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**Yucca Mountain Project Canister Material Corrosion Studies as Applied to the
Electrometallurgical Treatment Metallic Waste Form**

by

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YUCCA MOUNTAIN PROJECT CANISTER MATERIAL CORROSION STUDIES AS
APPLIED TO THE ELECTROMETALLURGICAL TREATMENT METALLIC WASTE
FORM

by

Dennis D. Keiser, Jr.

ABSTRACT

Yucca Mountain, Nevada is currently being evaluated as a potential site for a geologic repository. As part of the repository assessment activities, candidate materials are being tested for possible use as construction materials for waste package containers. A large portion of this testing effort is focused on determining the long range corrosion properties, in a Yucca Mountain environment, for those materials being considered. Along similar lines, Argonne National Laboratory is testing a metallic alloy waste form that also is scheduled for disposal in a geologic repository, like Yucca Mountain. Due to the fact that Argonne's waste form will require performance testing for an environment similar to what Yucca Mountain canister materials will require, this report was constructed to focus on the types of tests that have been conducted on candidate Yucca Mountain canister materials along with some of the results from these tests. Additionally, this report will discuss testing of Argonne's metal waste form in light of the Yucca Mountain activities.

I. INTRODUCTION

Beginning in 1981, a project was initiated to identify a corrosion-resistant metallic alloy that could be employed to contain high-level waste that is to be disposed of in Yucca Mountain [1]. Initially, there were 31 different alloys that were considered for use as canister materials [2]. This number was subsequently reduced to 17 and then six alloys, viz. the copper-based materials CDA 12 (oxygen free copper), CDA 613 (7% Al bronze), and CDA 715 (Cu-30Ni), and the austenitic materials Types 304L and 316L stainless steel, and Incoloy 825¹, because of their good corrosion resistance, their wide use in the marine, nuclear, and process industries, and their reasonable cost. Alloy C-4 has been mentioned as a possible nickel alloy, and Ti Grade 12 has been mentioned as a possible titanium-based material [3].

As recently as 1995, the official design concept for Yucca Mountain comprised a robust waste package design that employed carbon steel and Incoloy 825 along with other engineered barrier system components [4]. A multi-barrier waste container would be used where a thick layer (about 100 mm) of carbon steel corrosion-allowance material (CAM) would be the outer containment barrier, and a thin layer (about 20 mm) of Incoloy 825 corrosion-resistant material would be the inner containment barrier. To be finally selected, federal law requires that the containers provide "substantially complete containment" for a period of 300 to 1,000 years, with a very slow, controlled release of radionuclides allowed for the next 9,000 years [5]. No more than one part in 10^5 of the inventory of radionuclides present at 1,000 years after closure may be released annually from the engineered barrier system [6]. The final waste package design must have less than 1% of waste packages breached after 1,000 years in Yucca Mountain [4]. A "failure" is defined as having at least one pit penetration through the waste container [4]. Other requirements on the container, include retrievability for fifty years, compatibility with the waste forms and other repository components, provision for transportation and handling, reasonable cost and readily available technology [7].

In condensing down the number of alloys to be considered for use as canister materials, seven different criteria have been invoked by people involved in the selection process [7], viz., mechanical performance, chemical performance, predictability of performance, compatibility with other materials, fabricability, cost, and previous experience with the materials. Significant time has been spent investigating the various failure modes for the different materials. The

¹ A nominal composition range for Type 316L stainless steel is 16-18Cr, 10-14Ni, 2-3Mo, 2Mn, 1Si, 0.045P, 0.03S, 0.03C, bal. Fe; for Type 304L, a nominal composition range is 18-20Cr, 8-12Ni, 2Mn, 1Si, 0.045P, 0.03S, 0.03C, bal. Fe; and for Incoloy 825, a nominal composition is 42.0Ni, 30.0Fe, 21.5Cr, 3.0Mo, 2.25Cu, 0.90Ti, 0.50Mn, 0.25Si, 0.10Al, 0.03C, and 0.015S.

failure modes include: phase instability (can result in brittle structures that initiate cracks), crevice corrosion, pitting, microbially induced corrosion (MIC), uniform corrosion, stress corrosion cracking (SCC), hydrogen effects on corrosion, effects of various anions on corrosion, galvanic corrosion, sensitization, and the effects of irradiation on corrosion. A lot of effort has been expended to investigate the various corrosion modes on the many candidate alloys, including many different performance tests and some modeling.

McDeavitt et al. [8-11] have developed a stainless steel - zirconium metal waste form (MWF) alloy at Argonne National Laboratory (ANL) which, like the canister materials discussed above, may be emplaced in a geologic repository, such as Yucca Mountain. This metal alloy will contain cladding hulls, Zr, and noble metal fission products (e.g, Rh, Pd, Ru) that are residual from Argonne's electrometallurgical treatment of spent nuclear fuels. The alloy should remain inert to the environment for time frames exceeding those expected for the Yucca Mountain canister materials (up to 10,000 years), and as is the case for the final selected canister material, the metal waste form alloy must exhibit optimal corrosion behavior in the same type of aqueous and non-aqueous environments.

This report will discuss the major aspects of the Yucca Mountain canister material project in terms of the different types of corrosion that are of concern for a canister material disposed of in Yucca Mountain and the types of tests that have been and will be employed for judging candidate material performance, along with some results from these tests, particularly for the stainless steels (stainless steels will be a major component of the MWF alloy). This information will be compared to some preliminary results from corrosion testing of the MWF and will be applied to determining some additional corrosion tests that can be employed effectively to assess the corrosion performance of ANL's MWF in a repository environment.

II. THE YUCCA MOUNTAIN ENVIRONMENT

The proposed repository at Yucca Mountain is to be located in volcanic rock about 700 to 1400 feet above the water table and 300 to 1200 feet below ground [5]. The host rock contains many mineral oxides including silicon oxide (78-79 percent), aluminum oxide (12 percent), iron oxide (1 percent), phosphorous oxide (0.01 percent), and magnesium oxide (0.05 percent) [3]. Decay heat from the spent fuel will warm the containers and the surrounding rock to as much as 250°C after the repository is closed resulting in a "warm" air-steam environment for several hundred years (after 100 years, the temperature is expected to drop to about 150°C). The temperature is expected to plateau at slightly over 100°C over the next 1,000 years [3].

Canisters that contain vitrified waste are expected to have a temperature range of 90-140°C for the first 200 years then plateau at less than 60°C after 1,000 years [3]. For the extended dry repository configuration, low temperature oxidation of the canister materials is expected in the temperature range 30-340°C and possible metallurgical aging reactions in the range 120-350°C [12]. Eventually the containers will cool enough to allow the possibility of water contact. It has been suggested with thermo-hydrological modeling that the re-wetting period will occur beyond the regulatory period of 10,000 years [12]. However, this postulation is currently being challenged, and several scenarios are imagined that could lead to premature wetting of container surfaces [3].

The gamma radiation from the waste decay is expected to produce radiolytic alterations in the local environment in the early time period. The ground water at Yucca Mountain is near neutral in pH and fairly low in ionic content (about 10 ppm chloride, 20 ppm sulfate, 120 ppm bicarbonate, dissolved oxygen, and some nitrate). Potential increases in the concentration of solutes in the repository has been simulated by evaporation of J-13 well water [12]. 95% evaporation of J-13 well water at 90°C increases the pH to 9.5 and the chloride concentration to 750 ppm. The presence of materials like concrete will affect water pH. The presence of concrete could allow pH levels to get as high as 10 or higher [12]. The pressure will remain at slightly less than one atmosphere, with the boiling point of water at 96°C [13].

