CORROSION OF WASTE PACKAGES

J. Weeks, Chair
J. Moody, Co-Chair

CONSIDERATIONS IN ESTIMATING CORROSION OF METALLIC CONTAINERS IN NUCLEAR WASTE REPOSITORIES

J. C. Griess
Metals and Ceramics Division
Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

ABSTRACT

Metallic containers for high-level nuclear waste are expected to isolate waste from the repository environment for at least 1000 years. Forms of corrosive attack that could lead to premature failure of the containers and some of the difficulties in predicting corrosion behavior in repositories over long periods of time are discussed.

INTRODUCTION

Present plans for the disposal of high-level nuclear waste call for incorporating the waste in a solid matrix, such as borosilicate glass, before sealing it in a thin-walled stainless steel canister. The canister will then likely be placed in a relatively heavy-walled vessel, referred to as an overpack, before emplacement in an underground repository. A packing material will probably fill the annulus between the overpack and the geologic formation.

At some time after closure of the repository, ground water will contact the metallic waste containers. It is expected that the combined overpack and canister will completely isolate the waste from the ground water for a minimum of 1000 years. Depending on the loading of the canisters, the canister density in the repository and the thermal properties of the repository, wall temperatures of the overpack may reach 300°C shortly after emplacement, and temperatures in excess of 200°C may prevail for several decades. Although unlikely if properly designed, overpacks and canisters could fail by mechanical means, but it is much more likely that they will fail from chemical or corrosive degradation. This presentation is concerned with the problem of verifying the integrity of waste containers against corrosion penetration during very long periods of time.

CORROSION FAILURE MODES

All practical engineering materials are chemically reactive with repository environments. Consequently corrosion engineers can only hope to select materials on which corrosion processes are slow enough so that metal walls will last for the prescribed time. Control of the environment is not possible, except perhaps by selection of the packing material and the thermal loading of the canisters. In the following subsections some of the more common forms of corrosion are briefly discussed in relation to repository environments. While the composition of the ground water varies from repository to repository, the discussion is concerned with problems common to all repositories.

Uniform Corrosion

Materials seldom fail from uniform wall thinning; most failures result from highly localized attack. Uniform corrosion on highly resistant materials such as titanium and high nickel alloys is of minimal concern, but if the overpack is a carbon or low alloy steel, substantial general corrosion can be expected. Here the problem is in determining how much corrosion allowance to design into the overpack. Since corrosion tests can only be run for short times relative to 1000 years, extrapolation of these short term data to very long times is suspect. Prediction of corrosion damage for periods longer than the test period requires a detailed knowledge of the kinetics of the process and the assumption that the process does not change for the length of the prediction. Justifing the above assumption may be difficult.

Localized Corrosion

When the metallic waste containers are first breached, it is likely to be the result of localized corrosion. Initial contact of the waste form with repository ground water will probably occur through fine cracks or pits so that most of the container will still minimize dispersion of the waste. How fast radionuclides reach the geologic formation and how fast they move through the formation obviously depend on many factors, none of which is considered here.

The most common forms of localized corrosion are stress corrosion cracking, pitting, crevice corrosion, and intergranular corrosion. While other forms of localized attack exist, they appear to be of less concern in repositories than those listed above and are not considered here. Stress corrosion cracking, pitting, and crevice corrosion usually have induction periods before attack begins and once started, propagation proceeds by cell action involving clearly recognizable anodic and cathodic areas (occluded cells). It is not possible to measure or estimate induction periods in most cases, but in terms of 1000 years the induction period is likely to be unimportant, that is the induction period, if the material is susceptible, will be much shorter than 1000 years. However, if the induction period is of the order of a few years, susceptibility to localized corrosion could be overlooked in experimental programs. Intergranular corrosion, on the other hand, usually requires compositional differences between the grains and the grain boundaries and requires little or no induction period.

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Stress Corrosion Cracking

The induction period for cracks to initiate in a material can often be eliminated by using the constant-extension-rate test, and when the test is properly performed, it may show the susceptibility of a material to cracking in that environment. However, cracks sometimes begin at pits, and in these cases it may be the solution within the pit, which is of different composition than the bulk solution, that causes cracking. Under these conditions the constant-extension-rate test may yield misleading results.

Stress-corrosion cracking usually only occurs when the electrochemical potential of the metal or alloy is within certain specific ranges. Absorption of radiant energy by the solution in which the metal is immersed can change the potential of the metal and consequently its cracking behavior. Any evaluation of cracking susceptibility of a material must consider the effect of radiation from the waste package.

