THE JOINT EUROPEAN TESTING PROGRAM ON HLW CONTAINER MATERIALS

B. Haijtink
Commission of the European Communities
Rue de la Loi, 200
B - 1049 Brussels

A. Accary
Laboratory for Metallurgy
University of Clermont Ferrand II
F - 63000 Clermont-Ferrand

ABSTRACT

Within the framewark of the R & D program on Management and Storage of Radioactive Waste of the European Atomic Energy Community, one project is dedicated to the development of containers for vitrified high-level waste to be disposed of in geological formations. In particular, a joint testing program has been established for the assessment of the corrosion behavior of potential materials in the different disposal enviornmnets considered, respectively granite, salt and clay. As a result of previous screening tests on a number of materials, a detailed testing program is presently concentrated on three most promising reference materials, respectively Hastelloy C4, Ti-Pd (0.2%Pd) and a mild steel.

INTRODUCTION

The Commission of the European Communities has been participating, since 1978, in research programs aiming at the assessment of corrosion behavior of suitable materials for the manufacture of containers for geological disposal of vitrified high-level waste.

The research is being performed in the framework of cost-sharing contracts with research centers in various Member States of the European Communities as well as in the Joint Research Center of Euratom at Ispra in Italy. The role of the Commission, apart from financial support, is to coordinate the research projects and to promote exchange of information by organizing regular meetings between the participating laboratories. The scope of the program being limited in the first phase to testing and selecting suitable materials, has recently been enlarged to mathematical modelling of corrosion phenomena and to the identification of design features. This paper will, however, be limited to the corrosion testing program.

SELECTION OF MATERIALS

In the vitrification process of the high-level waste, the glass melt, e.g. in the French AVM process, is cast in a stainless steel canister which is generally considered as not being suitable for acting as a barrier for medium term in a geological disposal environment. Therefore the canister has to be protected by an overpack. One approach is to use a highly corrosion resistant material e.g. nickel based alloys, titanium alloys, etc. Another approach is to use metals or alloys, e.g. cast irons, carbon steels, etc., which have corrosion rates sufficiently low to ensure, when used at an appropriate thickness, containment for the desired period of time. These metals are called corrosion allowance metals.

In the past, over thirty different metallic alloys have been preselected and tested on their corrosion behavior in potential disposal enviornments likely to be faced with in the three geological formations, granite, salt and clay, considered in the Community R & D Program[1]. These screening tests, carried out at laboratory as well as in field experiments, permitted a further selection of most suitable materials with a view to limiting the number of materials being tested.

As a result, a more detailed joint testing program has been started in 1983 on three reference materials which were provided on a common basis, the samples of each material coming from one melt.

These reference materials are Hastelloy C4, Ti-Pd (0.2% Pd) and a mild steel (0.11 %C). Each participating laboratory is performing a number of tests on these materials, however may pursue on other candidate materials when found relevant.

TESTING PROGRAM

The corrosion testing program considers the potential disposal environments to be encountered in granite, salt and clay formations and to a minor part, in ocean sediments. Typical ground-waters, salt brines, interstitial clay waters as well as the host rock itself are used as test media. As reference temperatures 90°C and 170°C have been selected. Moreover, the influence of gamma radiation is being examined at typical doses of about 10^5 rad/hr. Finally, the possible effects of micro-organisms which might be present in the disposal environment are to be investigated.

In the tests generally no presence of backfilling or buffer materials is yet forseen, firstly as no reference backfill material could yet be defined and secondly a backfill material will be chosen among others, with a view to decreasing the agressivity of the environments, so the tests are done in the "worst conditions".

Various corrosion processes are analyzed such as general, pitting, crevice and stress corrosion.

Moreover, the formation of passivation layers in particular on the titanium alloy is being examined.

Below, the disposal environments studied are described in some more detail. Besides, some characteristical results obtained in the screening tests are presented. Results of the detailed testing program on the reference materials will become available in one year time.

DISPOSAL ENVIRONMENTS CONSIDERED

Granite Environment

Corrosion behavior in granitic environments is being examined by CEA (France) and UKAEA (UD) whereas the first is concentrating on corrosion resistant materials and the latter on corrosion allowance materials. Test solutions have been based on typical granite ground-water compositions like (units mg/l)

Cl^-	35	Na^+	106
F^-	1.9	Ca^{2+}	20
HCO_3^-	244	Mg^{2+}	6.1
$SO_4^=$	24	pH	9.4
SiO_3	19		

However, with a view to taking account of local modifications of the water composition due to e.g. radiolysis, and where accelerated tests are to be applied, the typical granitic water solutions are often artificially acidified and enriched with Cl^- ions. These accelerated tests are in particular necessary when corrosion phenomena have to be analyzed on highly corrosion resistant materials.

