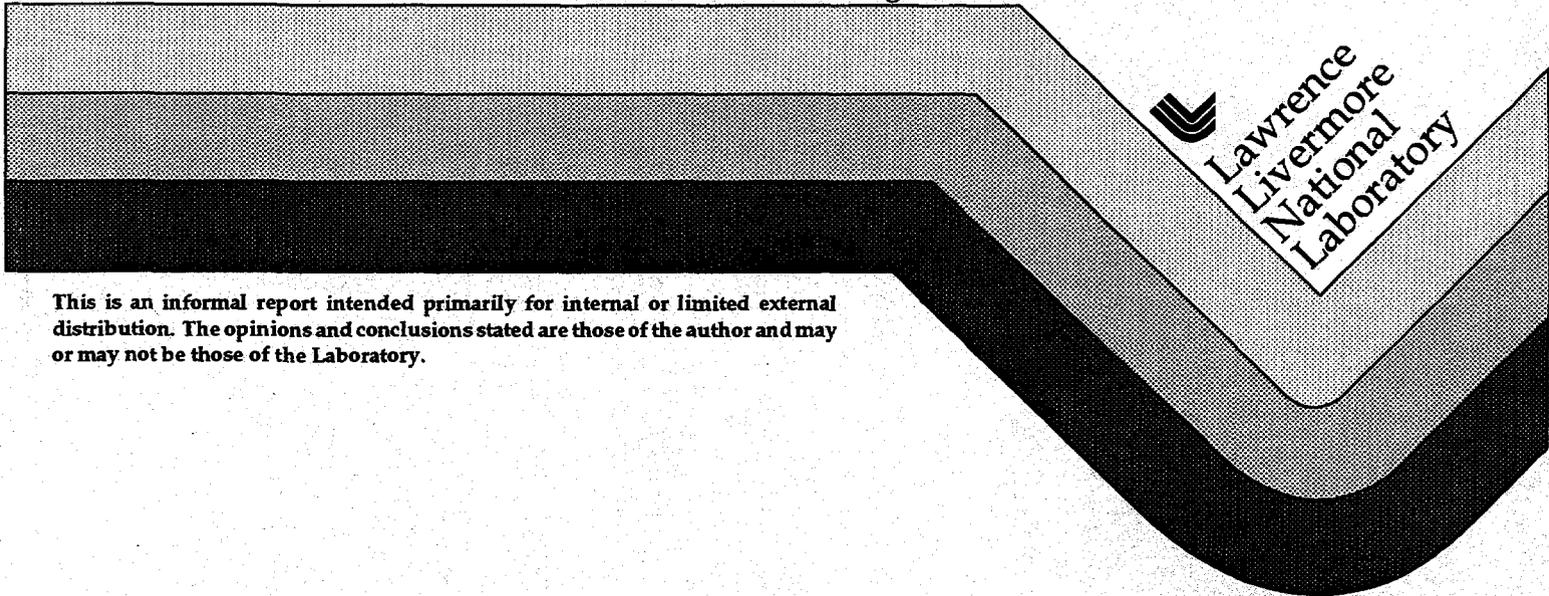# Engineered Materials Characterization Report for the Yucca Mountain Site Characterization Project

Volume 3: Corrosion and Data Modeling

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ENGINEERED MATERIALS CHARACTERIZATION REPORT FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

Volume 3

Corrosion Data and Modeling

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ENGINEERED MATERIALS CHARACTERIZATION REPORT FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

Volume 1   Introduction, History and Current Candidates

Abstract

Volume 2   Design Data

Abstract

1. Introduction
2. Current List of Candidate Materials
3. Degraded Materials Properties
4. Final Remarks
5 References
6. Tables and Figures

Volume 3   Corrosion Data and Modeling

Abstract

1. Degradation Mode Surveys
2. Results of Corrosion Testing
3. Radiation Effects on Corrosion
4. Modeling
5. References

Abstract

This three-volume report serves several purposes. The first volume provides an introduction to the engineered materials effort for the Yucca Mountain Site Characterization Project. It defines terms and outlines the history of selection and characterization of these materials. A summary of the recent engineered barrier materials characterization workshop is presented, and the current candidate materials are listed. The second volume tabulates design data for engineered materials, and the third volume is devoted to corrosion data, radiation effects on corrosion, and corrosion modeling. The second and third volumes are intended to be evolving documents, to which new data will be added as they become available from additional studies. The initial version of Volume 3 is devoted to information currently available for environments most similar to those expected in the potential Yucca Mountain repository. Each volume contains a separate list of references pertinent to it.

