container performance requirements and the container environment becomes available, the container design can be further refined.

3.1.1 The approach to screening and selection

As indicated in section 2, the design approach to a container was first to select one or more suitable construction materials. The requirements placed upon a container are diverse; those criteria most relevant to material choice are presented below.

- i) Container size. The minimum internal dimensions are fixed by the waste form. For the purposes of this design study the internal cavity required was taken as $\varnothing 450$ mm x 5000 mm, i.e. sufficient for spent fuel assemblies. The wall thickness will be determined by corrosion, radiation shielding and mechanical strength.
- ii) Lifetime. The current concept calls for a container life of up to 1000 years after closure. This is clearly one of the most difficult requirements to fulfil in particular as the main problem will be corrosion. The corrosion behaviour must be predicted over a space of time which are far in excess of the feasible duration of any experimental qualification programme.

The container material must also possess sufficient stability under the thermal and radiation exposure conditions within the repository.

- iii) Manufacture, sealing and testing. The manufacture and sealing of the container place important restrictions on the materials which can be used for the container. The waste also places some restriction on the manufacturing and sealing techniques in that the vitrified waste should not be heated above ca. 400°C to prevent crystallization of the glass. The waste itself is radioactive; fully automated sealing methods must be employed. The container must also be put through stringent quality checks. In particular the soundness of the seal will present severe testing problems. Only container concepts which are feasible with "state of the art" technology were considered.

A unique choice of material for the container under these conditions is not possible. Certain materials will be ideal on several points, but leave either open questions or unsurmountable problems in other areas. Any material choice at this stage must be provisional, nevertheless, each material chosen represents a container type which seems feasible taking into account present knowledge and state of the art technology.

3.2 Polymeric materials

Although many polymeric materials possess good resistance to neutral chloride solutions, no candidate material of this type could be identified.

In general, their long term stability at elevated temperatures (the temperature on the inner surface of the material may be well in excess of 140°C as polymers are in general poor heat conductors) and their resistance to radiation damage over the extended periods involved must be doubted.

The mechanical properties of most of these materials would also cause design problems.

3.3 Ceramics

Ceramics are an extremely attractive proposition for a waste container which must survive for several hundred years in an aqueous environment. They are highly stable chemically, particularly oxide ceramics, and are almost totally immune to dissolution in water or dilute chloride solutions within the temperature range in question. Ceramic materials in general suffer from lack of ductility. This brittle behaviour means that there is a significant risk of failure during encapsulation and handling. For the same reason, a ceramic container would be extremely sensitive to non uniform loading which may result from slight shifts in the repository over decades or centuries. There are also considerable problems manufacturing ceramic containers of the required size and quality.

Of all the ceramic materials, aluminium oxide (alumina) has received the most attention. The technology for its use is well-developed. The advantages and disadvantages of alumina will be briefly discussed; most of the points made, however, may be equally well applied to other ceramic materials.

Alumina is not thermodynamically stable in water. Hydration will occur leading to the formation of either $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Chemical corrosion may take place by either slow dissolution of the surface layer or flaking off of the hydrated oxide. Various immersion tests have shown that at 100°C in water, a corrosion rate of max. 0.007 mm/year may be expected.

The fracture properties of brittle materials are highly sensitive to surface or near surface defects. Such defects, mostly voids, are difficult to avoid in ceramics which normally have to be produced by high temperature sintering processes. Hot isostatic pressing (HIP) reduces this type of defect to a minimum. For alumina, a temperature of 1350°C at 100 bar pressure gives close to theoretical density and hence good fracture toughness properties. Production of canisters by the process is feasible although no facility exists at present which is large enough.

The description of the production process highlights one of the major problems with any alumina or indeed any ceramic container design, the problem of container closure. A homogenous seal is only possible by high temperature sintering, again 1350°C would be ideal for alumina, preferably also under pressure (HIP). This temperature need only be attained in the seal region but thermal stressing would require that the whole of the alumina body reach at least 900°C, and consequently the contents as well. Such temperatures could not be tolerated by the vitrified waste form.

Other sealing methods involving a sealant compound or ceramic-metal-ceramic seal are under investigation which could mean lower sealing temperatures. The integrity of these seals and equivalence of corrosion resistance to the alumina under repository conditions would still have to be proven.

While the container components could be pre-tested, a suitable quality control technique for the sealed container would have to be developed.

The ability of alumina containers to withstand transport accidents and the possibility of delayed fracture, i.e. crack growth with time emanating from voids under sustained tension, cannot at present be demonstrated, although improved fracture mechanics knowledge and testing techniques could provide an answer to these problems.

Alumina was not retained at this stage for experimental study in the Swiss programme for the above reasons, and also because the metal container lines identified were nearer realization. However, the rapid progress which may be expected in ceramic technology within the next few decades and the potential of ceramic materials and in particular alumina make it imperative to follow developments in this area on a medium to long-term basis.

3.4 Metallic Materials

Of the requirements presented at the beginning of this chapter, the corrosion resistance under repository conditions is probably the most restrictive on the possible choice of metallic materials for a container. The good general engineering properties of metals and alloys should allow a solution to the other points.

As discussed in section 2.1, the basic design criteria for the container material is that it should exhibit sufficient corrosion resistance to ensure a container life of 1000 years (maybe less) in a groundwater of composition similar to that for Bad Säckingen source water given in table 2.1 under the conservatively chosen conditions outlined in section 2.2, which include a surface temperature of up to 140°C for a limited period, and ground water flow rates of at most 10 Kg.m⁻²a⁻¹.

The corrosion forms which must be considered are:

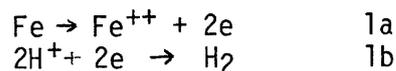
- i) general corrosion
- ii) localized corrosion - pitting or crevice corrosion
- iii) stress induced cracking - stress corrosion or hydrogen embrittlement.

Other corrosion forms, e.g. intergranular corrosion and galvanic corrosion, although they may be relevant in a detailed assessment, need not be given much attention in this first appraisal.

3.4.1 Iron and low alloy steels

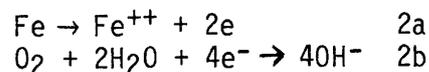
Iron and low alloy steels are the most widely used metallic materials because of their availability, low cost and adequate mechanical properties.

Iron is thermodynamically unstable in water and is expected to corrode according to the reaction.



In acid solutions iron is observed to corrode by this mechanism but above about pH 6 the cathodic partial reaction 1b is so slow that the corrosion rate via this mechanism is negligible in practical terms.

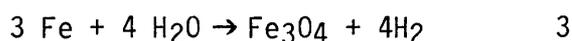
In water and dilute solutions above pH 6 the corrosion of iron depends upon the supply of dissolved oxygen via the reaction.



The final corrosion products are ferrous or ferric oxides and ferrous or ferric hydroxides or a combination of these. The products form poor protective films; at low oxygen concentrations the corrosion rate is observed to be proportional to the oxygen concentration; however, at higher oxygen concentrations the products have a limited passivating ability. The presence of

chloride at least at temperatures up to 100°C reduces the passivating ability of the corrosion products.

Above 100°C other corrosion products form which produce more protective films; in particular the direct formation of magnetite via a Schikorr type reaction



can build an effective passive film on iron. Magnetite will begin to form by this or other reactions above about 100°C. The higher the temperature the more likely it is that magnetite will build a passive film.

Corrosion rates reported for cast irons or low alloy steels in soils and natural waters, with chloride contents up to that of seawater vary enormously; 0.02 to 0.8 mm per year at 10-30°C would cover most of the quoted values. The literature is not always in agreement, but the general trends are that the highest corrosion rates were found in short term experiments in well aerated media with high chloride contents. Corrosion rates are much lower in low oxygen environments. Long term experiments tend to suggest that the corrosion rate falls with time for two reasons. The first is that the corrosion products can act as a barrier to diffusion. The second is that in chloride environments corrosion is uneven, shallow wide pits are common and in short term experiments dominate the penetration depth determination; the ratio maximum penetration to average corrosion loss falls with time.

Stress corrosion cracking may be disregarded for irons and low alloy steels under any conditions likely to be present in a repository. High strength steels are susceptible to hydrogen embrittlement. The hydrogen may come from the cathode corrosion reaction 1 b. Hydrogen embrittlement is restricted to steels with ultimate tensile strengths of 700 MPa or above, cast iron and low and medium strength steels are immune.

Production of containers of iron or low alloy steel should present no problems even in the very large sections required for a self-shielding container. Such large sections may also be sealed by welding. The technology for this exists and non-destructive testing of the seal should be feasible.

There is no firm evidence that the corrosion resistance of cast types is better or worse than that for wrought irons and steels, however, cast forms would be simpler to produce.

The decision whether to consider this material group for containers depends almost exclusively on the accuracy of corrosion rate forecasting under repository conditions. These should be determined experimentally. At this stage it seems probable that

the conditions expected within the repository would allow the use of an iron or steel container. The corrosion rate at lower temperatures is dependent upon the rate of delivery of suitable oxidants, by far the most likely is oxygen. The siting and design of the repository should ensure low ground water oxygen levels and a very low water flow rate past the container. pH values of 6 and below, necessary for acid corrosion by mechanism 1 are not to be expected. At higher temperatures direct reaction with water (reaction 3) may take place but the product, magnetite, normally forms a good protective layer which prevents further reaction. The net result should be acceptably low corrosion rates ensuring a lifetime of 1000 years with a reasonable wall thickness. Iron and low alloy steels have therefore been retained for further consideration and experimental study within the Swiss programme.

3.4.2 Stainless Steels

Stainless steels are a corrosion resistant family of iron based alloys containing a minimum of 12% chromium. They form a passive oxide film to which the stainless steels owe their corrosion resistance in aqueous solution. This passive film is responsible for the very low uniform corrosion rates, under 0.01 mm per year in water and most dilute aqueous solutions over a wide temperature and pH range. However, in common with most alloys that exhibit passivity, stainless steels may suffer from localized attack, pitting or crevice corrosion, particularly in the presence of aggressive ions of which the chloride ion is by far the most common.

High chloride levels and high temperatures promote pitting and crevice attack. Chromium and molybdenum are the most effective additions at reducing this form of attack. Nickel and nitrogen are also beneficial but less effective than chromium or molybdenum.

In the presence of tensile stresses, stainless steels in chloride solutions are also prone to stress corrosion, which is also more likely the higher the chloride concentration and temperature. The austenitic types are more predisposed to stress corrosion than ferritic or duplex varieties. Otherwise resistance to stress corrosion tends to parallel resistance to local attack.

Under the conditions prevailing in a repository, even such fairly highly alloyed types such as AISI-316 with 18% Cr, 12% Ni and 3% Mo are likely to exhibit local attack; penetration rates can be in excess of 1 mm per year. Higher alloyed types are available but even with chromium levels up to 28% local attack cannot be ruled out.

The technology exists for producing containers of stainless steel; cast grades are also available. Thick walled versions (> 100 mm) would also be possible. With grades superior to

AISI-316, there is less available experience. The highly alloyed steels for this reason and also for reason of cost would be more likely to be useful as thin corrosion resistant layers over an iron or mild steel container.

Stainless steels, in particular the highly alloyed varieties, may in practice possess adequate corrosion resistance, however, present knowledge suggests that localized attack cannot be disregarded. As more resistant alloys are available, stainless steels were not retained as an alternative in this programme.

3.4.3 Nickel alloys

The most corrosion resistant alloys in this group are nickel-chromium varieties often containing molybdenum. Chromium and molybdenum have an effect in nickel base alloys analagous to that in stainless steels.

Nickel-chromium alloys containing more than 50% nickel are thought to be immune to chloride induced stress corrosion cracking below 150°C. The nickel-iron-chromium alloys with 30-42% nickel, 30-50% iron and 5-30% chromium may be considered as very highly alloyed stainless steels. They are not credited with as good a chloride resistance as the nickel-chromium family of alloys.

The nickel-chromium alloys, as they also rely on a chromium based passive film for their corrosion resistance, are still liable to chloride promoted local attack. The pitting and crevice corrosion resistance in this group of alloys varies greatly, with Inconel 600 (76% Ni, 15% Cr and 8% Fe) only equivalent to the stainless steel AISI 316, whereas Inconel 625 (61% Ni, 21% Cr and 9% Mo), following the general rule that chromium and molybdenum are beneficial against this form of corrosion, is reported to be immune to attack by 1000 mg/l chloride at 200°C. Hastelloy C-276 (Ni, 15% Cr, 16% Mo, 5% Fe, 4% W) possesses equal chloride corrosion resistance to Inconel 625.