Immersion tests (up to 4 months) performed by CEA (Ref. 2) in acidified solutions (up to 10 and 30 g NaCl/liter) at 80 C on corrosion resistant materials gave general corrosion rates of about 0.15 μm/yr for Hastelloy C and Ti-Pd alloy, whereas no pitting corrosion was observed. At 170°C however, Hastelloy C4 showed being slightly susceptible to pitting corrosion. For the assessment of the stress corrosion susceptibility, a special testing machine was designed and built. The samples are submitted to a constant slow strain rate (e.g. $10^{-6}S^{-1}$) whereby the elctrode potential of the probe can be controlled.

Concerning the corrosion allowance materials, a number of carbon steels (cast and forged) have been tested by UKAEA at their laboratories at Harwell[3]. General corrosion rates were measured (e.g. in deaerated sea water at 90°C) yielding from about 10 m/yr without gamma radiation to about 40μm/yr with gamma radiation (gamma dose 10^5 rad/hr).

Concerning pitting corrosion penetration depths were measured as a function of time. It was concluded that the pit growth kinetics obeys the Romanoff law rather well, i.e. $P = KT^n$ where P is pit depth (mm), T the exposure time (year), and K and n are constants for which the following values are proposed : K = 2.9 and n = 0.44. This expression predicts a maximum penetration of 63 mm over 1000 years. Apart from laboratory experiments, field work is done at a site in Cornwall where specimens of carbon steels are incorporated in a test assembly mounted in an indirectly heated bore-hole.

The work done so far on carbon steels leads to the preliminary conclusion that a corrosion allowance of about 115 mm would take care of the general corrosion and pitting corrosion for a period in the order of 1000 years.

Environmental corrosion, to which steels in general are susceptible, is a process which cannot be accomodated by increasing the thickness because of the crack propagation velocity which is usually about 10^{-7} mm/s. Therefore, this process should be avoided either by showing that disposal environments will not support cracking or by using steels (e.g. low carbon steels) with a sufficient high threshold stress for cracking.

Salt Formation

The corrosion behavior in a saliferous enviornment is being examined by the Kernforschungszentrum, Karlsruhe (Germany)[4]. Immersion tests are performed in a brine without, and with gamma radiation (10^{-5} rad/hr) of the corroding medium. The brine has the following composition:

$MgCl^2$	$26.8^{W}/0$	KCl	$4.7\ ^{W}/0$
$MgSO_4$	$1.4^{W}/0$	NaCl	$1.4\ ^{W}/0$
H_2O	$65.7^{W}/0$		

The general corrosion, pitting corrosion and crevice corrosion are investigated on flat coupons and the stress corrosion on U-bend specimens. The mass losses are measured by gravimetry, the localized corrosions by metallography. In the brine, without gamma radiation general corrosion rates were measured for Hastelloy C4 as low as 0.05 μm/yr m/yr at 90°C to 0.15 m/yr at 170°C; for Ti-Pd alloy, the rates were about 0.3 μm/yr for both temperatures. For a mild steel, the values yielded from 55 μm/yr to 230 μm/yr. No local corrosion was observed.

Also under gamma radiation, the Ti-Pd alloy resisted to local corrosion whereas the general corrosion rates were not significantly increased. The other materials investigated show weight losses much larger than without irradiation and were also susceptible to local corrosion.

Besides the laboratory experiments at Karlsruhe, in situ experiments are being prepared to be performed at the Asse II salt mine. Welded tubes will be inserted in heated bore-holes (170°C) and plain material coupons will be buried in loose rock salt at rock temperature from 35°C to 40°C for a time period of 1 - 2 years.

Clay Formation

The corrosion behavior of candidate container materials for disposal of vitrified HLW in a plastic clay formation is being examined by SCK/CEN at Mol (Belguim)[5].

Material samples are tested in direct contact with the Boom clay, in humid clay atmospheres, in interstitial clay water and Antwerpian ground-water. Tests are being carried out both in laboratory at Mol and in an open clay pit at Terhaegen. Furthermore, a testing program is in preparation for being performed in the underground experimental laboratory excavated in the Boom clay at 220 m depth beneath the Mol site.

The screening tests performed in the various environments showed that Hastelloy C and Ti-Pd alloys behave very satisfactorily. Moreover, different trends could be identified with respect to the influence of temperature and humidity of the environment.

For Hastelloy C, tested in interstitial clay water at 25 C, uniform corrosion rates of about 1 m/yr were measured. These corrosion rates increase however drastically with exposure temperature. The same trend has been observed with tests in groundwater, with generally larger corrosion rates. At tests in direct contact with clay and in humid atmospheres the opposite trend was found due to the predominant influence of the relative humidity on corrosion.

The susceptibility to stress corrosion cracking is being evaluated using bend beem and U-bend devices and small sealed containers. Results of exposure times up to 3 - 4 years are now available, but some tests, in particular in situ at Terhaegen will continue in order to obtain results under long (up to 5 years) exposure times.

FORMATION OF PASSIVATION LAYERS

It is well known that at the surface of metals passive layers can be formed which have a protective effect. With a view to analyze the nature of the layers, relative concentration depth profiles of elements are determined using Glow Discharge Spectrometry[7]. G.D.S. spectres of surface films on Hastelloy C4 show three parts: the external part which is generally enriched in elements coming from the liquid or gas environment, the middle part, and the inner one enriched in elements coming from the alloy matrix. The composition depth profiles are being classified in several types depending on the more or less improverishment or enrichment of elements. In brine and clay water at 90 C, the depth profiles of elements become stationary after about 1000 hrs immersion.