Gamma radiation levels may be as high as 1×10^5 rads/h [13], but in general the initial gamma dose rate around the high-level radioactive waste containers will be in the 10^4 rad/hr range for spent fuel and in the 10^3 rad/hr range for borosilicate glass [14]. Gamma radiolysis of air and water in close proximity to the containers can result in the formation of a host of molecular species, like hydrogen, hydrogen peroxide, nitrate, nitrite, and hydrogen ions [15].

The composition of the initial air-water vapor mixture of Yucca Mountain will be a function of (1) the initial gas present, (2) the waste package temperature, (3) the gamma radiation levels (4) the material surface reactions, and (5) gas transport through the repository [16]. This initial air-water vapor mixture is not expected to cause localized attack. However, there are scenarios where aqueous phases can contact the metal surfaces such that localized attack is possible [1]. Pitting could occur on susceptible materials if certain ionic species are present in sufficient concentration in the water; micro-organisms can be present near the containers that will change chemical conditions locally such that they are more aggressive than the natural geochemical environment; and crevice corrosion will be an issue since some crevices will be present in any container design. Information on parameters in Yucca Mountain like temperature, rock

stability, water chemistry, flow rate, water contact mode, and effects of colloids, microbes, and other introduced materials will need to be determined to enable prediction of materials performance [12].

A. The Engineered Barrier System

As of 1995, an engineered barrier system (EBS) was to be used to contain the spent fuel and vitrified waste in Yucca Mountain [17]. The EBS consists of waste package materials (either fully corrosion resistant, corrosion allowable, or moderately corrosion resistant), basket materials, filler materials, packing materials, and/or backfill materials. The waste package container provides containment of the waste, and there are different containers for the spent nuclear fuel and the vitrified waste. The multi-purpose containers (MPC) that arrive at the repository with the spent fuel will each be enclosed in a multiple barrier disposal package, and four pour canisters, each of which contain vitrified waste, will be placed in a waste package container. The *basket* material will be used to separate spent nuclear fuel assemblies so as to prevent a criticality event. This material is a major conduit for heat transfer to the exterior environment since plans are to fill the waste package with inert gas. No basket material will be used for vitrified waste. As an option, *filler* material is being considered for use inside nuclear fuel waste packages to provide an additional barrier for controlled release and to provide some control of criticality. A *packing* material is to be used outside waste packages (both spent fuel and glass) to provide a medium for controlling the near waste package environment. Packing will serve to limit water contact with the container surface and to provide pH buffering and redox buffering to mitigate corrosion of the container. *Backfill* material would be used to fill the repository after waste packages are emplaced. This material would divert water away from the waste package and would raise the temperature of the containers because it would be selected due to its poor thermal conductivity.

Non-metallic barrier materials are also being proposed as an alternative to an all-metallic waste package container. If metals cannot meet demonstrated containment objectives, then a combination metal/non-metallic waste package may be used where the fracture toughness of the metal is applied with the chemical resistance of the non-metal (ceramics are the major non-metal candidate). The non-metal could either be a "stand-alone" barrier, or it could be applied as a coating onto the metal container.

III. CANISTER MATERIAL CORROSION IN A YUCCA MOUNTAIN ENVIRONMENT

The mechanisms for container material passivity and its breakdown in a Yucca Mountain environment are of particular importance [1]. For austenitic stainless steel alloys, the chromium content of the alloy is one of the most important considerations, since the passive films are Cr-rich. The excellent resistance of austenitic stainless steel alloys to corrosion is due to their capacity to build-up a film of chromium-oxide that is 10 to 50 Å thick [18]. At least 12 wt.% chromium is necessary for the formation of a protective film, and the films are generally described as hydrous oxides. As compared with the composition of the matrix, the films are enriched primarily, not just with chromium, but also with silicon and molybdenum. The molybdenum content is important as Mo seems to play an important role in the rapid reformation of the passive film if it is broken.

The maintenance of passivity is a dynamic process and relies on the continuous supply of a mild oxidant (such as dissolved oxygen). The film may be ruptured chemically or mechanically, and re-establishment of passivity depends on the competitive kinetics between processes favoring film breakdown and those favoring film repair. Under creviced conditions, the supply of oxidant is often inadequate because of geometric hindrance. Chloride ion (and to a lesser extent other halide ions) are well-known for their ability to destroy passive films, possibly by their preferential absorption into the film. For example, acid ferric chloride formed by evaporation and concentration of corrosion products from an outer carbon steel layer in a MPC are known to be extremely aggressive to even the most resistant nickel-base alloys [12]. Other ionic species aggravate or mollify the effect of chloride by their effect on pH or redox potential. While a mild oxidation is beneficial in promoting passivity (and therefore resistance to localized corrosion), strong oxidation destroys passivity (possibly by oxidation of Cr to the soluble hexavalent state). Many metallurgical features (grain size, grain boundary composition, inclusion kind and distribution, and so on) also play a role in strengthening or weakening the passive film. As a class, the Type 300-series austenitic stainless steels exhibit considerably better corrosion resistance than martensitic and ferritic stainless steels [19]. The carbon-steel materials that have been assessed as possible materials for nuclear waste containers also appear to develop a passive film, which has been determined to be Fe_3O_4 [20].

Nickel-base alloys generally passivate and retain passivity more readily than iron-base alloys. Incoloy 825 is the primary material for the inner container (Hastelloys C-4 and C-22 are alternates) [19]. The Ni content in this alloy is sufficient to prevent chloride-induced stress corrosion cracking, and in conjunction with the Mo and Cu, the Ni can provide sufficient

corrosion resistance in reducing environments such as sulfuric and phosphoric acids. The Mo enhances resistance to localized corrosion, and the high Cr content allows for superior corrosion resistance in a variety of oxidizing environments like nitric acid, nitrates, and oxidizing salts. The presence of Ti and a proper alloy heat treatment stabilizes the alloy against sensitization and intergranular attack.

A. Types of Corrosion Tests

Many different types of corrosion tests have been conducted on the various candidate canister materials. Probably the most universally applied tests have been the ones that employ an electrochemical cell and potentiostat. Electrochemical tests that have been performed include open circuit electrochemical potential (ECP) measurements, potentiodynamic (or potentiostatic) anodic polarization scans, and fixed-potential passive current density tests, with examples of these types of tests reported by Duquette et al. [21]. Glass et al. [22] employed two other types of electrochemical tests: Tafel extrapolation and linear polarization resistance. Huizinga and de Jong [23] have reported using cyclic polarization, staircase polarization, stepwise repassivation, and scratch repassivation methods for studying initiation, propagation, and repassivation of pitting for a variety of stainless steels. Drogowska et al. [24] invoked a voltammetric and *ac* impedance technique to investigate passive film formation on Type 304 stainless steel.

Potentiodynamic polarization curves are commonly generated to study the corrosion behavior of alloys. These curves are generated by applying a potential to a sample and continuously changing the potential in a pre-set pattern; the current response is then recorded. The measured current of a stainless steel, which has surface defects, scratches, and inclusions is the sum of several reactions [25].

The potentiostatic test involves applying a single value of potential to the working electrode for a long time and measuring the current as a function of time. In most cases, an anodic polarization curve is generated by anodically scanning a sample (working electrode) to specified potentials anodic to the corrosion potential (E_{corr}). To generate a cyclic curve, the direction of the scan can then be reversed back to more negative values.