Of the last two nickel base alloys mentioned, Inconel 625 should be somewhat cheaper and easier to process. Thick walled containers are not feasible in these materials. Difficulties in manufacture and high cost preclude this. Inconel 625 would be suitable as a corrosion resistant layer in combination with an iron or mild steel container for mechanical strength.

Inconel 625 is considered a suitable material for further consideration within the aims of this programme.

3.4.4 Aluminium and aluminium alloys

In neutral solutions, aluminium owes its good corrosion resistance to a passive oxide film. This film is increasingly soluble outside the pH range 4.5 to 8.5 such that in acid or alkaline conditions,

general corrosion rates increase. In general, the corrosion resistance of aluminium alloys decreases with increasing alloying element content.

Like other metals which rely on a passive film for their corrosion resistance, aluminium is susceptible to pitting and crevice corrosion. Solutions containing traces of heavy metal ions promote local attack on aluminium. Copper is most detrimental, but mercury, lead, nickel, cobalt, tin and silver also promote attack. Chloride and bicarbonate enhance this effect such that as little as 0.02 mg/l copper can initiate pits on aluminium. The resistance to pitting attack decreases with increasing temperature.

Stress corrosion cracking is not observed in pure aluminium, but aluminium alloys, particularly moderate and high strength precipitation hardening types, are susceptible in chloride solutions.

Aluminium and its alloys were rejected as candidate materials because of the danger of pitting or crevice attack; chloride and bicarbonate ions are very likely present in the groundwater and the lower safe limit for the heavy metals particularly over extended periods of time at higher temperatures are unknown.

3.4.5 Copper and copper alloys

Copper is a relatively noble metal, and is thermodynamically stable in pure oxygen free water (solubility less than 10^{-7} M/l as Cu^+), at least to 100°C and probably higher. Copper is, however, thermodynamically unstable in the systems $\text{Cu-H}_2\text{O-O}_2$, $\text{Cu-H}_2\text{O-S}^-$, $\text{Cu-H}_2\text{O-SO}_4^-$ and $\text{Cu-H}_2\text{O-NO}_3^-$. In practice the last two, sulphate and nitrate, are kinetically inhibited such that oxidation by these species is not observed. The corrosion rate of copper in oxygen or sulphide containing waters is dependent upon the rate of transport of these two species to the copper, as the corrosion products are ineffective as barrier layers. The chloride ion tends to promote local forms of corrosion. There is a suggestion that low chloride and low conductivity solutions produce deeper pits, whereas in sea water, copper forms shallow pits which with time coalesce to give a fairly uniform overall corrosion.

The copper alloys generally have similar general corrosion behaviour to copper. However, in addition, dezincification occurs in all zinc containing alloys, and analogous effects have been observed in the aluminium and tin bronzes. Copper-nickel alloys are more resistant to de-alloying forms of corrosion.

Stress corrosion cracking in copper and its alloys in aqueous solutions is restricted to solutions containing ammonia or an ammonium salt; oxygen is also normally required. Pure copper and copper-nickels are virtually immune, whereas copper-zinc alloys can be extremely sensitive to low ammonium ion concentrations.

There is little to choose between pure copper and copper-nickel alloys with ca. 40-65% nickel with respect to their corrosion behaviour as candidate materials for the container. Manufacture of such a container should present no grave problem. Both materials may be welded, although the high thermal conductivity of copper is a handicap and may cause difficulty in welding thick sections.

The use of copper as a container has been firmly proposed in the Swedish KBS report. They have made a very strong case for its suitability. The planned Swedish repository bears sufficient resemblance to the Swiss concept to assume that copper should also be suitable for inclusion as a possible container material within the Swiss programme.

3.4.6 Titanium and titanium alloys

Titanium is a very reactive metal; so reactive that in any environment containing available oxygen, e.g. water, it will form a protective oxide film. This oxide film is extremely resistant to chloride ions, and thus titanium has a high resistance to pitting and crevice attack by chloride.

Nevertheless, crevice corrosion has been reported in titanium alloys; α -titanium alloys are the most resistant, such as C.P. titanium, the Ti-Pd and Ti-Mo-Ni alloys. Of these the Ti-Pd and Ti-Mo-Ni are superior to C.P.Ti particularly at higher temperatures, C.P.Ti is resistant in seawater to about 130°C whereas the other two alloys are free from crevice effects up to temperatures in excess of 170°C.

In the absence of local attack, the general corrosion rate of titanium and its alloys in chloride containing aqueous media (up to saturated NaCl) remains below 0.006 mm per year up to 400°C. Under repository conditions, well under 0.006 mm per year is to be expected. This high corrosion resistance is retained under all but strongly acid or strongly alkaline conditions, i.e. pH < 2 and > 12.

Stress corrosion cracking and hydrogen embrittlement have been reported in titanium alloys. It is not yet clear whether these are related or independent phenomena in titanium as hydrogen production would accompany any anodic dissolution. Stress corrosion cracking has been observed in 3.5% NaCl at room temperature in $\alpha + \beta$ alloys, but is not reported for the highly corrosion resistant low oxygen C.P.Ti grades and Ti-Pd alloys.

Titanium alloys are particularly susceptible to hydrogen embrittlement effects. It is generally thought that hydrogen embrittlement effects only occur when the solubility limit of hydrogen is exceeded, and failure occurs through the brittle hydride. The solubility of hydrogen in titanium is very low;

titanium hydride may form at 200°C in some $\alpha + \beta$ alloys where the $\alpha - \beta$ phase boundary is a preferred site for hydride formation with as little as 10 $\mu\text{g/g}$ hydrogen, although embrittlement as such may not be noticeable at such extremely low hydrogen levels. α -Ti seems to tolerate higher hydrogen contents. The hydrogen solubility increases strongly with temperature, and the tolerance for dissolved hydrogen in parallel. α -Ti alloys are thought to be free from hydrogen embrittlement at hydrogen levels below about 100 $\mu\text{g/g}$. In production, hydrogen levels can be held below 10 $\mu\text{g/g}$.

Among the titanium alloys, the α types are to be preferred as they are more resistant to crevice attack and less sensitive to hydrogen effects. Ti-0.2% Pd and the near α Ti-Code-12 (Ti-Ni-Mo) have superior chloride corrosion resistance to C.P.Ti.

Both Ti-0.2% Pd and Ti-Code 12 may be suitable as container materials. The high corrosion resistance coupled with the relatively high material price and increased difficulty in producing thick walled sections means that these materials would probably be most effectively employed purely as a corrosion resistant layer. Both alloys may be welded, although some care is needed to prevent oxygen access to the weld zone.

Ti-Code 12 was chosen for inclusion in the current Swiss program. It was preferred to Ti-0.2% Pd as it possesses somewhat better mechanical properties and is significantly cheaper.

4. SUMMARY AND CONCLUSIONS - SECTIONS 1 - 3

In the previous chapters, the conditions expected within a repository were outlined, as were the requirements placed upon a high level waste container. The approach taken then was to look at the common engineering materials in order to attempt to identify suitable materials for a container. Only simple container designs were considered as a first step.

In general, only metallic materials were considered to possess the full range of properties required for a simple container design. Of the other materials, the ceramics because of their high chemical stability are attractive, but lack mechanical toughness.

A brief review of the most important metals and alloy systems identified some candidate materials; these were

- i) Cast irons, or cast or wrought low alloy steels
- ii) Copper
- iii) Inconel 625
- iv) Ti-Code 12.

The first two, low alloy irons or steels, and copper could be used to form monolithic containers. The corrosion resistance of the nickel and titanium alloy is such that the wall thickness allowance for corrosion would probably be much less than that required for strength or radiation shielding. In this case, although it would be possible to produce thick walled containers from these materials, they are probably best applied, if only for reasons of cost, as an outer corrosion resistant layer over a steel or iron inner container.

As it seems practicable to design a container on the basis of each material chosen, other materials with which less practical experience is available, and more sophisticated design approaches were not considered further.

5. BIBLIOGRAPHY SECTIONS 1-4

- /1/ Handling and Final Storage of Unreprocessed Spent Nuclear Fuel
Kärnbränslesäkerhet, Stockholm KBS-II Technical (1978)
- /2/ A Review of the Swedish KBS-II Plan for Disposal of Spent Nuclear Fuel
National Academy of Sciences, Washington D.C. 1980
- /3/ An Assessment of Materials for Nuclear Fuel Immobilization Containers
K. Nuttall, B. F. Urbanic
Atomic Energy of Canada Limited, AECL-6440 Sept. 1981
- /4/ Materials Considerations Relative to Multibarrier Waste Isolation
H. E. McCoy, J. C. Griess
Oak Ridge National Laboratory ORNL/TM-7770 July 1981
- /5/ A Design Study of Long Term Storage and Underground Disposal Systems for Highly Active Waste
W. B. Burton, J. R. Griffen
United Kingdom Atomic Energy Authority. ND-R-514(R)
June 1981
- /6/ Regulation of Geologic Repositories for the Disposal of High-Level Radioactive Wastes
L. A. White, M. J. Beu, D. M. Rohrer
Scientific Basis for Waste Management Vol. 2 (1980) p. 5
- /7/ Engineered Waste Package Conceptual Design. Spent Fuel (Form 1). Disposal in salt.
Westinghouse Electric Corporation, Advanced Energy Systems Division. AESD-TME-3087 March 1981
- /8/ Corrosion Resistant Metallic Canisters for Nuclear Waste Isolation
N. J. Magnani, J. W. Braithwaite
Scientific Basis for Nuclear Waste Management Vol. 2 (1980) p. 377
- /9/ Corrosion Resistance of Canisters for Final Disposal of Spent Nuclear Fuel
E. Mattsson
Scientific Basis for Nuclear Waste Management, Vol 1 (1978) p. 271.

- /10/ Nuclear Waste Canister Corrosion Studies Pertinent to Geological Isolation
J. W. Braithwaite, M. A. Molecke
Nuclear and Chemical Waste Management, Vol. 1,
pp. 37-50, 1980
- /11/ Korrosionsverhalten von unlegiertem Stahl, Stahlguss und Gusseisen als Endlagerbehälterwerkstoff in wasserführendem Granitgestein.
E. Heitz, D. zur Megede
NAGRA, NTB 82-08.
- /12/ Corrosion Resistance of Cast Irons and Titanium Alloys as Reference Engineered Metal Barriers for Use in Basalt Geologic Storage: A Literature Assessment
L. A. Charlot, R. E. Westerman
Pacific Northwest Laboratory PNL 3569 July 1981
- /13/ Copper as a Canister Material for Unreprocessed Nuclear Waste-Evaluation with respect to Corrosion.
Kärnbränslesäkerhet, Stockholm. KBS-Teknisk Rapport 90.
March 1978
- /14/ Zusammenfassende Zwischenbericht. Stand Juni 1981
Projekt Sicherheitsstudien Entsorgung (PSE)
PSE Berlin Okt. 1981
- /15/ Waste Package Materials Screening and Section.
D. P. Moak
Office of Nuclear Waste Isolation, Battelle, Columbus
ONWI-312, Oct. 1981
- /16/ Projektstudie für die Enlagerung von hochaktiven Abfällen in tiefliegenden Geologischen Formationen sowie für die Zwischenlagerung
NAGRA, NTB 80-02

6. APPRAISAL OF SELECTED MATERIALS AND OTHER FACTORS

6.1 Introduction

This section looks at the materials, container types and conditions within the repository more critically in order that problem areas be identified. This appraisal forms the framework for further effort within this programme, both experimental and in depth studies, with the aim of providing a sound basis for a conservative container design as part of the high level waste disposal feasibility study.

6.2 Container types

The materials identified in the previous sections lead to three different basic types of container if classified on their corrosion behaviour.

- i) Cheap material with poor general corrosion resistance but immune to stress induced cracking and with low pitting tendency. Life attained by thick section and suitable control (by repository siting and backfill) of the environment: -
low alloy irons and steels
- ii) Noble metal, thermodynamically stable in the system M-H₂O. Corrosion rate determined by availability of a suitable oxidant; i.e. transport controlled. Immune to stress induced cracking and with low pitting tendency: -
copper
- iii) Highly corrosion resistant metals, relying on a passive film for their corrosion resistance. Extremely low general corrosion rate suggests use as a corrosion resistant layer over a steel container which supplies the mechanical strength. These materials are not under all circumstances immune to stress induced cracking or local attack (pitting). Their resistance to these local failure modes under repository conditions must be demonstrated: -
Inconel 625, Ti-Code 12.

6.3 Container based on low alloy cast iron or steel

The suitability of this class of materials for high level waste containers has been the subject of several review articles and studies, both for use in crystalline rock /1-4/ and salt dome /5/ repository sites.