1. Degradation Mode Surveys

Surveys of degradation modes of a few candidate materials for high-level radioactive waste disposal containers were conducted by LLNL in 1988.[1,2] Materials that were surveyed include austenitic Types 304L and 316L stainless steels, high-nickel Alloy 825, and three copper-based alloys, namely CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni). The relevant modes of degradation which can be encountered under the potential repository environment were discussed in detail in these surveys, which were published in eight volumes as indicated below:

Volume 1 - Phase Stability
Volume 2 - Oxidation and Corrosion
Volume 3 - Localized Corrosion and Stress Corrosion Cracking of Austenitic
　　　　　　Alloys
Volume 4 - Stress Corrosion Cracking of Copper-Based Alloys
Volume 5 - Localized Corrosion of Copper-Based Alloys
Volume 6 - Effects of Hydrogen on Austenitic and Copper-Based Alloys
Volume 7 - Weldability of Austenitic Alloys
Volume 8 - Weldability of Copper-Based Alloys

To as practical an extent as possible, the literature was surveyed for and the results were applied to the physical, chemical, metallurgical, and mechanical conditions anticipated at the potential mined geologic repository. The candidate materials were ranked based on a broad range of environmental conditions as studied in numerous investigations cited in the literature. Based on this review, Alloy 825 and CDA 715 appear to possess superior overall properties for repository-relevant environmental conditions. For example, considering the metal alone as the thermodynamic system, Alloy 825 has a thermodynamically stable austenitic structure, whereas Types 304L and 316L stainless steels are metastable. CDA 715 is a simple solid solution of nickel in copper, and does not suffer from the problems of internal oxidation encountered with CDA 102; CDA 613 depends on iron precipitates for mechanical strength, which may grow in size over extended periods of time.

Although pitting and crevice corrosion may be encountered with all these candidate materials, Alloy 825 and CDA 715 seem to have the least susceptibility to these forms of degradation. In addition, Alloy 825 appears to be resistant to stress corrosion cracking under environmental conditions known to produce stress corrosion cracking in Types 304L and 316L stainless steels. Similarly, CDA 715 is the only copper-based alloy that appears to

possess favorable resistance to stress corrosion cracking over a broad range of environmental conditions known to cause failure in CDA 102 and CDA 613.

Degradation modes of four different nickel-chromium-molybdenum alloys were also surveyed by LLNL.[3,4] Materials included in this survey are Alloys C-276, C-4, C-22, and 625. The types of degradation covered in this study are general corrosion, localized corrosion including pitting and crevice corrosion, stress corrosion cracking in chloride environments, hydrogen embrittlement, and phase instability. While all four materials were found to exhibit significantly better corrosion resistance than the previously surveyed six austenitic and copper-based alloys, the corrosion resistances of these materials are expected to be almost indistinguishable from each other under the potential repository conditions. However, Alloy C-4 was judged to exhibit the best overall performance in view of its microstructural stability.

More recently, degradation modes of iron-based corrosion-allowance materials were also surveyed.[5] Based on this literature review it appears that the addition of chromium significantly enhances the oxidation resistance in these materials. As to the general corrosion resistance, the low alloy steels, plain carbon steels, cast steels, and cast irons seem to corrode at similar rates when exposed to an aqueous environment. However, in terms of total corrosion performance, the ranking of the investigated materials from most corrosion resistant to least corrosion resistant are austenitic cast iron, 12Cr, 9Cr-1Mo, carbon steel, low alloy steels, and cast iron.

2. Results of Corrosion Testing

The initial corrosion testing for selecting candidate materials was focused on a thin-walled single metal container design for emplacement in a vertical borehole. However, with the inception of the Advanced Conceptual Design (ACD) phase, the current design is centered around an all-metallic multibarrier waste package emplaced in a horizontal drift located in the unsaturated zone. Type 304L stainless steel was considered to be the reference material during the conceptual design phase. Alternate materials such as Types 316L, 317L, 321, and 347 stainless steels, and Alloy 825 were later included in the electrochemical corrosion test program.[6,7] Results indicated that the corrosion potentials of these materials were insensitive to temperature up to 90°C, and that spontaneous pitting did not occur when they were tested in J-13 water.