Current flowing between the working electrode and counter electrode is constantly monitored during the potentiodynamic polarization scan. Certain electrochemical values are of particular interest in such a scan, including the corrosion potential (E_{corr}), the pitting potential (E_p), and

the protection potential (E_{prot}). 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. At the corrosion potential, the current is zero because the anodic currents corresponding to oxidation reactions occurring spontaneously on the electrode just balance the cathodic currents corresponding to reduction reactions. As the potential is being scanned through the passive region, the current is relatively small in magnitude, and at the point where the passive film begins to breakdown, called the pitting potential, the current exhibits an abrupt increase. The pitting potential is the potential above which pits spontaneously initiate and grow. The protection potential is the potential below which pits that have previously initiated repassivate and no new pits form (also called the repassivation potential). At potentials between the pitting and protection potential, new pits are not initiated, but any previously initiated pits continue to grow. The pitting susceptibility of an alloy is determined by establishing the pitting and protection potential of an alloy relative to the corrosion potential. One important point is that the values for E_p , E_{prot} , and E_{corr} are in many cases dependent upon the particular electrochemical technique employed [22]. When generating potential curves as a function of current, the curves are generally considered reproducible for a corrosion potential of $\pm 20\text{mV}$ and a factor of 2 for current density at any potential [25].

Electrochemical corrosion rates can be determined by employing either Tafel extrapolation or linear polarization resistance (LPR). Tafel extrapolations involve scanning linearly the potential region to a few hundred millivolts anodic and cathodic of the corrosion potential. Plots are then constructed of the potential (or potential relative to the corrosion potential, e.g., overpotential) vs. the logarithm of the current. Extrapolations are then made of the linear segments of either anodic or cathodic branches back to the measured corrosion potential. The corrosion current is then obtained and converted to a corrosion rate in mils-per-year by using Faraday's Law. For the LPR method, linear polarization is measured at potential ranges close to, and on either side, of the corrosion potential ($\pm 10\text{ mV}$). Current-potential relationships are linearized and a "polarization resistance" is determined from current-potential plots. By knowing some electrochemical parameters (Tafel coefficients), a corrosion rate is calculated, in mA/cm^2 . This is converted to a corrosion rate, in mils-per-year, by using Faraday's law.

Electrochemical test results have shown that for the stainless steel candidate materials investigated (including Types 304L, 316L, 317L, 321, and 347 stainless steels, and Incoloy 825), the corrosion potentials were insensitive to temperature up to 90°C [22, 26]. Glass et al. reported tests of Types 304L and 316L stainless steels and Incoloy 825 in J-13 well water and found no dependence of the corrosion potential on temperature, in the temperature range of 50-

90°C. The values for E_{corr} for Type 316L stainless steel and Incoloy 825 were found to be fairly close, and generally more positive than those for Type 304L stainless steel. More noble corrosion potentials for the more highly alloyed materials was related to the well-acknowledged roles of Mo and Ni as passivating agents.

Immersion corrosion tests are another type of corrosion test employed to determine corrosion rates for various materials. In these tests, polished samples are placed in a selected solution, and either weight-loss or weight-gain is measured after a specified time period. In corrosion tests reported by Glass et al. [22], results from electrochemical tests and immersion tests of various stainless steels in J-13 well water were compared. It was shown that the electrochemical corrosion rates represented a conservative upper bound for corrosion rates. The corrosion rates determined by immersion tests were very much lower than the electrochemically measured rates. This appeared to result from the fact that it is difficult to measure absolute corrosion rates in a relatively benign environment by either weight-loss or electrochemical methods, and there are large differences in the methods used to determine the rates. There are differences in initial surface preparation and cleaning procedures, and "fresh" surfaces are used in electrochemical experiments, which may account for the observed discrepancies. A rule of thumb in corrosion measurements was described, where for corrosion rates of mils-per-year, one would expect an order of magnitude agreement between the two techniques. For the experiments described by Green et al., where the corrosion rates in the system were so low, reasonable agreement was believed to be obtained (though not within an order of magnitude). The Materials Characterization Center has outlined three kinds of corrosion tests for container materials of high level nuclear waste [27]. The reported tests were for materials to be used as part of the Basalt Waste Isolation Project. These tests included a static pressure vessel test, a flowby test, and an air/steam test, and the corrosion rates were determined by weight loss measurements.

B. Future Canister Material Testing

Estill et al. [28] have described a new facility that will be specifically configured to conduct corrosion tests on candidate canister materials. The test environments to which samples will be exposed include four solutions and the vapor phases above solutions. The solutions are as follows: (1) J-13 well water; (2) simulated concentrated J-13 well water, with which solution concentrating effects such as evaporation and boiling are simulated; (3) low pH (pH 2 to pH 3) water to simulate the effect of possible microbial metabolic products; and (4) high pH (pH 11 to pH 12) water to simulate the effect of contact with cementitious materials of construction.

pH is commonly varied in a solution by adding either hydrochloric acid or sodium hydroxide. Testing in high relative humidity vapor phases will be conducted to characterize the corrosion that may occur in materials that are covered with thin water layers. Thin water layers can cause accelerated corrosion of materials under the appropriate conditions [29]. Gdowski and Estill [30] have reported results from oxidation/corrosion tests on carbon steel, where samples were tested in a thermogravimetric analyzer exposed to humidified air.

Clarke et al. have discussed future corrosion experiments on candidate canister materials that are to be conducted to support predictive models for general oxidation and corrosion, for pit initiation and propagation, and for the initiation and propagation of stress corrosion cracks [7]. The tests are planned to be conducted in both the gaseous and aqueous bounding conditions expected at Yucca Mountain, both with and without the effects of gamma radiation. For general oxidation and corrosion studies, the types of experiments planned include weight gain tests of specimens in water and steam, corrosion potential measurements, electrochemical corrosion resistance tests in the aqueous phase, and the identification of corrosion products after exposure to a range of bounding environmental conditions. The initiation of pits will be studied, and local pitting potential and incubation time experiments using factorial designs will be applied to minimize the number of tests required. These designs also permit the determination of important two-factor and three-factor interactions, such as the effects of chloride, pH, and temperature. Optical techniques will be used to study pit propagation, in addition to weight loss measurements. These experiments will include the determination of pit depth as function of time, and the fractional coverage of the metal surface by the pits that form. Additionally, many experiments are planned or underway to study SCC initiation and propagation [7]. Bertocci et al. [31] have described current fluctuation experiments that can be employed to determine that time period just before stably growing pits develop on a corroding metal with a passive film.

Van Konynenburg et al. have recommended that future candidate container material testing should include a long-term testing component (up to 5 years) [12]. Test variables should include: various anticipated and unanticipated but credible environments, various alloys and other materials, and various specimen types. Duplicate tests will be required to determine reproducibility and give statistical significance. Accelerated, short-term corrosion tests would be helpful to evaluate long-term service behavior, but only if the mechanisms are identical. Therefore, mechanistic studies should be conducted. Of particular concern in testing materials is the effects of boiling and evaporation, which can concentrate solutes at the hot waste package surfaces and crevices, where heat transfer is limited.

The American Society for Testing and Materials (ASTM) has constructed a standard practice for developing methods that can aid one in predicting the long-term behavior of waste package materials and waste forms that will be employed when disposing of high-level nuclear waste in a geologic repository [32]. According to the practice, long-term predictions should be based on models derived from interpretation of data obtained from tests and appropriate analogs. The types of tests that are discussed include attribute tests, characterization tests, accelerated tests, service condition tests, analog tests, and confirmation tests. An attribute test is conducted to provide material property information that can be inputted into available behavior models. A characterization test allows for mechanistic understanding of alteration (examples of these types of tests were polarization tests, potential-pH diagrams, solubility analyses, and X-ray diffraction of corrosion layers). Accelerated tests employ independent variables that are set at values that result in increased rates of alteration, and any changes in alteration mechanisms must be accounted for. Service condition tests employ test variables that are in the range expected for actual service. Analog tests use materials whose compositions and material history are similar to those of the material of interest so that conclusions can be drawn that are relevant to the material of interest. Finally, confirmation tests are used to confirm predictions that have been made, based on available models.