The major concern with recommending cast iron or low alloy steel is to be able to demonstrate that they possess sufficient

corrosion resistance. They are otherwise ideal materials, in particular cast or wrought steels which can be easily welded.

The bulk of the data considered referred to either buried pipelines in soils (or experiments designed to simulate this) or from immersion tests in seawater. Short term experiments are difficult to interpret in the context of lifetime prediction to 1000 years. There are, however, two references to longer term studies, those of Romanoff at the National Bureau of Standards, Washington, in soils /6/, and of Southwell, Bultman and Alexander in tropical seawater /7/. Both looked at cast irons and plain carbon steels for up to 30 years in soil and 16 in seawater. The two studies show remarkably similar trends although the absolute values vary considerably, a factor of 16 alone between the most and least aggressive soil types. Southwell et al, for instance, found an average penetration 1.2 mm after 16 years with a maximum penetration of 2.6 mm for a 0.27 C cast steel. The difference between average and maximum values remained almost constant with time; after 1 year it was 1.3 mm, after 8 years 1.4 mm and after 16 years 1.5 mm, i.e. the average penetration is the determining factor for thick sections and long times. In both studies, the average penetration rate decreased with time, again taking the seawater data it was 0.18 mm/yr, 0.088 mm/yr and 0.068 mm/yr after 1, 8 and 16 years respectively.

These figures serve to illustrate the problems involved in testing cast irons and steels; the one year value of maximum penetration depth would, if extrapolated to 1000 years, have implied a wall thickness of 1422 mm; the 16 year data, one of 78 mm including an allowance of 10 mm for pitting. On the basis of the 16 year value, 0.27 C cast steel would be acceptable for a container material as aerated seawater at 25°C represents a fairly aggressive environment, but not unduly dissimilar to that in a repository.

The available data is ambivalent over the differences between the various plain carbon steels and cast irons. Data on low alloy varieties is scarce. No advantage could be seen in low alloy (< 5% alloy content) over plain carbon types.

Cast iron is an iron carbon alloy with minor additions of silicon, manganese and phosphorous. There are three major types, depending on the form of carbon. Flake graphite is found in gray irons, bound as cementite, Fe₃C, in white irons and as nodular graphite in ductile irons. Gray irons are brittle, ductility is better in white irons and the highest in nodular types. The better mechanical properties of nodular iron led to its inclusion within this programme in preference to grey or white types. Nodular cast iron is also easier to weld although as with all cast irons, welding is not as simple as for cast steels.

A cast steel GS-40* and a nodular cast iron GGG-40* were chosen for the experimental part of the programme.

6.4 Container based on copper

Copper was the material of choice for containers in the Swedish KBS-II proposal /8,9/. It was demonstrated that the corrosion rate would depend on the rate of transport of oxygen and/or sulphide to the container. The Swedish analysis was considered to be realistic in two review studies /10,11/.

There are, however, some points which were not adequately discussed in the KBS report or on which directly relevant data was not available. These are i) the morphology of the corrosion attack, ii) stress corrosion cracking of copper, and iii) welding of thick sections.

As with iron or carbon steel, the morphology of the corrosion attack is important. The estimation of the pitting factor, ratio of deepest pit to general corrosion loss, was based on the work of Denison and Romanoff /12/ who studied the corrosion of copper in various soils. The KBS study assumed the worst case pitting factor of 25. This is a very high value for a non passivating metal. The pitting factor should be determined under repository conditions, in particular the variation with time is important. The argument is the same as that for iron and carbon steels in section 6.2. For a factor which so directly affects the wall thickness requirement, the available data is unsatisfactory.

Stress corrosion cracking (SCC) is a catastrophic mode of failure which can occur in environments where a metal is otherwise resistant to uniform attack. The KBS authors assumed that high purity copper is virtually immune to SCC. There are, however, isolated reports in the literature of SCC of pure copper /e.g. 13-15/. The presence of cupric ammonia ion or cupric nitrate may promote SCC at concentrations down to 0.01 N. It is unlikely that the containers will be exposed to such environments and high tensile stresses should not be present as they will be relieved by creep at temperatures over 100°C. Nevertheless, SCC should be considered before copper can finally be recommended.

The best method to seal a copper canister would be by welding. The KBS proposal suggests electron beam welding for their 200 mm thick containers. Such welds have to be demonstrated; at present it is not clear if quality electron beam welds at even 100 mm wall thickness can be routinely achieved. A certain amount of development work is necessary. Copper can also be welded by more conventional electric arc methods but the deposition rate is limited by the high thermal conductivity of copper; the large shrinkage as the weld metal cools could lead to distortion or internal cracking.

* Designation according to DIN 17006

6.5 Container based on a corrosion resistant barrier layer

The two most promising materials for this container type are Inconel 625 and Ti-Code 12. Of these two materials Inconel 625 is more likely to suffer from pitting or crevice corrosion to which Ti-Code 12 is more resistant, whereas Ti-Code 12 is suspect to hydrogen embrittlement but Inconel 625 should be immune from stress assisted cracking.

It was decided to actively pursue only one of these two materials. Ti-Code 12 was chosen less on technical grounds but more for the reason that this alloy is featured in the American programmes where it is preferred over the nickel base alloys because nickel is a strategic element i.e. likely to be in short supply in crisis periods /16/.

6.5.1 Ti-Code 12 as a corrosion resistant container case

The resistance of Ti-Code 12 to pitting or crevice attack is amongst the highest of all titanium alloys available and is immune to this form of attack at temperatures under 170°C /17/.

Titanium and its alloys are susceptible to stress assisted cracking in chloride environments. In general the α and near- α alloys such as C.P.Ti and Ti-0.2% Pd are thought to be more resistant. Ti-Code 12 is a new alloy and insufficient data is available although since it has been included as the titanium alloy of choice in an American programme the alloy is under intense study /18/.

Nuttall and Urbanic have included a good short review of stress corrosion cracking, hydrogen embrittlement and delayed failure of titanium alloys in their assessment of materials for nuclear fuel immobilization containers /19/. Hydrogen is suspected of playing a role in all three phenomena. Hydrogen embrittlement is noticeable at high strain rates and is attributed to brittle failure of titanium hydride already present in the structure. Stress corrosion cracking and delayed fracture are associated with slow strain rates, for stress corrosion cracking the source of hydrogen is external, from corrosion at the crack tip, and for delayed fracture internal hydrogen is the important parameter. The hydrides probably form only at or near the crack tip.

The discussion of delayed failure is probably the most relevant for the use of titanium alloys as container materials. The α alloys are reported to have a higher resistance to hydrogen which may be attributed to a higher solubility for hydrogen in the phase. Titanium hydride forms preferentially at α - β grain boundaries and is thought to form at these sites at very low hydrogen levels /20/. This process may be localized, hydride

formation only occurring in the stress field associated with a crack tip /21/. Hydrogen solubility increases rapidly with temperature, the higher mean temperatures expected in a Swiss repository are thus beneficial, nevertheless, at ambient temperatures delayed cracking has been observed in α - β alloys with as little as 7 $\mu\text{g/g}$ hydrogen /22/. This problem must be looked at carefully as Ti-Code is a near α alloy i.e. in the annealed state contains a small percentage of β phase.

6.6 Other factors

6.6.1 Radiation

The contents of the container are radioactive and this has certain consequences on container design.

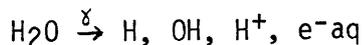
The container may be required to be self-shielding for one of two reasons:

- i) for safety reasons
- ii) increased corrosion under radiation

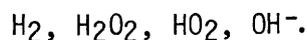
Point i) will not be considered here further as any specification will be based upon a regulatory or operational requirement rather than endanger the integrity or performance of the container as such. It should be noted, however, that the wall thickness of the container may well be determined by a self-shielding requirement.

The effect of radiation on corrosion is first and foremost attributable to radiolysis of the medium itself.

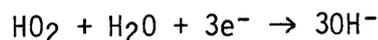
The absorption of γ -radiation in water leads to the formation of radicals, protons and free electrons



which via biomolecular recombinations lead to the formation of the more stable species

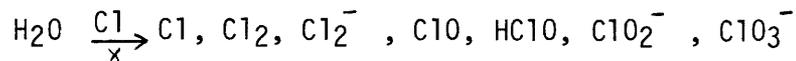


The radiolysis products are formed in the whole solution volume, species evolved in the neighbourhood of the metal surface particularly within the diffuse double layer may reach the metal surface and act as cathodic depolarizers.



Should the stable radiolysis products H_2 and H_2O_2 reach sufficient concentrations, they may control the redox potential of the solution. In particular H_2O_2 is more electrochemically active than H_2 and with increasing H_2O_2 concentration will become potential controlling. $E(H_2O_2) = 0.835 - 0.059 \text{ pH (V)}$.

In the presence of other ions in solutions the recombination chain of the radicals may be modified; of particular importance are the radiolysis products in the presence of chloride ions which are expected to be present in the repository groundwater.



Some of these products are strong oxidizers.

Radiolysis may accelerate or retard corrosion depending on the nature of the metal. Radiolysis may well be beneficial in the case of titanium, the oxidising conditions prevailing after radiolysis should promote passive film formation. The corrosion rates of iron or copper may be expected to increase via cathodic depolarization or increased supply of oxidants.

There is some evidence of this in the literature, γ -radiation was shown to increase the corrosion of mild steel but to have no effect on titanium or Inconel 625. /18/. Bjalabzesky investigated corrosion of copper in 1 M HCl. He found that the corrosion rate increased by a factor of 4.5 if the solution only was irradiated and by a factor of 6 if the specimen itself was irradiated /23/. The effect of radiation on corrosion will be discussed in more detail in Part II.

6.5.2 Welding

The waste containers will have to be sealed. This will most likely be accomplished by welding. Development of suitable methods and testing procedures will be necessary but bearing in mind the reservations expressed over the welding of copper (see 7.3), state of the art technology should suffice. However, container design and engineering can only be considered when a definitive concept has to be implemented.

The welding process involves the production of molten metal at the site to be joined. This can also be accompanied by metallurgical changes in the heat affected zone neighbouring the weld. The process may also require the addition of a material of a different composition, e.g. in the case of welding of nodular iron the filler metal is plain carbon steel. It is possible that the inhomogeneity associated with welding could locally change the corrosion behaviour, a factor which cannot be disregarded.

6.6.3 Bentonite

In most high level waste disposal schemes, the backfill is an important integral part of the barrier system. The material of choice for the backfill immediately surrounding the container is sodium or calcium bentonite.

The bentonite is to be placed around the container in the form of highly compacted blocks of dry bentonite. The gaps between the blocks will probably be filled with bentonite powder as far as this is possible. The advantages of highly compacted bentonite applied in this fashion are: -

- i) its ability to swell and flow as it takes up water. The bentonite will swell until it has filled all voids and cracks around the container.
- ii) once all voids and spaces are filled, and provided the bentonite is constrained, the water content will only go on increasing until it reaches an equilibrium value at a certain swelling pressure. At low water contents, the permeability of the bentonite is very low, which means correspondingly low flow rates of water past the container. The reduction of water flow is of utmost importance as the main means of transport of radioactivity out of the repository is via water soluble species.
- iii) bentonite is known to be a cationic ion exchanger; as many of the most important waste products are cations, the transport of these will be further retarded.

A more detailed appraisal of the material is available in the KBS II study /8/. The various forms of bentonite and minerals with similar properties are also the subject of a NAGRA research programme /24,25/. These studies have concentrated on the above-mentioned properties of bentonite as they are the most relevant in the overall safety analysis.

Less attention has been paid to the effect of bentonite on the corrosion of the container. Qualitatively the presence of highly

compacted bentonite around the container should prove beneficial. This is attributed to the low water permeability and hence low rate of transport of oxidants to the container surface and to the ability of bentonite to maintain a slightly alkaline pH (\sim pH9). However, the nature of the chemical interaction of bentonite with groundwater is still not sufficiently understood to be able to say with all certainty that bentonite has a neutral or positive effect on the corrosion resistance of the candidate container materials.

7. EXPERIMENTAL

7.1 Introduction

This experimental programme was designed to provide experimental verification with respect to the forecasts made from the literature survey, and cover the main problems identified by this survey in order that more relevant supporting data is available for the nuclear waste feasibility study (see section 1.3). On conclusion of this first set of experiments, a provisional, conservative container design fulfilling the requirements put upon the container within the framework of this study should be possible. The current aim is not to optimize a design concept; this will be the purpose of in-depth studies of points already raised in this study and those identified as a result of this preliminary experimental programme, and will form a continuation of this project.