The corrosion potential is the electrical potential that a metal assumes, relative to a standard electrode, as it undergoes corrosion in the medium of interest. This potential is a result of the balance between cathodic and

anodic reactions, and its value is used to determine the status of the corrosion processes. As the chloride content is increased in J-13 water, the corrosion potential of these materials became more negative, and they exhibited enhanced susceptibility to pitting corrosion. With respect to general corrosion, no significant difference in corrosion rate was observed based on weight-loss measurements and electrochemical tests in J-13 water at temperatures up to 100°C for all materials tested. All materials showed sufficiently low corrosion rates with no indication of spontaneous pitting, suggesting that any one of these candidate materials could meet the requirement of 300-1000 year substantially complete containment. Later, stress corrosion cracking tests of Type 304L stainless steel were performed[8,9] at PNL and LLNL under irradiated and non-irradiated conditions incorporating U-bend and slow strain rate specimens. This material was susceptible to stress corrosion cracking when exposed to an irradiated crushed tuff rock environment containing air and water vapor at 90°C. A similar exposure at 50°C did not exhibit any failure after a 25-month test duration. Solution-annealed Types 304L and 316L stainless steels were tested at 150°C and 95°C in J-13 water, with neither material showing any evidence of stress corrosion cracking. However, a sensitized Type 304 stainless steel did exhibit stress corrosion cracking in J-13 well water at 150°C.

In view of the superior corrosion resistance of Alloy 825, additional efforts were focused on evaluating its resistance to localized corrosion, including pitting.[10,11] Electrochemical polarization techniques were used to determine the critical potential for passive film breakdown, a process that leads to localized attack such as pitting corrosion. Results indicated that Alloy 825 becomes susceptible to pitting attack in aggressive environments containing high chloride concentrations (10,000 ppm) at a low pH of 2.5, with the critical pitting potential approching the corrosion potential.

Stress corrosion cracking tests of six candidate container materials were performed[12] at Argonne National Laboratory (ANL) by using slow strain rate tests in simulated J-13 water at 93°C. These materials included Types 304L and 316L stainless steels, Alloy 825, and three copper-based alloys, namely CDA 122 (P-deoxidized Cu), CDA 614 (Al bronze), and CDA 715 (Cu-30%Ni). In addition, fracture-mechanics-type crack growth rate (CGR) tests were also conducted[12-14] incorporating Types 304L and 316L stainless steels and Alloy 825 at temperatures below boiling at ambient pressure in simulated J-13 well water. Crack growth rates using one-inch-thick compact tension specimens were measured at various load ratios. However, environmentally-assisted crack growth was not observed in any of the three materials under the test conditions investigated.

7

Limited corrosion tests of low carbon structural steels such as AISI 1020 and ASTM A-36 were performed in J-13 well water and in saturated steam at 100°C.[15] Tests were conducted in air-sparged J-13 water to attain more oxidizing conditions representative of irradiated aqueous environments. A limited number of irradiation corrosion and stress corrosion cracking tests were also performed. Results indicated that the maximum corrosion rate occurs at 70-80°C, where the flux of oxygen to the steel surface is at a maximum. Carbon steels appeared to be resistant to stress corrosion cracking, but showed localized corrosion, with the localized corrosion factor being on the order of 1-3 times the general corrosion rate. The crevice corrosion rate was found to be as high as 15 times the general corrosion rate in wet steam conditions. A 9Cr-1Mo steel was excluded from this testing since this material is known to undergo hydrogen embrittlement in the welded condition. Although a post-weld thermal treatment can reduce the susceptibility to hydrogen embrittlement due to the formation of tempered martensite, this extra operation was considered to be impractical and costly.

With respect to copper-based waste package container materials, numerous feasibility assessment studies[16-20] have been completed. Based on the evaluations made so far, all three copper-based materials (CDA 102, CDA 613, and CDA 715) appear to be adequate for use as container materials, but questions regarding the relevance and effects of gamma radiation on corrosion behavior remain a big issue. In order to address this issue, all three materials were tested[19] in 0.1 N $NaNO_3$ at 95°C. The interest in nitrate solutions stems from the radiolytic effects on the expected environment. Even though the potential repository environment is expected to be unsaturated, in the presence of a liquid phase the fixed nitrogen will exist in it as nitrite and nitrate ions. The total amount of nitrite and nitrate that can be produced is limited by the gamma radiation dose rate, and the volume of air irradiated. If a thin water film on the waste package container is irradiated in contact with a relatively thicker air space, it is possible to achieve a significant concentration of nitrate in the relatively small amount of water in the film. Results indicate that although all three copper-based materials are somewhat susceptible to pitting in 0.1 N $NaNO_3$ at 95° C, at high (oxidizing) potentials, stable and protective passive films formed on the alloy surface would provide resistance to both general and pitting corrosion.