C. Forms of Corrosion

1. Uniform Corrosion and Oxidation

The rate of attack of general corrosion and oxidation of a canister material is usually orders of magnitude less than the rates of attack due to pitting and SCC. In fact, it is usually assumed that container life will probably be limited by some form of localized attack. For low-carbon structural steels, the localized corrosion factor has been determined to be 1-3 times the general corrosion rate [33]. Both atmospheric and aqueous corrosion are assumed to be the least significant modes of degradation [34]. Table 1 shows uniform corrosion rates for some austenitic candidate materials in J-13 well water along with oxidation rates. In relation to pH values, only at a pH value of 2 or below will uniform corrosion appear to be significant for a material like Type 304 stainless steel [35]. The pH value of ground water in a disposal environment should be higher than 2. In alkaline water, austenitic stainless steels will not suffer attack in ground water with pH lower than 10. In the presence of an aqueous phase containing dissolved halide ions, oxygen, and other species, rates of localized corrosion (LC) are more likely to limit container life. Oversby et al. have argued that uniform corrosion is the most likely mechanism for container degradation [36], and that by extrapolating data for the

average uniform corrosion rate (0.15 $\mu\text{m}/\text{yr}$) to obtain the time necessary to corrode through 1 cm of metal, a predicted package would have a lifetime of 67,000 years.

In reported immersion tests that investigated general corrosion rates of Types 304L, 316L, 317L, 321, and 347 stainless steels and Incoloy 825 in J-13 water in the 50 to 100°C range, the corrosion rate was found to be independent of temperature and the corrosion was uniformly distributed over the exposed surface [22]. No significant difference in corrosion rates were observed for Types 304L, 316L, and 317L stainless steels in 50, 70, 80, 90, and 100°C J-13 water at exposure times of 3,548 and 5,000 hours. An average of the data gave a corrosion rate of 0.19 $\pm$ 0.04 $\mu\text{m}/\text{yr}$. After including available data for tests run for 7,500 hours of exposure, the rate is 0.15 $\pm$ $\mu\text{m}/\text{yr}$. The total range of measured corrosion rates was 0.025 to 0.36 $\mu\text{m}/\text{yr}$. In general, the low alloy steels, plain carbon steels, cast steels, and cast irons

Table I. General Corrosion and Oxidation Rates of Candidate Austenitic Stainless Steels in J-13 Well Water at Different Temperatures [14].

Alloy	Temp (°C)	Time (hr)	Medium	Corrosion rate	(microns/yr.)
				Ave.	Std. dev. ^a
304L	50	11,512	water	0.133	0.018
316L	50	11,512	water	0.154	0.008
825	50	11,512	water	0.211	0.013
304L	80	11,056	water	0.085	0.001
316L	80	11,056	water	0.109	0.005
825	80	11,056	water	0.109	0.012
304L	100	10,360	water	0.072	0.023
316L	100	10,360	water	0.037	0.011
825	100	10,360	water	0.049	0.019
304L	100	10,456	saturated steam	0.102	ND
316L	100	10,456	saturated steam	0.099	ND
825	100	10,456	unsaturated steam	0.030	ND
304L	150	3,808	unsaturated steam	0.071	ND
316L	150	3,808	unsaturated steam	0.064	ND
825	150	3,808	unsaturated steam	0.030	ND

^a Average of three replicate samples of each alloy in each condition.

ND- Not Determined

seem to corrode at similar rates when exposed to an aqueous environment [26]. The ranking of the investigated materials from most corrosion resistant to least corrosion resistant are austenitic cast iron, 12 Cr steels, 9Cr-1Mo steels, carbon steel, low alloy steels, and cast iron. For the samples of Types 304L, 316L, 317L, 321, and 347 stainless steels and Incoloy 825 tested in a 100°C saturated steam environment for 7,500 hours, there was a range of corrosion rates between 0.037 to 0.31 $\mu\text{m}/\text{yr}$ and an average of 0.16 $\pm$ 0.03 $\mu\text{m}/\text{yr}$ [37].

With respect to oxidation behavior, it has been reported that additions of chromium significantly enhance the oxidation resistance in the assessed container materials [26]. Oxidation rates ranged from 0.0001 to 0.008 $\mu\text{m}/\text{yr}$ were measured for samples of Types 304L, 316L, 317L, 321, and 347 stainless steels and Incoloy 825 tested in 150°C unsaturated steam for 3800 hours [37]. Rates under "wet" steam conditions overlapped those from the fully immersed conditions, and rates obtained under "dry" steam conditions were substantially lower. Tests in the presence of gamma radiation gave similar results to those without radiation. Corrosion results have been reported for low-alloy steel and cast carbon steel specimens tested in moist air at 150, 200, 250, and 300°C at atmospheric pressure [38]. For specimens exposed to the moist air environment for one, four, ten, 18, and 25 months, the corrosion of both materials essentially stopped when tested at 150 and 200°C. At 250°C, low-alloy steel exhibited accelerating corrosion, and carbon steel corroded almost linearly. The total penetration for 25 months for both alloys was less than 0.002 mm. On the 300°C specimens, magnetite (Fe_3O_4) and hematite (Fe_2O_3) were identified, and the ratio of hematite to magnetite in the corrosion product film increased with exposure time.

The nature of the oxide layers that form on particular alloys helps determine the overall corrosion performance of the material. Stable, adherent, continuous, and protective oxide layers make materials, like Ni-Cr-Mo alloys, very corrosion resistant [39]. Passive films of austenitic stainless steels in acidic solutions exhibit a marked enrichment of chromium and an increase in the film thickness with potential has been observed [40]. Higher Cr^{3+} content in the passive film is linked to lower film thickness and higher content of OH^- in the film [40]. The complex oxide formed for many stainless steels is $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ [41]. Differences in corrosion resistance within an alloy family indicate that structural and/or compositional differences exist in oxide layers. For example, increasing the Mo concentration in a Ni-Cr-Mo alloy produces an alloy more resistant to localized corrosion. For AISI 1020 carbon steel tested at 65°C in a thermogravimetric analyzer and exposed to air at various relative humidities, an inner oxide of Fe_3O_4 and an outer oxide of a powdery Fe_2O_3 and/or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ develops, and a critical relative humidity exists at 75-85% where oxidation/corrosion changes from dry

oxidation to aqueous film electrochemical corrosion [30]. It appears that water film corrosion rates can be 10 to 100 times faster than "dry" oxidation rates at similar temperatures [30]. Oxide layers, in general, are looked at as a semiconducting material, with significantly different electronic and structural properties from the underlying metallic material's properties [39]. Ionic and electronic transport are required for growth of an oxide layer to occur. Minority alloy species may significantly affect the oxide layer properties.

2. Localized Corrosion

Ionic and molecular species present in aqueous environments (water and moisture films) can serve as promoters, depolarizers, or inhibitors of localized corrosion (LC) in austenitic materials [42]. For example, F^- , Cl^- , Br^- , and $S_2O_3^{2-}$ can induce localized breakdown of passive films, thereby initiating pit formation; such species are known as promoters [5]. Halide ions are generally thought to participate in localized corrosion by acting as electrical conductors, aggressive species, and solvating ions [43]. For stainless steels, the order of aggressiveness of halides decreases with increasing size of halide [43]. Anodic dissolution at the bases of pits and at crack tips can be enhanced by a number of depolarizers, including O_2 , H^+ , Fe^{3+} , Cu^{2+} , and Hg^{2+} . The cathodic reduction of depolarizers on surfaces outside of crevices, pits, and cracks can galvanically couple with anodic dissolution and oxidation processes that occur inside pits [5]. In contrast to Cl^- , ions such as NO_3^- , I^- , and acetate are known inhibitors of pitting of austenitic stainless steels. These inhibitors compete with halide ions for adsorption sites on the metal oxide film and base metal. In alkaline media, OH^- , H^+ , and PO_4^- can serve as promoter, depolarizer, and buffer, respectively [5]. In general, inhibitors enhance the resistance to film attack by facilitating film formation and thickening and densifying the protective film [39].