The main areas of concern were identified and discussed in section 6. The experimental programme stems mainly from this appraisal. In addition, two aspects not emphasized within the report so far were included within the experimental programme. These were the interaction of molten lead with container materials and the fuel element casing (section 7.5), and galvanic corrosion between the elements of multilayer designs (section 7.6).

The aims and methods employed for each part of the experimental programme are briefly described below. More detailed description of methods, along with the results and conclusions will be reported in Part II.

Note

Preliminary results and a description of the materials under investigation are given in the Appendices to Part I.

7.2 Immersion Corrosion Testing

On the basis of a literature evaluation, four materials have been retained within this programme for further consideration. These are cast steel, nodular cast iron, copper and Ti-Code 12. On the basis of the literature data it is expected that containers of these materials or with these materials as the corrosion resistant component will have a life of up to 1000 years, under repository conditions as described in section 2.

The data available does not pertain to repository conditions; the choice of materials is thus based on an interpretation of the current data to forecast behaviour under repository conditions. For cast steel, nodular iron and copper, the thickness of material required for corrosion resistance depends upon a reasonably reliable estimate of the average corrosion rate for the full lifespan, and the morphology of corrosion attack (pitting factor). Ti-code 12 is predicted to be free from pitting or crevice corrosion problems.

The present immersion corrosion testing programme has the following aims:

- i) to test that the assumptions as to material suitability were correct when exposed under conditions more closely resembling those likely to prevail in the repository.
- ii) to provide reference values of corrosion rate as a basis for the corrosion allowance for the provisional container designs.

7.2.1 Materials

All four materials are to be tested. The specimen set for each medium/time combination also includes welded specimens as the corrosion behaviour in the weld zone may be different from that of the bulk material.

7.2.2 Experimental

The test medium is Bad Säcningen source water; typical analyses are given in section 2.2.4. Bad Säcningen source water contains a considerable amount of dissolved oxygen, up to 7.1 mg/l. In general, however, groundwater in crystalline bedrock is virtually oxygen-free, less than 0.01 mg/l /2,4,8/, and this is expected to be the case for the bedrock groundwater in Northern Switzerland. However, oxygen is present in the repository on closure, thus, two levels of dissolved oxygen are used in the experimental programme, air saturated and 0.1 mg/l.

Measurements are to be carried out at two standard temperatures, 140°C, which is the highest temperature allowable at the container surface and 80°C, as representative of the conditions during the slow thermal decay period.

Additional experiments at 80 °C will be carried out in air saturated Bad Säcningen water with an additional 15 g/l chloride ion.

7.3 Stress assisted cracking

In section 6, Ti-Code-12 was identified as the most likely of the candidate materials to be endangered by some form of stress assisted cracking. Some doubts were also expressed as to the correctness of the assumption that high purity coppers are immune to stress corrosion cracking. On the other hand, there was no reference to stress corrosion under conditions approaching those expected for the cast steel and nodular iron grades chosen. Testing, thus, concentrates on Ti-Code-12 and copper.

Two methods are employed to test for stress assisted cracking of the candidate materials.

- i) four point bending test
- ii) constant extension rate test (CERT)

7.3.1 Four point bending test

The four point bending test is a well established test method for stress assisted cracking. A bar shaped specimen is stressed in a four point loading jig to a certain stress level and then exposed to the test medium for a range of times.

7.3.2 Constant extension rate test (CERT)

The constant extension rate test, CERT, often also called the slow strain rate test, SSR, is a test method for the investigation of susceptibility to stress induced cracking. It is particularly suited for testing whether stress assisted cracking with a certain material/medium combination is a possibility or not. The advantages and limitations of the test method are discussed by Parkins in a review article /26/.

Only copper and Ti-Code 12 are to be tested by the CERT method. The test medium is Bad Säckingen water at 80 C with two levels of oxygen, air saturated and 0.1 mg/l. Three strain rates are planned, 10^{-5} , 10^{-6} and 2×10^{-7} sec⁻¹ (nominal).

Ammonium ions are known to promote stress corrosion cracking of copper alloys and are suspected of producing the same in high purity coppers. For this reason additional CERT tests at one strain rate (10^{-6} sec⁻¹) in the air saturated test medium with two levels of NH₄⁺ additions are planned.

The effect of increased chloride levels on both copper and Ti-Code 12 will also be investigated.

7.4 Corrosion in Bentonite

Bentonite is known to interact with water and dissolved ions; however, it is not possible to predict the effects of these interactions on the corrosion rate of container materials by water saturated compact bentonite.

It is thus necessary to approach this problem empirically and to perform corrosion exposure tests on coupons of all four materials embedded in highly compacted bentonite saturated with Bad Säkingen water.

The bentonite swelling pressure apparatus developed at the Institut für Grundbau und Bodenmechanik at the Eidgenössische Technische Hochschule, Zurich was adopted for this purpose. (Fig. 7.1).

The following test conditions were defined for the first series of tests

- i) Temperature 140°C
- ii) Bentonite - Sodium bentonite MX-80 compacted in air. /24/
- iii) Medium - Bad Säkingen water under nitrogen
- iv) Pressure difference across bentonite - 90 bar
- v) Water content of compacted bentonite - 30 wt %
- iv) Test periods - 500 and 1500 h.

The high water content (saturated) and high pressure drop across the specimen were chosen in order to provide more severe conditions than those expected in the repository.

7.5 Effect of molten lead on canister materials and Zircaloy fuel element cladding

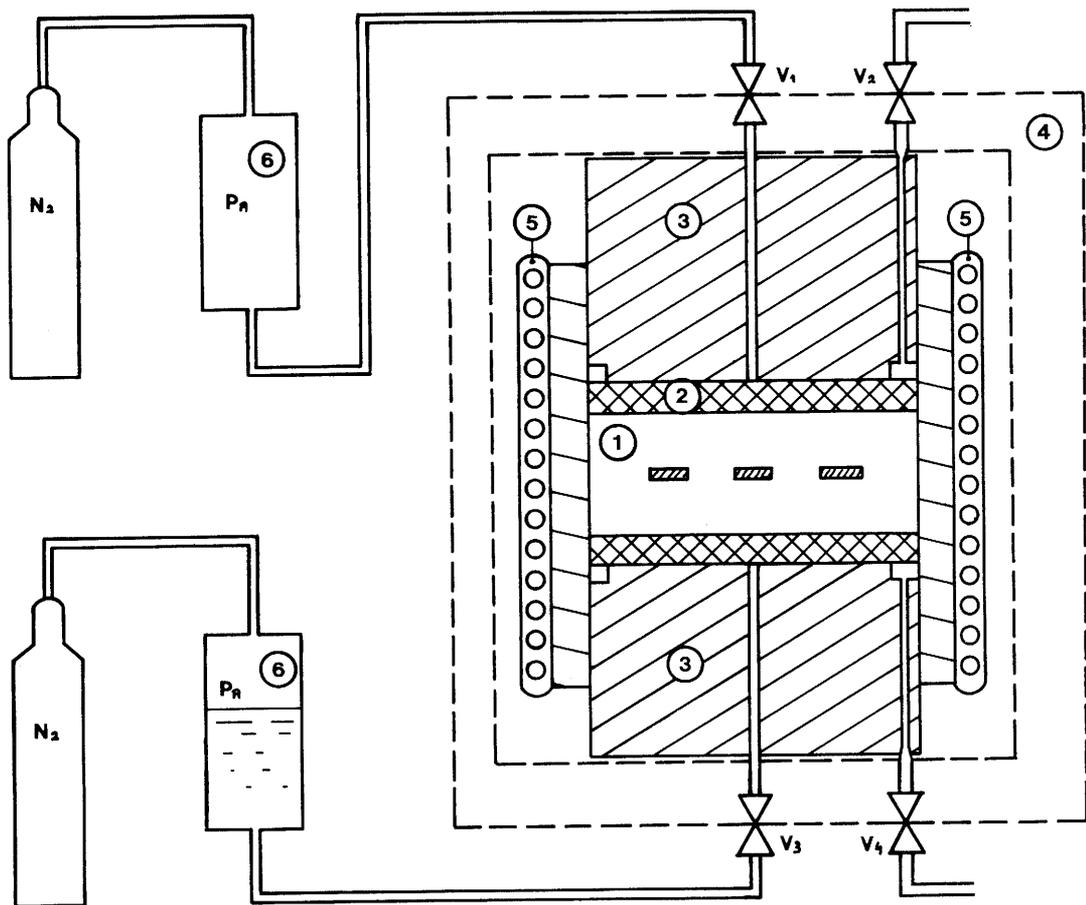
It has been proposed /8/ that in the case of direct disposal of spent fuel elements these be encapsulated in lead. The method envisaged is to heat the container and contents to around 400°C and then introduce molten lead to fill the internal cavities. Molten lead would thus be in direct contact with the container material and its contents for at least several hours and possibly up to two days. The purpose of this experimental part of the programme is to check if the candidate materials copper and Ti-Code 12 and also the fuel element cladding, Zircaloy-2 are susceptible to any form of attack in molten lead. Cast steel and nodular cast iron are immune to degradation by molten lead.

7.5.1 Experimental

Both externally stressed and unstressed specimens are to be immersed in molten lead for 14 days. The stressed specimens will, if they have not failed, be examined for signs of liquid metal cracking, and both types of specimen for dissolution or grain boundary penetration by the lead.

7.6 Corrosion Performance of a Multi-Layer Container

Several container concepts are possible with the four materials remaining under consideration in the Nagra programme. Although emphasis has been placed upon simple design where a single



- | | |
|---|-----------------|
| 1. Corrosion specimens
in bentonite block | 4. Load frame |
| 2. Sintered discs
50 μm pores, AISI 316 | 5. Heating coil |
| 3. End blocks with inlet
and outlet channels | 6. Reservoirs |
| | V. Valves |

Fig. 7.1 IGB-ETHZ bentonite swelling pressure apparatus

corrosion resistant layer, Ti-Code 12, or the container itself, copper, cast steel, nodular cast iron, provides the necessary corrosion resistance, multi-layer concepts may have significant advantages. In particular the outer layer may continue to provide protection for an inner container even after it has been breached. Such protection is achieved when the inner container is galvanically protected by the outer layer.

7.6.1 Experimental

The following material combinations are to be tested:

copper/cast steel
copper/cast nodular iron
Ti-Code 12/cast steel
Ti-Code 12/cast nodular iron
copper/lead

The experiments will be carried out in Bad Säckingen water with 0.1 mg/l dissolved oxygen at 140 C. The galvanic current between the two materials at a surface area ratio of 1:1 will be measured for a minimum of 200 hours if the current attains a constant value, otherwise to a maximum of 1000 hours.

References

- /1/ Korrosionsverhalten von unlegiertem Stahl, Stahlguss und Gusseisen als Endlagerbehälterwerkstoff in wasserführendem Granitgestein
E. Heitz, D. zur Megede NAGRA NTB 82-08
- /2/ Corrosion Resistance of Cast Irons and Titanium Alloys as Reference Engineered Metal Barriers for Use in Basalt Geologic Storage: A Literature Assessment
L.A. Charlot, R. G. Westerman
Pacific Northwest Laboratory PNL-3569 July 1981
- /3/ A Design Study of Long Term Storage and Underground Disposal Systems for Highly Active Waste.
W.R. Burton, J.R. Griffin
United Kingdom Atomic Energy Authority ND-R-514(R) June 1981
- /4/ An Assessment of Materials for Nuclear Fuel Immobilization Containers
K. Nuttall, V.F. Urbanic
Atomic Energy of Canada Ltd. AECL-6440 Sept. 1981
- /5/ Engineered Waste Package, Conceptual Design Spent Fuel (Form 1) Disposal in Salt
Westinghouse Electric Corporation AESD-TME-3087 Mar. 1981
- /6/ Performance of Ductile Iron Pipe in Soils
J. Am. Water Works Assoc. June 1968, p. 645
- /7/ Corrosion of Metals in Tropical Environments
C.R. Southwell, J.D. Buttman, A.L. Alexander
Materials Performance. July 1976
- /8/ Handling and Final Storage of Unreprocessed Spent Nuclear Fuel
Kärnbränslesäkerhet, Stockholm KBS-II Technical (1978)
- /9/ Copper as a Canister Material Waste - Evaluation with respect to Corrosion
Kärnbränslesäkerhet, Stockholm. KBS-Teknisk Rapport 90 March 1978
- /10/ A Review of the Swedish KBS-II Plan for Disposal of Spent Nuclear Fuel
National Academy of Sciences, Washington D.C. 1980
- /11/ Beurteilung von Konditionierungsverfahren zur Endlagerung nicht-wiederaufbereiteter Brennelemente
Alusuisse-Sulzer-NAGRA Bericht June 1981
- /12/ Soil-corrosion studies 1946 and 1948: Copper alloys, Lead and Zinc
J. Res. Nat. Bur. Stand. 44 259 (1950)