Pitting

For each material that is subject to pitting in an environment there presumably exists an electrochemical potential below which pitting will not occur. This potential is specific for each system and is temperature dependent. If the system can be defined, including radiation intensity, electrochemical methods can be used to determine whether or not pitting is possible.

Conventional pitting studies stop while pits are relatively shallow, but for waste packages the behavior of deep pits is important. Some questions peculiar to waste packages have apparently not been addressed. For example, since the growth of a pit is supported by cathodic processes occurring on surfaces adjacent to it, will there be sufficient reducible substances present in the repository ground water and will the conductivity of the water be great enough to continue to support a pit as it deepens and becomes larger? If the overpack is embedded in a plastic material like wet bentonite, the pit is likely to be filled with bentonite and solid corrosion products that may further reduce the effective conductivity of the solution within the pit. What effect, if any, will radiation have on pit growth under these conditions? These and other concerns need to be investigated before the possibility of waste package failure by pitting can be evaluated.

Crevice Corrosion

The effect of radiation on crevice corrosion should be the same as in pitting because once started, the corrosion mechanism is similar in both cases. An additional consideration with crevice corrosion is that a greater variety of ions is capable of producing crevice corrosion than is the case for pitting. During crevice corrosion the crevice area is the anode and the freely exposed area adjacent to the crevice is the cathode. Since in a waste package the entire metal surface is a "crevice" and the concentration of radiolysis products is approximately the same on all surfaces, can crevice corrosion, as we usually think of it, start and propagate? The answer to this question will probably depend on the specific material and environment considered.

Intergranular Corrosion

Compositional differences within an alloy that could lead to intergranular attack can be evaluated by standard laboratory tests or by metallography. If such compositional differences exist, testing in simulated repository ground water should reveal any tendency to intergranular corrosion. In the case of waste packages where relatively high temperatures will prevail for long times, the possibility of forming a new phase that could produce susceptibility to intergranular attack where none existed originally cannot be ignored. Low temperature sensitization of austenitic stainless steels is one example. However, equilibrium thermodynamics should be useful in determining whether other phases are possible, although its use will not provide information about rates of formation or distribution within the alloy.

Weld Associated Corrosion

Welding a material may influence its corrosion behavior by producing changes in the microstructure in the heat-affected zone, by causing tensile stresses and by introducing galvanic effects if the composition of the weld metal is different from the base metal. While none of these effects produces a new form of corrosion, a knowledge of overall weld behavior is essential in evaluating the life of waste containers.

Hydrogen Embrittlement

Some of the materials considered for waste packages are subject to embrittlement when exposed to gaseous hydrogen or when hydrogen is electrochemically discharged on their surfaces. Titanium and zirconium can dissolve hydrogen and when the solubility is exceeded an embrittling hydride phase forms. At temperatures above 250°C hydrogen can enter steels and react with carbon to form methane that embrittles the steel. Obviously, the possibility of hydrogen effects on waste packages must be considered. However, the consequences of embrittlement of an overpack in a sealed repository are not completely clear. Assuming no seismic activity, embrittlement should have no adverse effect on the waste package if the forces acting on the overpack are isostatic.

UNCERTAINTIES IN ASSESSING CORROSION DAMAGE IN REPOSITORIES

Listed below are some unknowns that make estimating the life of metallic waste packages difficult. Some have been mentioned above and others are obvious. Appropriate experimental programs may resolve some of the uncertainties but in others consensus opinions of experts may prove to be of more value than relatively short experimental programs.

1. Changes in the environment.
2. Permeability of the repository to hydrogen and steam.
3. Microstructural changes in the overpack and canister material.
4. Inadequate corrosion data base.
    a. effect of time
    b. effect of heat flux
    c. effect of welds
    d. effect of radiation
    e. effect of hydrogen

An understanding of the above points is necessary to be able to estimate the life of waste packages. From a corrosion standpoint the most important unanswered question is how to conduct meaningful short-term tests that can be used to reliably predict long-term performance.

Corrosion engineers are unaccustomed to thinking in terms of 1000 years, and even their predictions for very much shorter periods have been far from infallible. One needs only to look at the unanticipated corrosion problems experienced by the major producer of high level nuclear waste, the nuclear power industry, as proof. The selection of materials for waste packages that will not be breached for 1000 years or more represents a major challenge to corrosion engineers. Only future generations will know how well we met the challenge.