Corrosion of Type 304 stainless steel in aqueous chloride solution of phosphoric acid can be inhibited by chromium, molybdenum, nitrogen, tungsten, and boron anion additions, and, in general, the resistance of an alloy to localized corrosion can be enhanced by increasing the molybdenum and chromium content [34, 44]. A "pitting resistance equivalent" (PRE) has been empirically linked to the corrosion characteristics of an alloy, where $PRE = \%Cr + 3.3 \times \%Mo + 30 \times \%N$, and $\%Cr$ = percentage by mass of Cr, $\%Mo$ = percentage by mass of Mo, and $\%N$ = percentage by mass of N [23]. Researchers have tried to correlate the corrosion resistance of an alloy with its Cr, Mo, and N content, and the PRE value can serve as a rough guideline for making alloy comparisons. The presence of Mo in alloys exposed to a corrosive media has been correlated with the formation of $Fe_2(MoO_4)_3$ which appears to slow corrosion rates [45].

In Type 316 alloy, molybdenum was found to affect the composition and growth rate of oxides, to decrease the dissolution rate of chromium in the transpassive region, and to inhibit penetration of Cl^- through the oxide film. Based on electrochemical tests, Incoloy 825 is reportedly more resistant to localized corrosion than either Type 304L or 316L stainless steel [46].

For general corrosion it is meaningful to measure corrosion rate, but for localized corrosion the probability of corrosion is more important [25]. McCright et al. [47] have described "critical environmental parameters" that bound the resistance of a material to localized corrosion, where a threshold is identified between susceptibility and effective immunity to localized attack. Critical chloride ion concentrations (higher chloride contents increase susceptibility), critical pH (acidic pH values favor localized attack), and critical temperature (higher temperatures increase susceptibility) are important parameters for enveloping the localized corrosion susceptibility of austenitic materials exposed to aqueous solutions. The parameters mentioned above are interrelated, and a useful index that relates them is the "critical" electrochemical potential on the metal surface where the usually protective film breaks down and corrosive attack initiates in the film denuded locations. Some other parameters that can be related through the electrochemical potential include: the effect of gamma radiation (from radioactive decay of spent nuclear fuel and vitrified reprocessed waste inside the container), and the effect of oxidizing species in the environment (e.g., nitrate ion is naturally present in the groundwater and ferric ion would be introduced due to the corrosion of carbon steel or cast iron boreliners). Microbiological organisms that produce acid-forming metabolism products would also result in more aggressive environmental conditions. Sharland and Newton [48] have tried to determine a "critical" solution composition which results in the breakdown of the passive film within the crevice, and whether such a condition is achievable for a range of repository conditions, types of steels and canister designs.

A. Crevice Corrosion

During uniform aqueous phase corrosion, dissolved oxygen is cathodically reduced and metal cations are anodically dissolved. These reactions proceed at rates independent of location on an exposed metal's surface. In contrast, the reduction of oxygen in a crevice may eventually cease due to the lack of reactant, if mass transport rates are insufficient to replenish it. As a result, only the anodic dissolution of metal occurs at a noticeable rate in a crevice, which results in an excess of positive charge (M^{Z+}). Halide ions, like Cl^- , tend to migrate to crevices to balance the excess positive charge and an unfavorable localized chemistry results.

As shown above, the halide salt hydrolyzes in water forming a precipitate and free acid. Repassivation in this type of environment (high-chloride, low-pH) is virtually impossible, and the anodic dissolution of most metal is accelerated.

In addition to the large differences in concentration that exist inside and outside of a crevice, there exist large differences in current density. On metal surfaces outside of the crevice, oxygen reduction occurs at relatively low current densities. Inside the crevice, the current densities are large due to the small active area. Therefore, the penetration rates inside a crevice are very large. During handling and emplacement of containers, it is important to limit the amount of scratches and other surface defects so as to lessen the number of sites on the container surface that would be prone to localized corrosion. It has been suggested that crevice attack initiates more easily than pitting corrosion on stainless steel [48]. The crevice corrosion rate for low carbon structural steels can be as high as 15 times the general corrosion rate in wet steam conditions [33].

B. Pitting Corrosion

Pitting corrosion occurs when there is a passive film on the metal surface and enough aggressive ions (e.g., OH^- , Cl^- , SO_4^{2-}) are in the electrolyte to cause local breakdown of the film. Local acidity develops in occluded areas because the migration of Cl^- and SO_4^{2-} into active sites results in formation of FeCl_2 and FeSO_4 which hydrolyze to produce HCl and H_2SO_4 . This maintains acidity of the sites. Only at the end of the initiation step does Fe^{2+} appear as a corrosion product from the pits, whereas Fe^{3+} production continues from the remaining passive surface [49]. During propagation, the external passive surface acts as a cathode to the anodic occluded sites. For a corrosion current to flow, a potential gradient must exist between the anode and cathode sites. To maintain a potential gradient, an oxidizing agent more powerful than water must be present in the bulk electrolyte. Anodic dissolution kinetics in the localized corrosion areas are likely to be under activation control. Charge and mass transport within the corrosion sites will occur by diffusion, and, for the charged species, by migration. Pits nucleate at various sites on the passive film. Besides halide nuclei, pits can nucleate at voids and sulfide inclusions in the alloy surface [5]. Manganese sulphide inclusions play a major role as potential initiation sites of localized corrosion in stainless steels [50].

In electrochemical corrosion tests, the difference between the pitting potential, E_p , and the corrosion potential, E_{corr} , serves as a quantitative measure of the susceptibility of an alloy to pitting; the greater the difference, the greater the resistance to pitting [34]. Similarly, the difference between the pitting potential and the repassivation potential, E_{rp} , serves as a measure of the resistance of an alloy to crevice corrosion. The repassivation potential, E_{rp} , has been determined to be useful parameter for predicting the long-term localized corrosion behavior of alloys [51, 52], and it is defined as that potential below which thermodynamically unstable material remains protected by a passive film. Detailed investigations of the pitting behavior of materials of interest (including Types 304L, 316L, 317L, 321, and 347 stainless steels and Incoloy 825) showed that spontaneous pitting did not occur for tests conducted in J-13 well water [26]. Whereas, Lukezich et al. reported that pitting did occur for Type 316L stainless steel in J-13 well water at 95°C [53]. The austenitic candidates Types 304L and 316L stainless steels and Incoloy 825 demonstrate pitting and crevice corrosion in chloride-containing environments [46]. Incoloy 825 had greater resistance to pitting and crevice corrosion than either Types 304L or 316L stainless steels. Acidic environments were found to be more aggressive to Incoloy 825 than a neutral environment [47]. The difference between E_p and E_{corr} is lower for the acidic solutions than for the near-neutral solutions. A sharp decrease in the potential difference is also noted for the high chloride solutions (greater than 10,000 ppm), and the difference in the potentials approaches zero. Alkali additions were found to mollify some of the effect of chloride and temperature. In general, a decrease in pH to more acidic conditions raises the corrosion potential and lowers the pitting potential. This decreases the resistance to pitting, especially in high-chloride solutions.

Since canisters will experience high-temperature air environments, Glass et al. [22] have investigated how thermally formed films on stainless steels affect pitting susceptibility in chloride media. It has been reported that Type 304L stainless steel has a maximum sensitivity to pitting that occurs following oxidation in dry air at 300°C [22]. Supposedly, this is due to a change in the semiconducting properties of the oxide film. Oxide films formed on Type 304L stainless steel in dry air at 650°C for 1 hour have been found to inhibit overall pitting in 1,000 ppm Cl^- media at 90°C.