- /13/ Two Cases of Stress Corrosion Cracking in Copper Tubing
H.L. Logan, G.M. Ugiansky
Materials Protection p. 79 May 1965
- /14/ Transgranular Cracking of Copper in 1 M NaNO₂ Solution
S.P. Pednekar, A.K. Agrawal, H.E. Chaung, R.W. Staehle
J. Electrochem Soc. 126 70 (1979)
- /15/ Stress Corrosion Cracking of Pure Copper in Dilute Ammoniacal
Solutions
Y. Suzuki, Y. Hisamatsu
Corros. Sci. 21 353 (1981)
- /16/ Materials Considerations Relative to Multibarrier Waste Isolation
H.E. McCoy, J.C. Griess
Oak Ridge National Laboratory ORNL/TM-7770 July 1981
- /17/ Titanium Alloy Corrosion in Nuclear Waste Environments
J.W. Braithwaite, N.J. Magnani, J.W. Munford
Paper 213, Corrosion/80, Chicago, Illinois, March 3-7, 1980
- /18/ Container Assessment - Corrosion Study of HLW Container Materials
Quarterly Progress Reports, July - September 1981,
Oct. - Dec. 1981
U.S. Nuclear Regulating Commission NUREG/CR-2317
- /19/ An Assessment of Materials for Nuclear Immobilization Containers
K. Nuttall, V.F. Urbanic
Atomic Energy of Canada Ltd. AECL-6440 Sept. 1981
- /20/ The Hydrogen Embrittlement of Titanium Alloys
D.N. Williams
J. Inst. Met. 91 147 (1962)
- /21/ Mechanisms of Hydrogen Induced Delayed Cracking in Hydride Forming
Materials
R. Dutton, K. Nuttall, M.P. Pub, L.A. Simpson
Met. Trans. 8A 1553 (1977)
- /22/ Effects of Hydrogen in Titanium Alloys on Subcritical Crack Growth
under Sustained Load
D.N. Williams
Mat. Sci and Eng. 24 53 (1976)
- /23/ Korrosion durch radioaktive Strahlung
A.V. Galobzesky
Akademie-Verlag GmbH; Berlin (DDR) 1971

- /24/ Bereitstellung der Bentonite für die Laboruntermischungen
M. Müller-Vonmoos, G. Kahr, NAGRA NTB 82-04 Jan. 1982.
- /25/ Herstellung und Homogenität Hochverdichteter Bentonitproben
F. Bucher, P. Jeger, G. Kahr, J. Lehner NAGRA NTB 82-05 Dec. 1982
- /26/ Development of Strain-Rate Testing and its Implications. R.N.
Parkins. Stress Corrosion Cracking - The Slow Strain Rate
Technique, ASTM STP 665 G.M. Ugiansky and J.H. Payer, Eds.,
American Society for Testing and Materials, 1979,pp 5-25.

APPENDIX A - MATERIALS

A.1. Copper

All experiments were performed on specimens taken from a 14 mm thick plate of phosphorus de-oxidised copper with a phosphorus content of 0.007%.

The microstructure is shown in figure 7.1; the tensile test parameters are given in table A.1. The micrograph in figure A.1 is from a section parallel to the plate surface; the rolling and transverse directions are identical.



Fig. A.1 Microstructure of Copper

Yield strength (0.2%) N/mm ²	Tensile Strength N/mm ²	Elongation %	Reduction of area %	Direction
180	228	44.8	89	Rolling
188	231	48.5	87	Rolling
169	228	49.0	86	Rolling
176	234	42.8	85	Transverse
181	233	46.5	86	Transverse
173	234	46.5	85	Transverve

Table A.1 Room temperature tensile properties of copper

A.2. Cast steel and nodular cast iron

Two slabs each of GGG40 and GS40 of dimensions 500 mm x 500 mm x 40 mm were cast for use as specimen material. The chemical compositions and tensile properties are given in table A.2 and A.3 respectively.

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 A.2 Chemical composition of GS 40 and GGG 40

Material	Yield Strength (0.2%) N/mm ²	Tensile Strength (N/mm ²)	Elongation %	Reduction of area %
GS 40	262	487	28.5	56
	262	483	29.8	58
GGG 40	279	427	21.8	23
	280	433	23.5	21

Table A.3 Room temperature tensile properties of cast steel (GS 40) and nodular iron (GGG 40)

A.3. Ti-Code-12

The Ti-Code-12 was supplied in the form of 9.6 mm thick sheet material. The chemical composition is given in table A.4 and mechanical properties in table A.5.

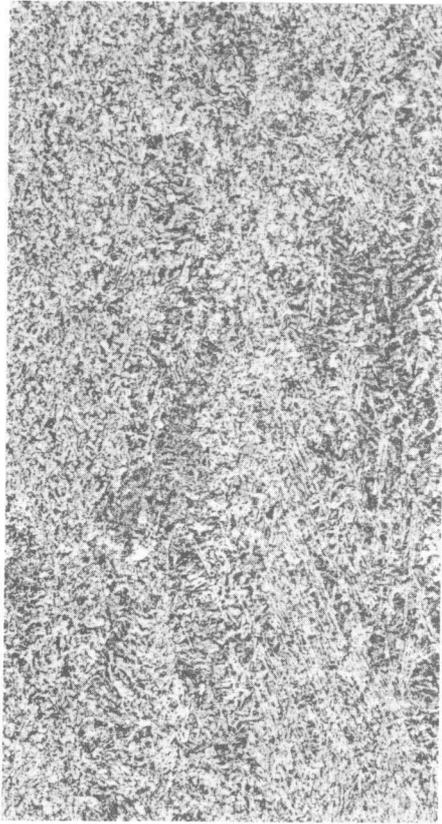
C	Fe	N	Mo	M	O	Ni	Ti
0.013	0.11	0.009	0.26	0.006	0.13	0.69	bal.

Table A.4 Chemical composition of Ti-Code-12

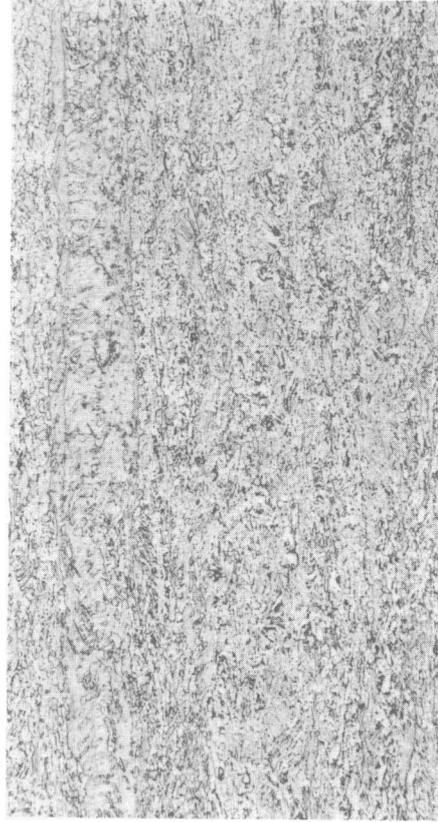
Yield Strength (0.2%) N/mm ²	Tensile Strength N/mm ²	Elongation %	Reduction of area %	Direction
476	545	22	42	Rolling
455	552	21	43	Rolling
496	641	22	48	Transverse
490	565	23	47	Transverse

Table A.5 Room temperature tensile properties of Ti-Code-12

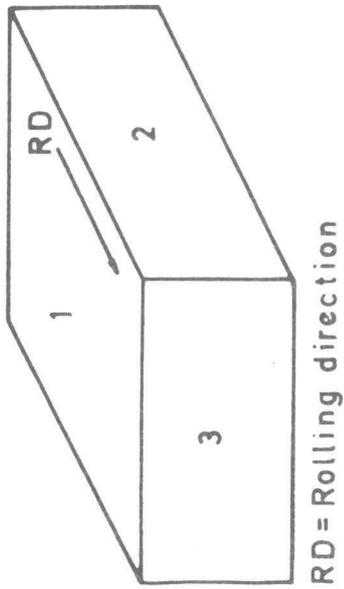
Some directional inhomogeneity is evident from the tensile values, and is also visible in the microstructure (figs. A.2 b-d and A.3 b-d).



b) Face 1



c) Face 2

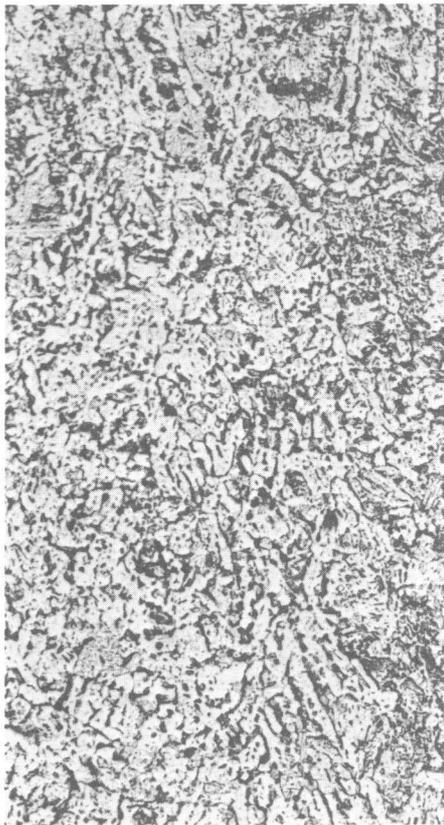


a)

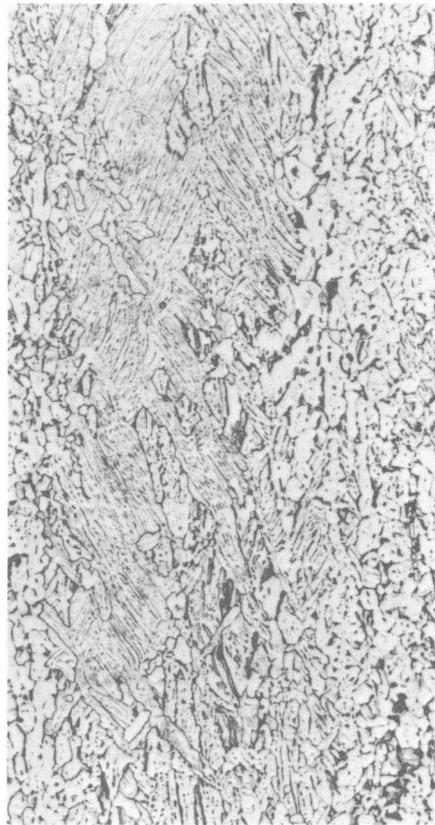


d) Face 3

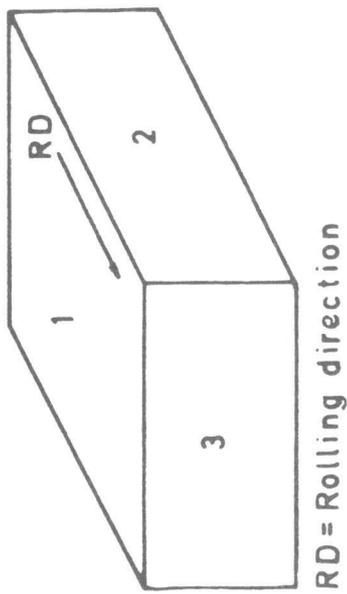
Fig. A.2 Microstructure of Ti-Cøde 12. Magnification 50x



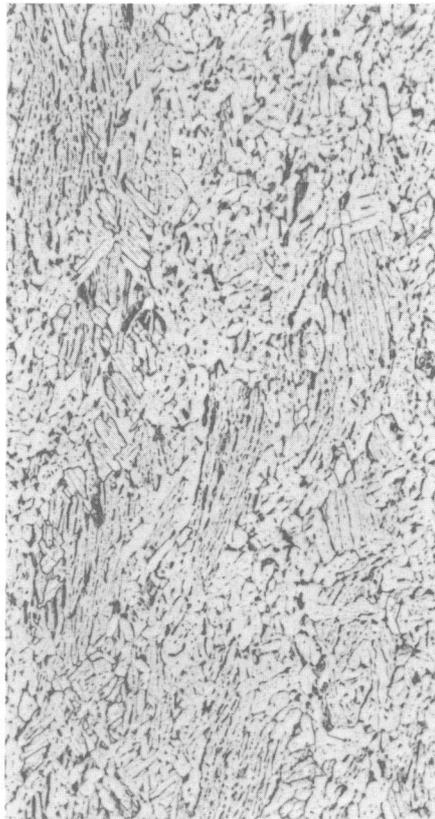
b) Face 1



c) Face 2



a)



d) Face 3

Fig. A.3 Microstructure of Ti-Code 12. Magnification 200X.