In the case of Ti-Pd alloy electron patterns have shown that the protective film has an amorphous structure. Besides Ti and Pd whose contents are significantly decreased, the presence of elements coming from solution, like Mg, Ca, Si, Na, is very apparent. G.D.S. also appears a powerful technique for determining the distribution of hydrogen through the passive films. Hydrogen level detected is relatively uniform during sputtering, suggesting that the whole film is hydrated to some extent. The nucleation and growth of the layer as well as the potential problem of film break away should be further examined.

APPLICABILITY OF RESULTS

Conceptual plans for the disposal of nuclear waste into geological formations envisage waste isolation in containers for several hundred years. It is obvious that real time tests for the assessment of material behavior are not applicable. Theoretical extrapolation from short term tests with multiplication factors of more than 100 to be credible must therefore be based on a perfect knowledge of the fundamental mechanisms involved in the corrosion process which is not yet sufficiently available to justify this procedure.

Another problem is the disposal environment which is not only site specific but will also vary during disposal time. Therefore test conditions are selected out of a number of varieties which might occur in the disposal environments in such a way that usually the "worst conditions" are considered. In the same way, "overtests" or "accelerated tests" are applied in which the "amount of corrosion" under aggravated conditions is the one which would be expected over a long period. However, exact relationship between short-term tests and long-term service can only be known if theoretical extrapolation has proved reliable.

Modelling of corrosion behavior, in particular general corrosion, for the evaluation of long term behavior has started, however more experimental results are necessary for a better validation of the models. Validation may also be obtained by analysis of archeological metallic objects submitted to corrosion for well-known periods under well defined conditions. This procedure is applicable only to metals or alloys used or existing several centuries ago. It is therefore practically restricted to iron and copper based alloys[8].

The detailed testing program is however believed

- to provide a large number of results concerning the response of most promising materials to the different environments;
- to identify disposal environments in which materials behave satisfactory (particularly important for local corrosion phenomena);
- to develop and validate theoretical models.

CONCLUSION

Within the framework of the R & D Program on Management and Storage of Radioactive Waste of the European Atomic Energy Community a number of research centers in various Member States is participating in a coordinated project for the assessment of corrosion behavior of promising container materials for geological disposal of vitrified high-level waste.

Two kinds of materials are tested, respectively corrosion resistant materials and corrosion allowance materials, in potential disposal environments likely to be encountered in the three geological formations considered in the Community R & D Program namely granite, salt and clay.

Besides classification of the materials with respect to their suitability, the results should also improve the credibility of theoretical models for the prediction of long term behavior.

From the results obtained so far, it appears that with gamma radiation, only Ti-Pd alloy may remain free from local corrosion phenomena, so that this alloy seems to be suitable as overpack material. Hastelloy C4 could be used for an overpack when shielded against gamma radiation. A possible concept would be a container made from a thick-walled, inexpensive material, e.g. mild steel coated with Hastelloy C4.

From a point of view of simplicity of design, manufacture feasibility and mechanical stability, the use of a thick-walled one-layer overpack from a corrosion allowance material seems attractive. Mild steel may, also for economical reasons appear to be a good choice.

REFERENCES

1. B. HAIJTINK, "Corrosion of Potential Materials for Containers and Repository Structures for the Disposal of Highly Radioactive Waste in Geological Formations", EUR 6698 EN. European Appl. Res. Rept. Vol. 2, no 2 (1980).

2. G. PLANTE et al., "Etude de Corrosion des Matériaux de Conteneurs Pour le Stockage des Déchets Radioactifs en Sites Granitiques", EUR 8762 FR (1984).

3. G. P. MARSH et al., "Corrosion Assessment of Metal Overpacks for Radioactive Waste Disposal", EUR 8658 EN. European Appl. Res. Rept. Vol. 5, No. 2, (1983).

4. E. SMAILOS et al., "Korrosionsuntersuchungen an Verpackungsmaterialen für Hochaktive Abfälle", EUR 8657 DE. European Appl. Res. Rept. Vol. 5, No. 2 (1983).

5. R. HEREMANS et al., "R & D Programme on Radioactive Waste Disposal Into a Clay Formation", Ch. VII: Corrosion of Structural and Canister Materials in Clay Environments, EUR 9077 EN (1984).

6. F. LANZA et al., "Corrosion Behavior of Low-carbon Steel in Sub-seabed Sediments", EUR 8586 EN (1983).

7. K. VU QUANG et al., "Etude de Films Superficiels et du Comportement Électrochimique de Certains Alliages à Base de Ni et à Base de Ti", EUR 9136 EN (1984).

8. A. ACCARY, B. HAIJTINK, "La Paléométallurgie - Outil de Prévision", Proceedings of Journées de Paléométallurgie, Compiègne, France, Feb. 22-23, 1983.