3. Galvanic Corrosion

Local galvanic cells in specific regions of the container materials are of concern [56]. These cells can be initiated due to compositional and microstructural differences made by various fabrication processes used to make different parts of the container. For example, if filler weld

metal is used, compositional and microstructural inhomogeneities between the filler and the base metal can create a galvanic effect. This effect can be particularly egregious if the filler metal is anodic to the base metal, since the attack would be focused over a small area. Additionally, contact between the container and borehole liner creates a potential galvanic cell if electrochemically dissimilar metals are used and if an electrolyte is present.

4. Sensitization

Sensitization is when a material becomes susceptible to intergranular stress corrosion cracking due to precipitation of $M_{23}Cr_6$ carbides at grain boundaries during heat treatment. Chromium carbide precipitation in stainless steels occurs in the temperature range of 500 to 850°C (during pouring of vitrified glass into a canister the outside canister walls can reach 550°C [54]), and the rate of precipitation is controlled by chromium diffusion [5]. It is generally accepted that the mechanism for sensitization is the creation of a narrow chromium-depleted zone that forms contiguous to the carbides. Chromium is the element responsible for the formation of stable passive films in stainless steels, and localized depletion of this element adjacent to grain boundaries results in the establishment of an active path (one which does not repassivate) into the bulk material. To combat sensitization, carbon levels are reduced in the material, or strong carbide forming elements are added, like titanium or niobium. Yet, even in cases where a low carbon material is employed, sensitization can occur. Sensitization has been observed in low-carbon Incoloy 825 heat-treated in the 600 to 800°C range [55].

Sensitized structures may be problematic in oxidizing environments, particularly in cases where gamma radiation from waste forms generates radiolysis reactions in the water, which will likely make the water more oxidizing [54].

5. Microbially Induced Corrosion (MIC)

The presence of certain kinds of microbiological organisms can lead to a more acidic condition in a solution, and typically the measured pH is 2 (or less) in the region near bacteria colonies that attack metals [47]. Bacteria can contribute to anodic dissolution of metals through production of acidic substances, such as CO_2 , or organic acids such as acetate, butyrate, and other short-chain fatty acids [3]. Production of these substances increases the proton concentration and decreases the local pH. Some well-known micro-organisms oxidize and reduce the various oxidation states of sulfur and iron, and make the environment hostile to metals and alloys [56].

Certain micro-organisms can survive and propagate in environments previously thought to be too harsh for these organisms [56]. The micro-organisms can remain dormant for long periods of time under unfavorable conditions and become active when conditions are favorable. Microbes need water and temperatures below 100°C to grow [12]. Propagation of microbes may not be favorable when the container environment is relatively hot and dry, but when water re-enters the environment and the temperature declines below 100°C, microbe development may be favored. At this point, microbially-induced pitting corrosion of canister materials will have to be considered. In fact, MIC is considered a possible degradation mode in the entire temperature range from 30-120°C [12]. It has been surmised that during construction of a repository microbiological organisms may be introduced through drilling fluids, fuels for powered vehicles, and other human activity.

Although MIC has been observed for Type 300-series stainless steels, Incoloy 825 is reportedly immune to microbiological problems [18]. On the other hand, Van Konynenburg et al. claim that Incoloy 825 is generally resistant to MIC, but not immune [12]. Generally, exposure of stainless steels to aqueous environments, after detectable biofilms have formed, will result in an increase in E_{corr} [55].

6. Stress Corrosion Cracking

SCC was not reported in the literature for Incoloy 825. The candidates are ranked as follows: Incoloy 825 (best) > Type 316L > Type 304L (worst) [18]. Much of the data is for solutions having higher ionic strengths than expected in the groundwater near the repository. However, these data are believed to be relevant since refluxing can concentrate water falling onto container surfaces. Carbon steels proved to be resistant to stress corrosion cracking, but not localized corrosion [33]. It has been suggested that a critical potential for SCC can be related to a repassivation potential for crevice corrosion, E_{rcrev} , so as to provide a unified bounding parameter for localized corrosion and for SCC [3].

7. Effects of Hydrogen

Hydrogen can be present as a water or water vapor radiolysis product, and atomic hydrogen is absorbed by many stainless steels. It enters the lattice and causes loss of ductility and tensile strength. Bacteria that produce acid byproducts could also be a source of hydrogen, and some bacteria produce sulfides that prevent the transformation of atomic hydrogen to molecular

hydrogen [3]. Even though hydrogen can be adsorbed on austenitic stainless steels, diffusion rates are less than for ferritic or martensitic steels, and, as a result, austenitic steels are less prone to hydrogen embrittlement than other steels [3]. Hydrogen is expected to build up in and around a steel container over time in repository, and this build up can shift cathodic and anodic equilibrium potentials [57]. Formation of a hydrogen-dominated gas phase is considered to be a distinct possibility.

8. Effects of Anions

The effects of various anions on corrosion behavior in aqueous solution has been reported for a variety of potential canister materials that are being considered for deployment in Yucca Mountain. In general, iron and steel are susceptible to moisture, particularly when combined with chloride, sulfate, ammonium, formate, acetate ions, or formaldehyde [58]. The major anions suspected to be present in deep ground waters, in terms of their concentration with or without dissolved oxygen, include HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , and CO_3^- . Due to evaporation and radiolysis effects, it has been determined that J-13 well water may "concentrate" in an actual repository environment [22]. For samples tested in J-13 well water with increasing chloride content and at temperatures up to 100°C , no significant differences in the general corrosion rate were observed for the materials tested: Types 304L, 316L, 317L, 321, and 347 stainless steels [26]. The corrosion potential for the materials tested did become more negative, and they exhibited enhanced susceptibility to pitting corrosion. It was determined that all materials showed low corrosion rates and no evidence of spontaneous pitting, and on this basis, any one of the materials could serve as a candidate canister material.

Data reported for Type 316L stainless steel tested in a solution ten times more concentrated in Cl^- than J-13 well water indicated no significant effect on the electrochemical corrosion behavior (with respect to tests in normal J-13 well water), and due to the apparent superior corrosion resistance of Incoloy 825, more detailed investigations of pitting were conducted [47, 59]. It was reported that Incoloy 825 is susceptible to pitting attack in aggressive environments with high chloride contents (10,000 ppm) at a low pH of 2.5. Glass et al. [22] reported that an increase in Cl^- alone in J-13 well water creates a more aggressive solution towards austenitic stainless steels. As a result, E_{corr} and E_p values get more negative and the alloy becomes more susceptible to pitting, and for samples tested in J-13 water with more than 75 ppm of NaCl added, electrochemically measured corrosion rates increase. Beavers et al. [60] found that for 304L stainless steel tested in J-13 well water the pitting potential was increased by adding the passivating agents HCO_3 and NO_3 and by elevating the pH. E_{prot}

was only affected by NO_3 and Cl^- ; it increased with increasing NO_3 content and decreased with increasing Cl^- content. Incoloy 825 was reported to be susceptible to pitting in J-13 well water with the chloride concentration increased by 1,000 times (to 6400 ppm) [53].