APPENDIX B - WELDS

B.1. Welding of cast steel

The two slabs of cast steel GS 40 were welded together. The geometry of the weld site is given in figure B.1.

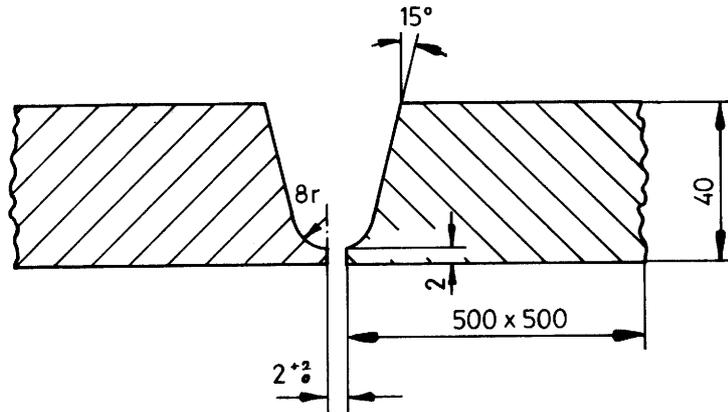


Fig. B.1. Weld site preparation cast steel and nodular iron

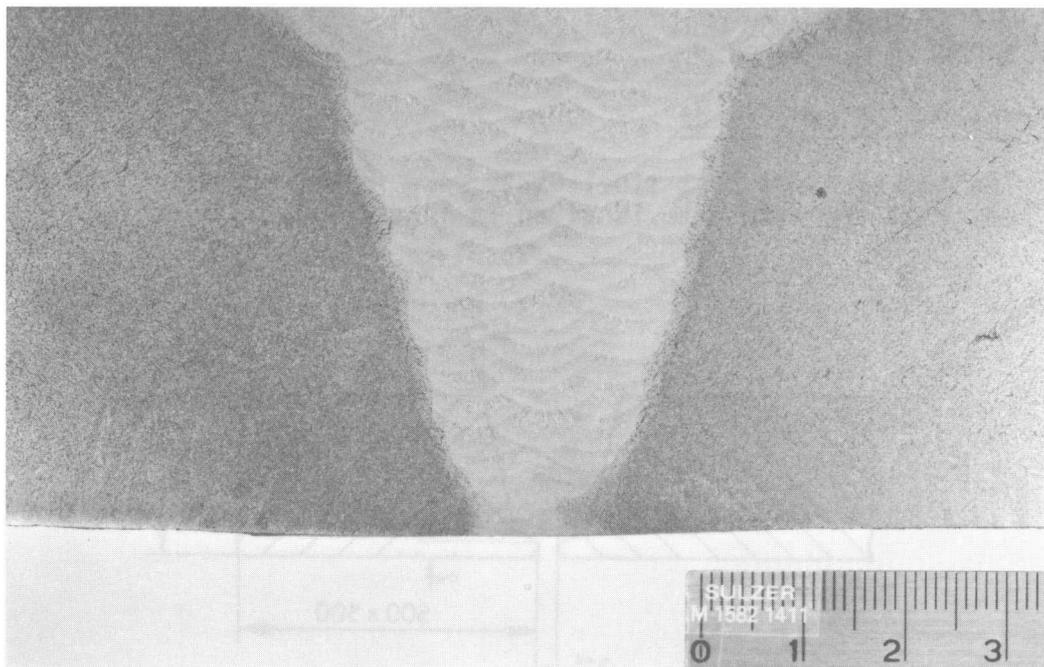
Weld details: -

preheat 120 C, TIG + E + UP
 filler metal: TIG: DMO-IG, 0 2.4 mm.
 E: Supratherme, 0 2.5-6.0 mm
 UP: S 3, 0 4.0 mm + LW 280.

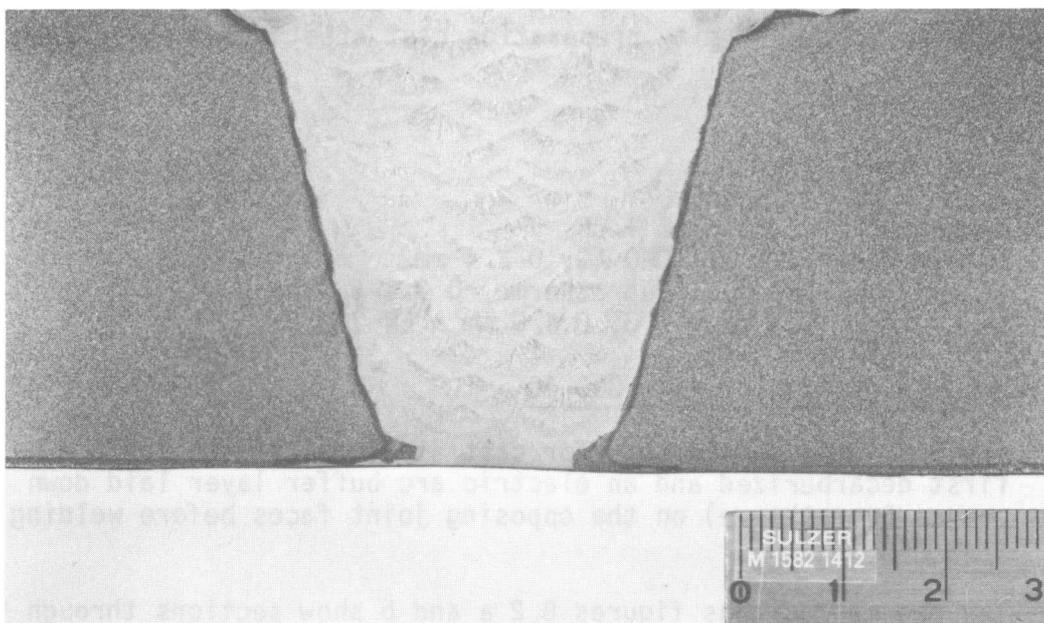
B.2. Welding of nodular iron GGG 40

Process identical to that for cast steel except the surface was first decarburized and an electric arc buffer layer laid down (3 passes Supratherme) on the opposing joint faces before welding them together.

The two macrographs figures B.2 a and b show sections through the weld of cast steel (a) and nodular iron (b). The decarburized zone (etched dark) and the weld metal buffer layer, which are necessary in order to be able to weld nodular iron, are clearly visible. After application of the buffer layer the nodular iron could be welded as for cast steel. This preparation of the nodular iron weld surfaces may be carried out in advance, such that the repository facility itself the handling of cast steel or nodular iron containers would be practically identical.



a)



b)

Fig. B.2 Macrographs of cast steel (a), and nodular cast iron (b) welds

B.3. Electron beam weld in copper

Unlike electric arc fusion welding of thicker sections, no gap as in figure B.1. is required for electron beam welding. The two pieces should be as close a fit as possible, and no filler metal is needed. For the purposes of this programme, a satisfactory simulation of an electron beam weld could be made by a weld run in the full material i.e. by omitting the joint. A cross section of such a mock weld is shown in figure B.3. The U-shaped lines in these micrographs mark the successive solidification fronts as the pulsed beam progresses along the weld line. The spike (void) at the root of the weld is typical of such mock welds.

B.4. Electron beam weld in Ti-Code 12

A simulated weld was produced as for copper. The weld is shown in cross section in figure B.4.

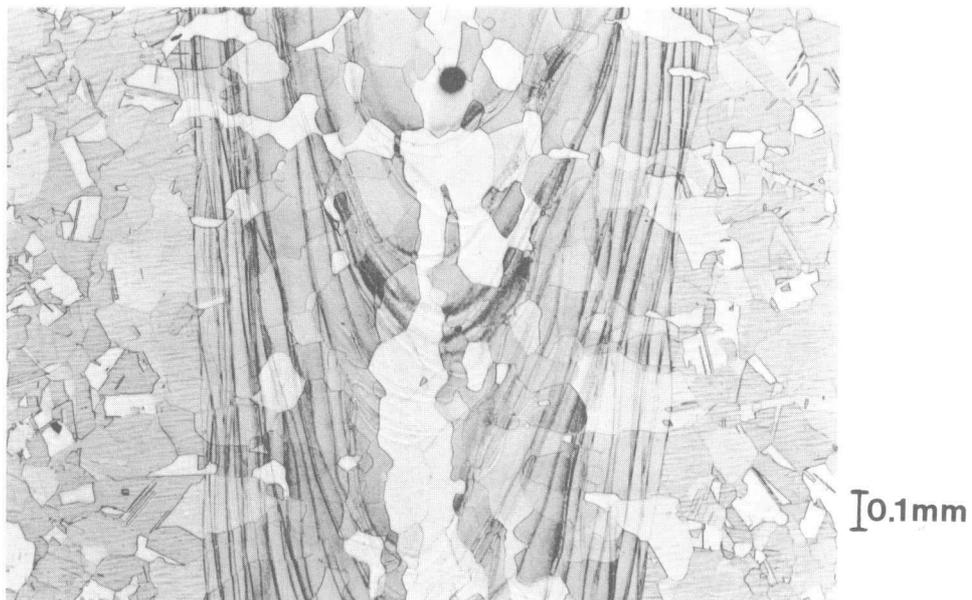
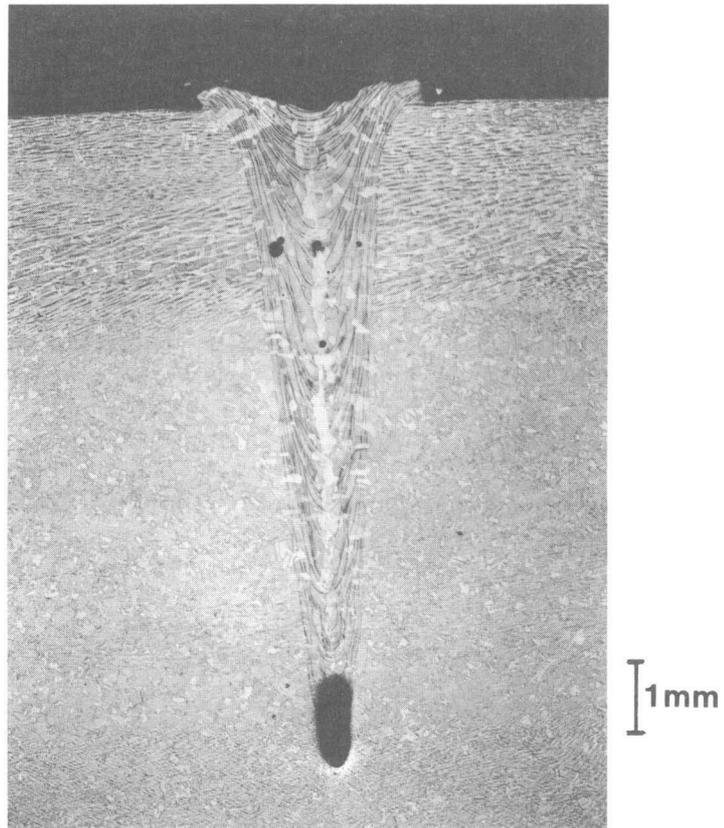


Fig. B. 3. Cross section through electron beam weld in copper

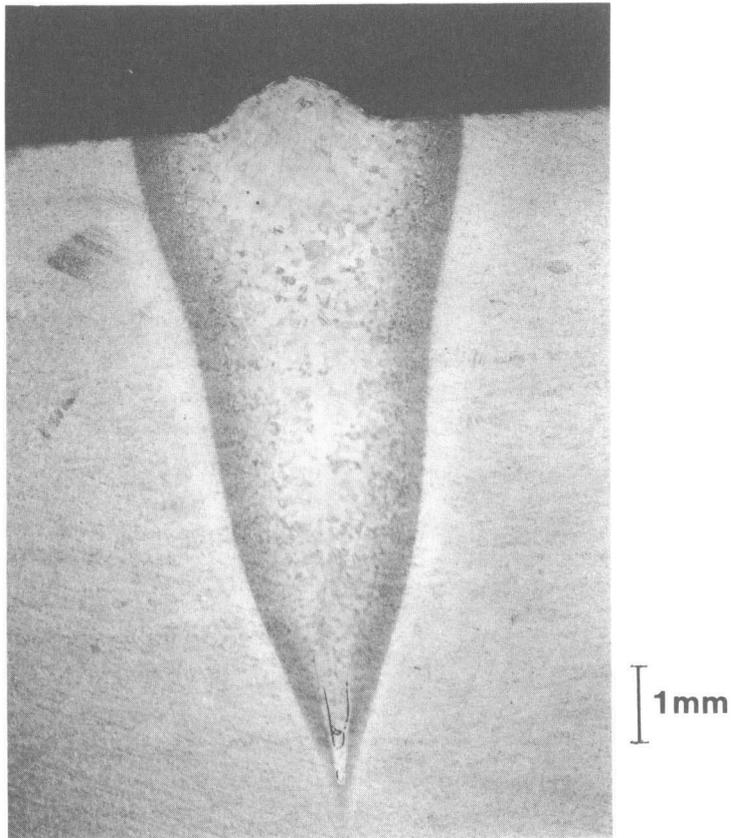


Fig. B.4 Cross section through electron beam weld in Ti-Code 12

APPENDIX C - RESULTS

C.1. Introduction

This appendix presents the results from the experimental programme as available March 31, 1983. For a full description of the experimental techniques, detailed presentation of results and discussion, the reader is referred to Part II of this report.