3. Radiation Effects on Corrosion

Several investigations were performed[21-27] to evaluate the effects of gamma radiation on the corrosion mechanisms of candidate waste package container

materials. Results[21] indicate that for Types 304L and 316L stainless steels, the corrosion potential is shifted in the positive direction as the gamma radiation is introduced. These potential shifts are attributed to the radiation-induced production of hydrogen peroxide. The results of potentiodynamic anodic polarization study indicate that for Types 304L and 316L stainless steel, the pitting potentials were almost unchanged when tested in chloride media under gamma radiation. However, since the corrosion potential is increased under gamma irradiation, the difference between the pitting and corrosion potentials is decreased significantly compared to the value without irradiation. Thus, the susceptibility to pitting corrosion is increased. Similar behavior has also been observed[22] for copper and its alloys, which are known to be very catalytic toward the decomposition of hydrogen peroxide. In solution, the surfaces of copper and its alloys appear to be more oxidized in irradiated environments than those of austenitic stainless steels. As to the corrosion potential shifts, the same general behavior as for stainless steels is observed. However, the corrosion potentials then decline to relatively less positive values, possibly due to a reduced efficiency for catalytic decomposition of hydrogen peroxide.

Pure copper and copper-based materials such as CDA 101/102, CDA 613/614, and CDA 715 were corrosion tested[23,24] at the Westinghouse Hanford Company under gamma irradiation. These materials were tested in moist air at 95 and 150°C, and in J-13 water at 95°C for periods of up to 16 months. The susceptibilities to general corrosion, crevice corrosion, and stress corrosion cracking were evaluated. None of these materials exhibited any significant corrosion tendency. In general, the pure copper was corroded most uniformly, while the corrosion data for CDA 715 were least reproducible.

More recently, numerous investigations were conducted[25-27] to evaluate the effects of temperature, relative humidity, and gamma dose rate on the corrosion behavior of candidate container materials. Corrosion rates of copper-based materials were found to be influenced by all three parameters. The effect of moisture content was most significant in that nitrate phase, principally $Cu_2NO_3(OH)_3$, as well as copper oxides, were evident at both intermediate and low moisture contents. No nitrates, however, were observed at higher temperature (150°C) and relative humidity (100%). While both general and localized (pitting) corrosion were observed with pure copper and its alloys, Alloy 825 did not suffer from these degradation modes. This is consistent with experience, since Alloy 825 tends to resist attack by NO_3 and nitric acids.

4. Modeling

Literature review on mechanisms and models of localized corrosion and stress corrosion cracking of container materials was performed.[28] These models fell into the following categories:

(a) Initiation of pits on passive surfaces of austenitics
(b) Propagation of pits on active metal surfaces
(c) Propagation of pits on surfaces covered by salt films
(d) Initiation of cracks at pits
(e) Propagation of cracks on active metal surfaces
(f) Propagation of cracks due to periodic fracture of passive films at crack tips
(g) Propagation of cracks due to film-induced cleavage of the base metal
(h) Crevice corrosion on active metal surfaces, and
(i) Crevices that behave like active-passive concentration cells

The modeling efforts were further extended[29,30] by additional literature search to predict the long-term performance of candidate materials, in particular the propensities to oxidation, uniform corrosion, and localized corrosion including pitting and stress corrosion cracking. Based on this review, the following needs have been identified:

(a) Development of a model of local environment, which will enable the prediction of temperature of the container wall, the levels of species in ground water concentrated by thermal refluxing, the concentrations of radiolysis products, and the effects of microbial growth on the local environment.
(b) Quantification of corrosion parameters, where applicable.
(c) Development of models to predict the initiation and propagation of localized attack such as pitting corrosion.
(d) Determination of crevice geometries
(e) Introduction of statistical techniques to model development.

In recent years, stochastic models of pitting corrosion have been explored,[31] and found to be potentially useful in predicting damage of waste package container materials. These computer models include simple phenomenological relationships describing the environmental dependence of the stochastic parameters, and can simulate pit initiation and propagation under various environmental conditions. These models have been found useful in providing insights into the pit nucleation and growth mechanisms. Furthermore, these models should provide quantitative information needed in developing performance assessment codes for the entire waste repository system. However, very little quantitative validation of these models has been

performed because of a lack of available data. Thus, a significant amount of experimental effort should be initiated immediately for further development and testing of these models, in particular, the determination of the pit depth distributions as functions of time and potential repository environment.

Acknowledgment

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