9. Effects of Phase Stability

Bullen et al. [61] conducted a literature review looking at phase stability of the metal-barrier candidate materials. They reported that both Type 304L and 316L stainless steels are metastable because of the possible existence of body-centered cubic (α , ferrite) and face-centered cubic (γ , austenite) phases. Whereas, the austenite phase in Incoloy 825 is thermodynamically stable when the metal itself constitutes the thermodynamic system under consideration. As temperature is lowered from, let us say 650°C , both Types 304L and 316L stainless steels move from the austenite region through a martensite-plus-austenite region to a martensite region. Furthermore, martensitic transformations have been observed in Types 304L and 316L stainless steels, but no such transformations have been observed in Incoloy 825. With respect to carbide formation, it was suggested that if enough M_{23}C_6 carbides form, the previously stable austenite in a material like Type 304 stainless steel can transform into another phase. For austenitic materials, like Types 304L and 316L stainless steels, exposed to lower temperature and long times ($t > 1500$ hours), M_{23}C_6 can precipitate at grain boundaries. Such precipitation could be relevant for the time period of interest for container retrieval ($t \approx 450,000$ hours).

Generally, the corrosion resistance of a stainless steel is at its best when the material is single phase and homogeneous [62]. In practice, few cast alloys are homogeneous in composition, due to segregation during solidification. In most cases, microsegregation of the major alloying elements does not usually lead to significant changes in the overall corrosion resistance, except for some changes in corrosion rates that may occur under extremely corrosive conditions. When second phases are present, partitioning of alloy constituents has occurred, and in austenitic stainless steel the most likely second phase is δ -ferrite, which is higher in chromium and molybdenum and lower in nickel content than austenite. As a result, δ -ferrite has different corrosion characteristics than does austenite. In some cases, ferrite will corrode at a faster rate than austenite, and in other cases the reverse will be true. Generally, both phases have good resistance to corrosion and in most environments no attack occurs on either phase. Selective leaching, which is the removal of a less noble element from a solid alloy (e.g., dezincification from brass), does not occur for Type 304 and other Fe-Cr-Ni stainless steels [35].

10. Effects of Radiation

The effect of gamma radiation is most important for canisters that contain spent fuel, particularly in the earlier part of the containment period when the radiation field is the highest. The primary radiolytic products from interaction of ionizing radiation and air are oxygen, nitrogen, carbon dioxide, and water [16]. Only nitrogen oxides are important for dry air since there is no source of hydrogen or OH. The most important of these is nitrous oxide and nitrogen dioxide [16]. When considering air and air/water systems together, the most important radiolytic products are the oxidation products of nitrogen (NO, N₂O, NO₂, N₂O₅, HNO₂, and HNO₃), the reduction products of nitrogen (ammonia), and ozone [16]. Many of the chemical species formed by radiolysis are quite oxidizing to container materials (ozone, oxygen, oxides of nitrogen, nitric acid, hydrogen peroxide, and a number of free radicals) [56], and these products have the potential to concentrate in droplets that condense on canister materials [63]. Specifically, irradiation of air with water can form nitric acid which will attack the inner components of the waste package, and radiation will form nitric acid within moisture layers that could affect corrosion rates [12]. Dissolved CO₂ from air in water can form formic acid and oxalic acid. Particularly for copper-based materials radiolysis reactions can increase the oxidation rate and the general aqueous corrosion rate. Hydrogen is produced by the radiolytic decomposition of water or water vapor, and atomic hydrogen is absorbed by many metals. In susceptible structures, like martensite, hydrogen can cause embrittlement.

Reportedly, irradiation of pure water (de-ionized water with 0.0005M K₂SO₄ as the reference solution) at 50°C results in a shift in the electrochemical potential for Type 316SS of approximately 100mV in the active direction and nearly an order of magnitude increase in the passive current density as compared to non-irradiated conditions [21]. This active shift was attributed to a net increase in the reducing power of the solution, by the production of reducing radiolytic species.

Corrosion tests on 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 [33]. Tests were performed in air-sparged J-13 water to increase the oxidizing conditions of the water, thereby representing an irradiated aqueous environment. Results showed that the maximum corrosion rate occurs at 70-80°C, where the flux of oxygen to the steel surface is at a maximum.

For an investigation performed to assess the effects of gamma radiation on the corrosion mechanisms of candidate canister materials, it was determined that for Types 304L and 316L

stainless steels the corrosion potentials are shifted in the positive direction as the gamma radiation is introduced [15]. Such a potential shift is attributed to the production of hydrogen peroxide due to radiation. For Types 304L and 316L stainless steels in a potentiodynamic study, pitting potentials were almost unchanged when tested in a chloride media under gamma radiation. Nevertheless, since the corrosion potential is increased due to gamma radiation, the difference between the pitting and corrosion potentials is decreased significantly compared to values without irradiation. Therefore, the result is increased susceptibility to pitting corrosion.

In corrosion tests performed under simultaneous irradiation conditions by Juhas et al. [64], Type 304L stainless steel corrosion coupons were tested for one year at room temperature and 1×10^5 rads/hr in partially aerated (5 ppm O₂) J-13 water in contact with crushed Topopah Spring tuff (this represented rock found at Yucca Mountain). A non-irradiated test was conducted for control. Many of the dissolved ionic species in the J-13 water were concentrated by a factor of about two in the irradiated vessel as compared to the unirradiated vessel. The irradiated solution was relatively depleted in dissolved sulfate and oxygen, maybe due to enhanced corrosion rate of the vessel wall which was Type 304 stainless steel. Weight loss measurements on the specimens showed barely detectable corrosion for either the irradiated or non-irradiated material. It was suggested that gamma radiation may even enhance the stability of the passive film by making the environment more uniformly oxidizing, even in creviced areas.

Some reported investigations have looked at the effects of temperature, relative humidity, and gamma dose rate on the corrosion behavior of candidate container materials, primarily copper-based. One particular investigation reported little if any general or localized corrosion for Incoloy 825 in short-term, irradiated, moist-air experiments (up to 100% relative humidity) [65].

D. Favored Canister Materials

Based on the reported degradation mode investigations regarding the performance of Types 304L and 316L stainless steels and Incoloy 825, Table II can be constructed for alloy comparison [5].

Table II. Comparisons of candidate materials from information presented and analyzed in Degradation Modes Surveys [5].

Phenomenon	Most Resistant	Least Resistant
Phase Stability	Incoloy 825	304L
Oxidation/General Corrosion	IN 825, 316L	304L
Hydrogen Effects	IN 825, 316L	304L
Pitting Corrosion	Incoloy 825	304L
Crevice Corrosion	Incoloy 825	304L
Stress Corrosion Cracking	Incoloy 825	304L
Welding Effects (Sensitization)	Incoloy 825	316L
Radiation Enhanced Corrosion	Incoloy 825	304L
Microbial Enhanced Corrosion	Incoloy 825	304L

IV. MODELING OF CANISTER MATERIAL DEGRADATION

Predictive modeling is a major component of the Yucca Mountain canister qualification program. The models under study fall into the following categories: (1) pit initiation on passive austenite surfaces; (2) propagation of pits on active metal surfaces; (3) propagation of pits on surfaces covered by salt films; (4) crack initiation at pits; (5) propagation of cracks on active metal surfaces; (6) propagation of cracks due to periodic fracture of passive films at crack tips; (7) propagation of cracks due to film-induced cleavage of the base metal; (8) crevice corrosion on active metal surfaces; and (9) crevices that behave like active-passive concentration cells [7, 26]. Most of the models are applicable to worst case scenarios such as when a concentrated electrolyte contacts the container surface. For example, condensation may dissolve salt scales that form as a result of refluxing of groundwater on the hot container wall.

For predicting long term corrosion of canister materials, Marsh [66] has supported development of a mechanistic approach in order to complement experimental data. Two experimental approaches have been used for predicting long term corrosion of canister materials: (a) accelerated tests or (b) simulation tests. With (a) the procedure is to expose specimens to an electrolyte containing what are considered to be the main corrosion agents from the expected repository environment. Acceleration can be affected by increasing the temperature over that anticipated in the repository, by applying electrochemical polarization, by

concentrating the electrolyte, etc. Such tests are usually applied to demonstrate that a material is resistant to a particular form of attack. In the alternative simulation tests (b) every effort is made to reproduce the repository environment as closely as possible. These tests are used to investigate what forms of corrosion will occur under repository conditions, and to evaluate their rates of propagation so that the necessary corrosion allowance can be estimated.