C.2. Immersion Corrosion TestingC.2.1. Introduction

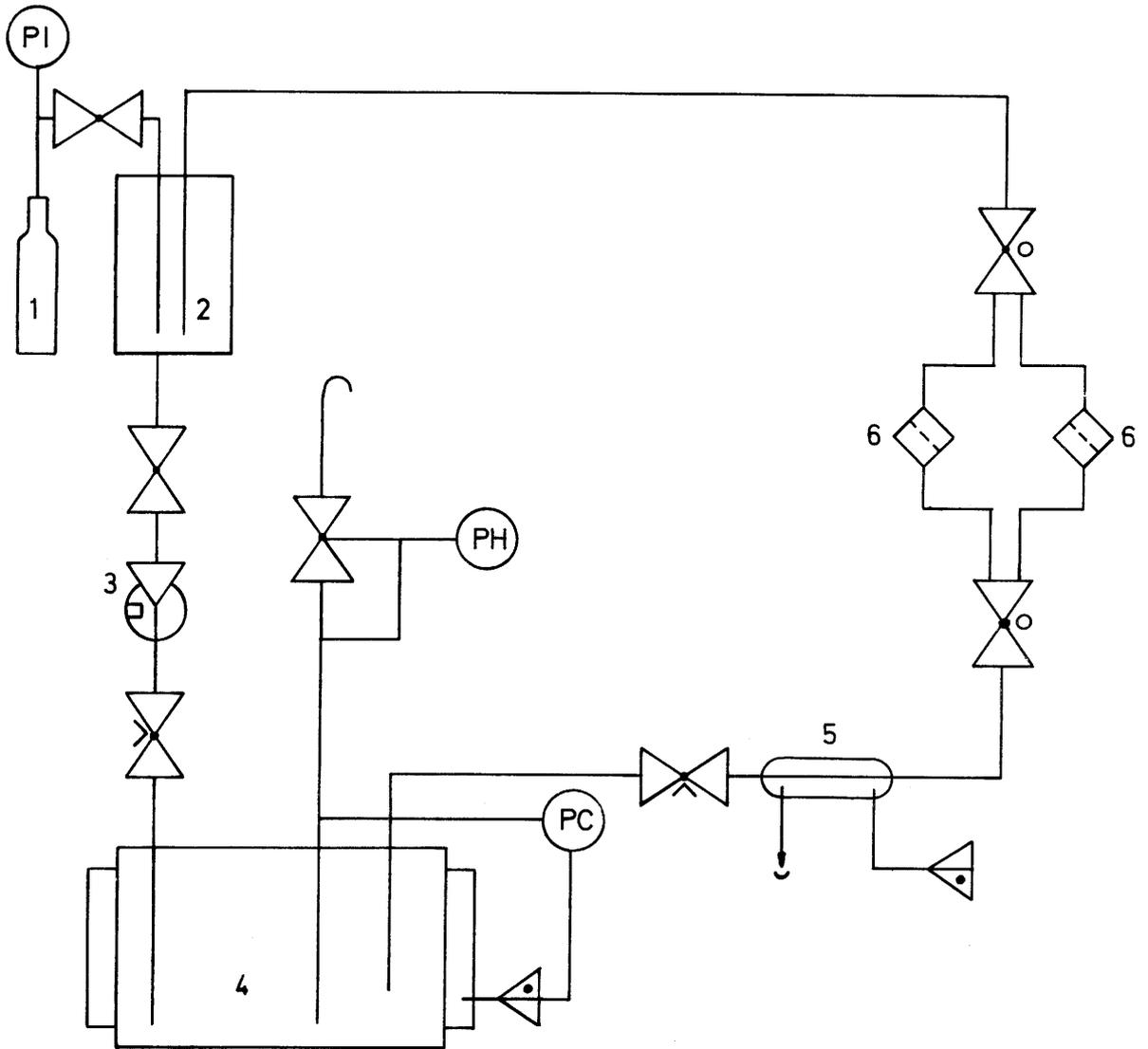
Immersion corrosion tests on Bad Säckingén water are intended primarily to experimentally verify that the corrosion rates forecast from the literature values are applicable to Swiss repository conditions.

Corrosion specimens from the test welds in the candidate materials were also corrosion tested to check whether or not the welding process has any effect on the corrosion resistance.

C.2.2. Experimental

The 140°C exposures were carried out in a refreshing autoclave system (see figure C.1.). The 80°C experiments were carried out in an analogous, but simplified test circuit operating at atmospheric pressure. In both cases the oxygen concentration is set by bubbling an appropriate nitrogen/oxygen gas mixture through the sealed reservoir.

The specimens were 30 x 20 x 2 mm in the case of the plain corrosion specimens and 150 x 20 x 2 mm for the specimens taken from the weld.



- | | |
|----------------|------------------------------|
| 1. Gas mixture | 5. Heat exchanger |
| 2. Reservoir | 6. Filter |
| 3. Pump | PI. Gas cylinder |
| 4. Autoclave | pressure gauge |
| PH and PC | Over-pressure safety cutouts |

Fig. C.1. Refreshing autoclave system

C.2.3. Results

The results from the very first tests on cast steel and cast nodular iron are given, as the values obtained here are critical to the retention of these materials in the Swiss programme.

The specimens were evaluated in two ways

i) weight loss

At both 80°C and 140°C the corrosion product on the iron based materials could not be completely removed by ultrasonic agitation, by means of a nylon brush or by rubbing with a rubber eraser. Cathodic polarization in 30% oxalic acid at 50°C at a current of 15 mA/cm² removed the corrosion product. On blank specimens this method produced a weight loss which did not exceed the equivalent of a corrosion rate of 1 m/yr.

ii) metallographic examination.

The results from the weight loss determination for GS 40 and GGG 40 at 80°C in Bad Säckingen water containing 0.1 mg/l O₂ after 500 hours exposure gave average corrosion rates of 41 µm/yr and 48 µm/yr respectively. At 140°C in the same medium after 630 hrs. the corrosion rate was measured as ca. 12 µm/yr for GS 40.

On heating, calcium carbonate precipitates out from Bad Säckingen water, some of which attaches itself to the specimen surface. More was observed on the specimen at 80°C than 140°C.

Cross sections of GS 40 exposed at 80°C in Bad Säckingen water with 0.1 mg/l O₂ were not uniformly corroded. The thick calcium carbonate layer is clearly visible in figures C.2 a and b. At holidays in this layer, the steel was pitted, the pits containing a thick layer of corrosion products. Beneath the carbonate, the corrosion product layer is much thinner, and in some instances is absent altogether, e.g. left hand side of figure C.2b. It was assumed that in the absence of a corrosion layer the surface at this point was unattacked. Measured from this point the deepest pit found was 12 µm deep after 500 hours, i.e. equivalent to a maximum penetration rate of 204 µm/yr. At 140°C the corrosion appears to be more uniform such that the maximum penetration rate does not greatly exceed the average corrosion rate.

No evidence of increased corrosion due to welding was found.

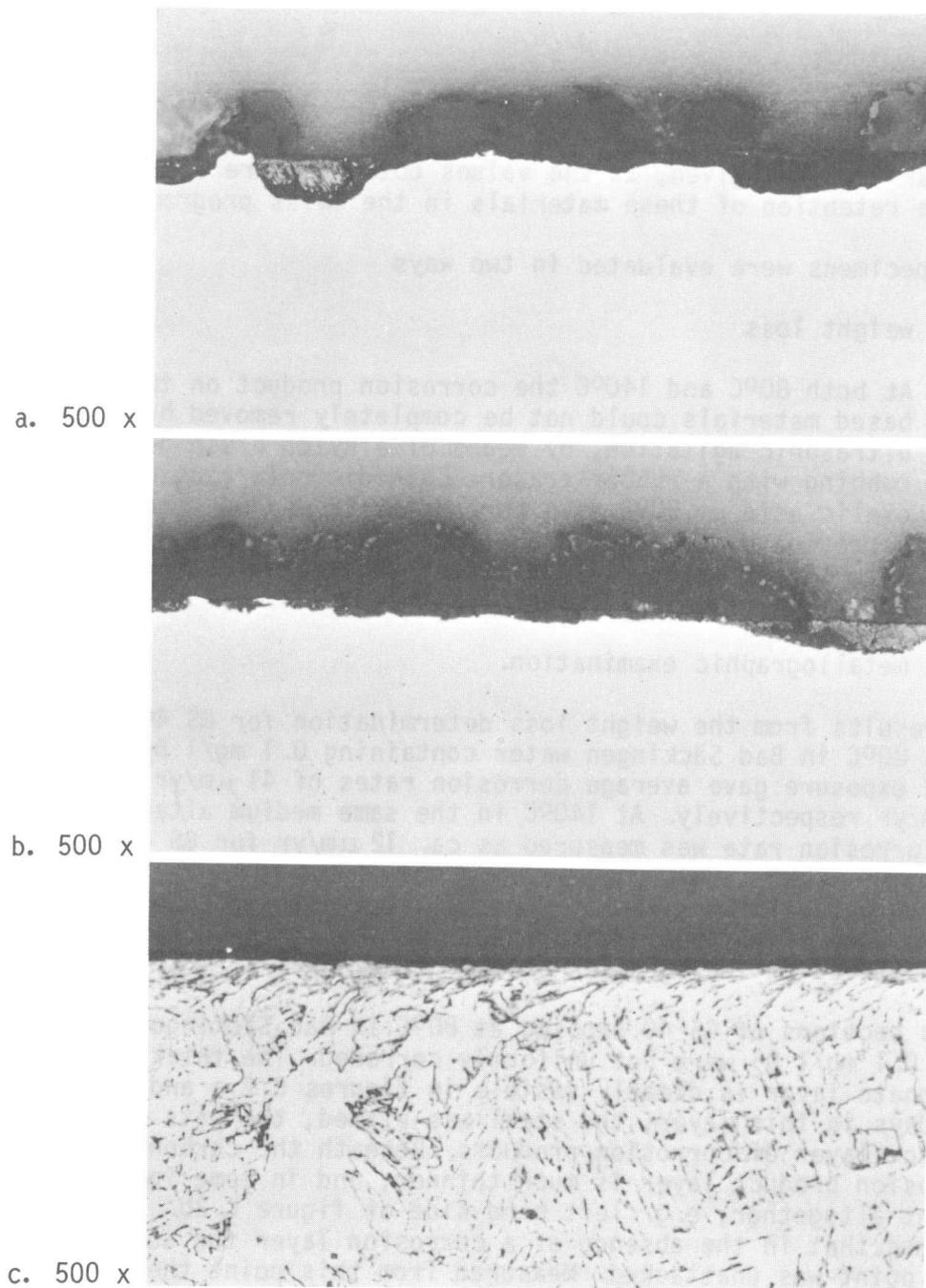


Fig. C.2

- a.b. Cast steel exposed to Bad Säckingen water, 0.1 mg/l O₂ at 80 C for 500 h
- c. As a and b but exposed for 630h at 140 C

C. 2. 4. Comment

The results seem to confirm the forecasts made in section 6. The corrosion rate is lower at 140°C than at 80°C where a maximum penetration rate of 204 µm/year predicted from the 500 hour data was observed. If a linear extrapolation to 1000 years holds, then 204 µm/year max. penetration is near the upper acceptable limit, whereas if the predicted reduction of both average and maximum penetration rates with time are confirmed by longer term tests then both cast steel and nodular iron would be fully adequate as container materials.

C. 3. Stress assisted cracking

C. 3. 1. Four point bending test

The four point bending specimens are tested under the same conditions as the immersion test specimens. The specimens were loaded to 90% of their room temperature 0.2% yield strength. The results so far are presented in table C.1. No evidence of stress corrosion cracking was found.

Medium: Säckingen Water		Cracks found	Yes, No: test time
O ₂	Temp.	Cast steel	Nodular iron
0.1 mg/l	80°C	No: 600 h	No: 600 h
0.1 mg/l	80°C	No: 1600 h	No: 1600 h
0.1 mg/l	140°C	No: 630 h	

Table C.1 Four point bend test results

C. 3. 2 Constant extension rate testing (CERT)

With this method, tensile specimens are slowly strained while exposed to the test medium. The tensile properties are then compared to the values obtained in an inert medium. The most sensitive indicator of stress corrosion sensitivity is the reduction of area, (R.A.).

The results are presented in tabular form, for copper in table C2, and Ti-Code 12 in table C3 for specimens with their axis in the rolling direction and in the transverse direction.

Medium	Temp °C	Strain rate sec ⁻¹	<u>R. A. medium</u> R. A. reference	%
Säckingen water air saturated	80	1x10 ⁻⁵	99	
		1x10 ⁻⁶	100	
		2x10 ⁻⁷	100	
Säckingen water 0.1 mg/l O ₂	80	1x10 ⁻⁵	99	
		1x10 ⁻⁶	100	
		2x10 ⁻⁷	103	
Säckingen water air saturated + 15 g/l Cl	80	1x10 ⁻⁵	101	
		1x10 ⁻⁶	100	
Säckingen water air saturated +100 mg/l NH ₄	80	1x10 ⁻⁵	99	
		1x10 ⁻⁶	98	
Säckingen water air saturated + 300 mg/l NH ₄	80	1x10 ⁻⁵	99	
		1x10 ⁻⁶	104	

Table C.2 CERT results on copper

Medium	Temp °C	Strain rate sec ⁻¹	<u>R. A. medium</u> R. A. reference	%	Direction
Säckingen water air saturated	80	1x10 ⁻⁵	103		rolling
	80	1x10 ⁻⁶	105		rolling
	80	2x10 ⁻⁷			rolling
	80	1x10 ⁻⁵	100		transverse
	80	1x10 ⁻⁶	100		transverse
	80	2x10 ⁻⁷			transverse
Säckingen water 0.1 mg/l O ₂	80	1x10 ⁻⁵	103		rolling
	80	1x10 ⁻⁶	103		rolling
	80	2x10 ⁻⁷			rolling
	80	1x10 ⁻⁵	97		transverse
	80	1x10 ⁻⁶	100		transverse
	80	2x10 ⁻⁷			transverse

Table C.3 CERT results on Ti-Code 12

C. 3. 3. Comment on CERT results

With the CERT method, the reduction of area (R.A.) is considered to be the most sensitive parameter for environmentally induced stress assisted cracking. This is the parameter quoted in the tables expressed as a percentage of the R.A. value in a neutral medium, which in this case was deionised water. There is no evidence of stress induced cracking either for copper or Ti-Code 12; the results are all within normal experimental scatter.

C. 4. Corrosion in Bentonite

C. 4. 1 Experimental conditions

These are given in section 7.4. The IGB swelling pressure apparatus used for these experiments is illustrated in figure 7.1.

C. 4. 2. Handling

The preparation and handling of the bentonite blocks with their embedded corrosion specimens caused some problems as a saturated water content of 30% is near the upper limit attainable with pre-compacted bentonite. Higher water contents would require different handling procedures to those used at the IGB for swelling pressure measurements. The corrosion specimens were inserted by simply pre-pressing half the weighted bentonite charge before laying the specimen 10x10x2 mm on the packed bentonite, covering with the rest of the charge, and finally compressing to the required as-pressed density. The saturated water content is dependent upon the as-pressed density and the water content of the 110°C air dried bentonite powder. All bentonite specimens produced lay within the range indicated in figure C. 3.

Preliminary experiments had shown that the bentonite with an as-pressed density of ca. $1.63 \times 10^6 \text{ g/m}^3$ is porous enough to allow a high water flow rate through the sample if the full 90 bar pressure difference is immediately applied. The mechanism of water uptake appears to be rapid flow into the bentonite and flooding of the pores in the compressed bentonite, followed by absorption of water into the bentonite structure which causes the bentonite to swell and fill the pores.

In this experiment Bad Säckingen water was introduced at low pressure (~ 5 bar) from one side of the bentonite block via valve V_3 (fig. 7.7). About 2 hours later the bentonite had swollen sufficiently to sustain the full 90 bar pressure difference, i.e. $P_A = 10$ bar, $P_B = 100$ bar. The specimen was then brought to the test temperature of 140°C

C. 4. 3. Results

Material	Exposure Period. hours	Average Corr. rate $\mu\text{m}/\text{yr}$
Cu	720	1
Cu	744	1
Cu	744	1
GGG 40	720	11
GGG 40	744	27
GS 40	720	8
GS 40	744	16
Ti-Code 12	720	1

Table C. 4. Results of corrosion tests in bentonite at 140°C

C. 4. 4. Comments

The results from the corrosion testing in bentonite should be compared to those obtained from immersion testing at the same temperature. Only one result is available from the immersion at 140°C, that for GS 40 where a corrosion rate equivalent to 12 $\mu\text{m}/\text{yr}$ was found. The rate for GS 40 in bentonite is almost identical despite some important differences in the experimental conditions. With the immersion tests, oxygen is continuously supplied albeit at a concentration of only 0.1 mg/l and at a rate of 0.5 l/h fresh solution, whereas in the bentonite once the oxygen trapped within the pores has been displaced or consumed, the oxygen level should tend to zero. A possible explanation of the similarity in corrosion rate is that diffusion in the oxide film is rate limiting and that corrosion either by oxygen or direct by water (Schikorr) proceed at similar rates. Further clarification of this point must await the completion of the experimental programme.

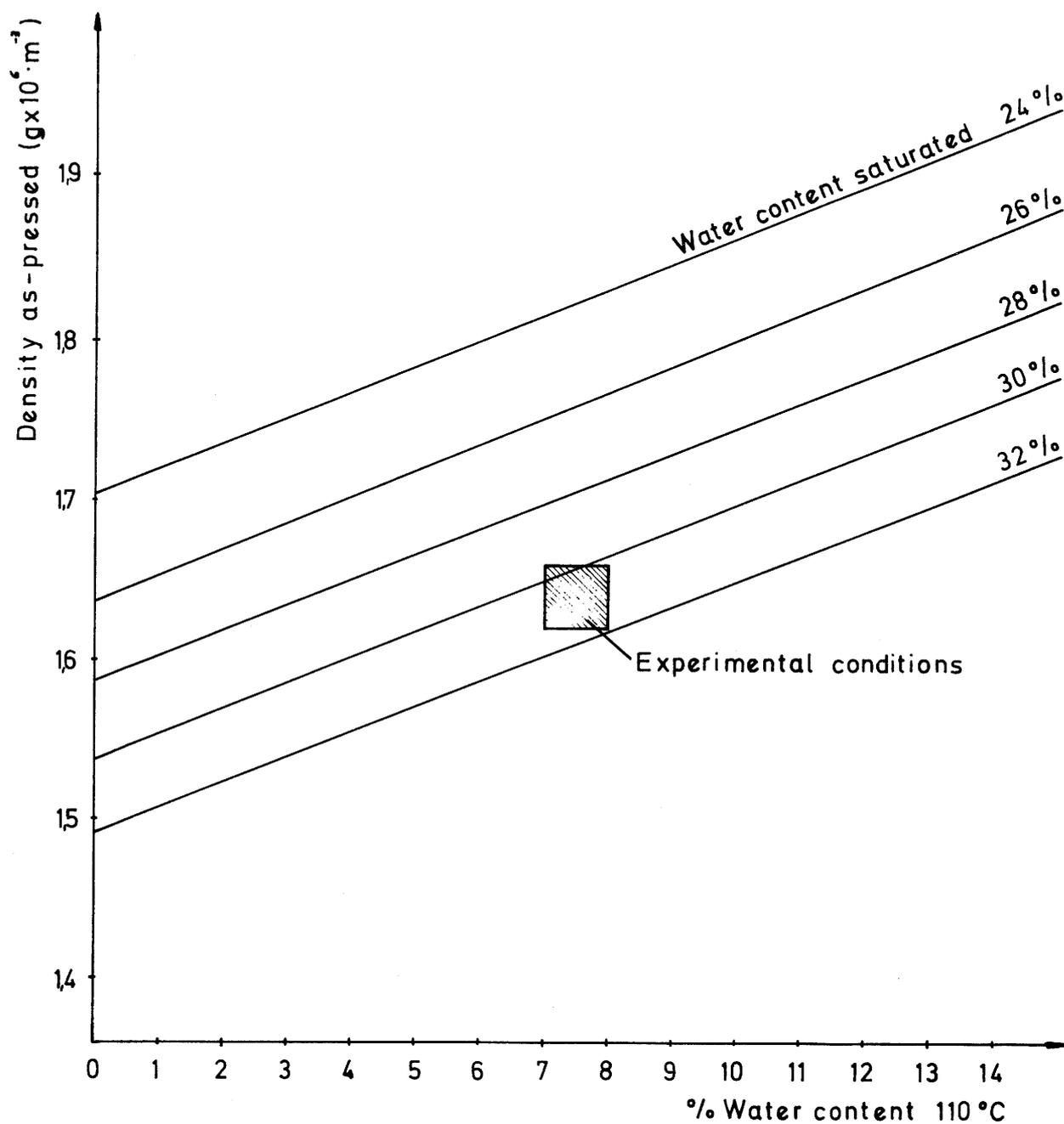


Fig. C. 3. Relationship between water content of 110°C air dried sodium bentonite MX-80, the as-pressed density and the saturated water content as established in the IGB apparatus

C.5. Effect of molten lead on canister materials and Zircaloy fuel element cladding

C.5.1 Experimental

Specimens of copper, Zircaloy-2 and Ti-Code 12 were immersed loaded and unloaded in a molten lead bath. In the case of the stressed specimens, the load applied was 80% of the 0.2% yield stress at 350°C, i.e. 76, 112 and 80 N/mm² for copper, Zircaloy 2 and Ti-Code 12 respectively. The experiment was terminated at 500 h immersion.

C.5.2. Results

At 350°C the creep rate of copper is so high, about 1% extension after 18 h. that the use of loaded specimens was not possible. Copper is soluble in molten lead, corrosion rates of 0.09 - 0.23 mm per day were observed. (Fig. C.4).

Zircaloy-2 is resistant to molten lead. There was no evidence of liquid metal embrittlement on the stressed specimens. Cross sections of the Zircaloy specimens failed to reveal any evidence of surface attack or penetration via the grain boundaries or by bulk diffusion of lead into the Zircaloy.

The experiment on Ti-Code 12 is in preparation and will be reported in Part II.

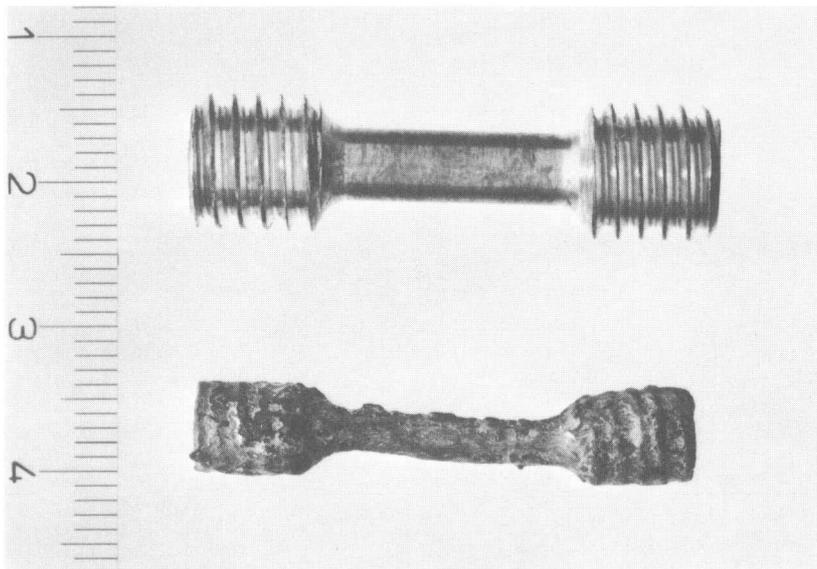


Fig. C.4 Appearance of copper specimen after two weeks immersion in molten lead.