The draw-back with both of the above techniques, according to Marsh, is that they do not provide a convincing answer to the problem of long term extrapolation. While the accelerated tests (a) may show that the material is immune to a particular form of attack for the duration of the test, how do we know the same is true for 1,000 years? Similarly with the simulation tests, how do we gain assurance that the corrosion processes observed in tests lasting a maximum of 4-5 years will be the same as those operating on containers over 1,000 years? Corrosion products could alter the environment pH and absorb certain ions preferentially changing the balance of aggressive to passivating ions. Such questions can only be answered if a sound mechanistic knowledge exists of (1) the prerequisites for a particular corrosion process and of (2) the rate controlling parameters for those corrosion processes which are considered to be viable.

With regards to pitting, available models fall into two broad classes: initiation and propagation [5]. Pit initiation models allow for the prediction of how environment may affect critical pitting potential and induction time. Once initiation has occurred, it is necessary to calculate the penetration rate. Sharland divided the localized corrosion modeling efforts into three categories: (1) initiation phenomena, (2) early growth processes which may lead to self-perpetuating corrosion cells that include ion migration and repassivation effects, and (3) propagation phenomena associated with cavity enlargement [66]. Models exist that can be used to calculate pH depression in a pit, the concentration of specific species in a pit, and the propagation rate. Marsh et al. [68] have modeled the oxygen transport in a repository setting, since the supply of oxygen will be one factor that will determine how long pits will continue to propagate in canister materials. Additionally, Marsh et al. [20] have modeled the fraction of a containers life where localized corrosion may occur. They showed that the period of possible localized attack is strongly dependent on the passive film leakage current, the radiation dose rate, and the oxygen diffusion coefficient.

Stochastic probability theory is used to explain variations that are observed in critical pitting potentials, and have proven useful in shedding light on pit nucleation and growth mechanisms. These models have the potential to provide quantitative information needed for developing

performance assessment codes for the entire waste repository system [26]. Yet, much quantitative validation of these models remains, in particular, "the determination of the pit depth distribution as a function of time and potential repository environment." Stochastic models have been presented that simulate the effects of electrochemical potential, chloride ion concentration, and temperature on the aqueous pitting corrosion behavior of container materials [69]. Also, stochastic models have been constructed to simulate waste package degradation. These models incorporate individual models for humid-air general corrosion of the outer barrier, humid-air pitting corrosion of the outer barrier, aqueous general corrosion of the outer barrier, aqueous pitting corrosion of the outer barrier, and aqueous pitting corrosion of the inner barrier [70]. To calculate the evolution of the pit depth distribution, a model has been constructed that combines elements of the deterministic and stochastic aspects of pit growth [71].

Crevice corrosion models of canister materials have generally been constructed to predict the evolution of the solution composition within the crevice [48]. They have tried to ascertain either a limiting composition resulting from mass-transfer considerations or a "critical solution composition" (defined in terms of pH and chloride concentration) that causes the film to breakdown and initiate rapid corrosion.

Farmer et al. [5] have listed several needs in the area of corrosion modeling of canister materials. These needs include: (1) A model of the local environment around a canister must be developed. This model should be capable of predicting the temperature of the container wall, the levels of species in ground water that have been concentrated by thermal refluxing, the concentrations of radiolysis products, and the effects of microbial growth on the local environment; (2) parameters in corrosion models should be quantified for the candidate materials, where appropriate; (3) possible crevice geometries must be determined; and, (4) statistical techniques should be introduced into models. McNeil has stated that the corrosion community has reached the limit as far as modeling pit initiation is concerned, at least until considerable experimental data is generated [72].

Preliminary performance assessments have been conducted on waste package materials. Initial results show that waste containers will fail within 100 years if the packages are wet at the boiling temperature, and no failures will occur after one million years if the containers are hot and dry [12]. Of course some important effects were ignored in making the million year prediction, including: delayed resaturation will occur for the dry case, galvanic interactions can be present between dissimilar materials, MIC may be active, the geochemistry may be altered,

and manmade materials will be introduced. It is clear these models are oversimplified, and data continues to be generated to validate these models. Walton and Sagar's canister corrosion model determined that substantial changes in the system being modeled will occur due to the canister corrosion process [57]. Consequently, caution must be applied in extrapolating short empirical studies for prediction of long-term behavior. According to Ricker, "...it may very well be possible to use electrochemical measurements in a laboratory to predict behavior in service, only if the variations in the environmental constituents that influence the corrosion rate are known and the interactions between the material and the environment are also understood" [73].

Stahl et al. [74] modeled the performance of a corrosion-allowable container in Yucca Mountain as a function of thermal loading. They claim that the worst aqueous corrosion is observed above about 60°C. The corrosion rate in neutral pH aqueous environments is governed by the oxygen content in the water; as temperature increases, the diffusion of oxygen increases, but the solubility of oxygen decreases. A maximum in corrosion rate occurs at around 80°C. The aggressive zone for aqueous corrosion exists from 60°C to the boiling point. Based on the modeling efforts completed by Stahl et al. for waste containers with various thermal loadings, containers can supposedly survive the 1,000 year containment period, and in terms of oxidation behavior, the hottest waste container is predicted to display only 4 μm of penetration in 100,000 years.

V. CORROSION OF A METALLIC WASTE FORM

It is clear that a lot of information exists about the possible corrosion behavior of steels in a repository setting, and it is potentially useful to extend the application of this information to the possible corrosion behavior of the metal waste form, which can contain up to 85 wt.% stainless steel, in a geologic repository. The MWF alloy that will be cast for treated stainless-steel clad fuel elements will have as a base stainless steel ($\approx$ 80-85 wt.%), viz. Types 304, 316, D9, or HT9 stainless steels, with the other major component being zirconium (15 wt.%), giving a nominal alloy composition of stainless steel - 15 wt.% Zr (SS-15Zr) [8-11]. Additionally, a small amount of noble metal fission products (up to 4 wt.%) will be incorporated. The microstructure of the metal waste form, with this composition, is a eutectic-type structure that consists of an Fe_2Zr phase and a ferrite phase with some retained austenite (10-15%). For light-water reactor fuel elements that are clad with Zircaloy, 90+% of the alloy will constitute zirconium, and the balance will be stainless steel components (Fe, Ni, Cr, etc.) and noble metal fission products. The nominal composition is Zr-8 wt.% stainless steel (Zr-

8SS). This alloy has a microstructure consisting of islands of major α -Zr phase and the inter- α -Zr phases Fe_2Zr and FeZr_2 . The phases that compose both MWF alloys should remain stable and corrosion resistant for an exceedingly long time (approximately 10,000 years).

Even though ANL's MWF may not have to meet the same requirements as the Yucca Mountain canister materials discussed earlier (e.g., the MWF will not be required to support a load), many of the same environmental conditions mentioned above will impact the performance of an alloy waste form. The forms of corrosion that will be of particular interest will be those that directly affect the waste form's ability to retain fission products over very long time frames, including uniform corrosion, oxidation, localized corrosion (including crevice and pitting corrosion), galvanic corrosion, and MIC. Some specific factors that will affect the MWF in the context of corrosion performance include: the presence of anions, radiation, changing temperature, changing pH, the presence of hydrogen, and the stability of alloy phases.

Most of the same forms of corrosion that directly affect corrosion rate of potential Yucca Mountain canister materials will also affect the corrosion behavior of the MWF in a geologic repository. Uniform corrosion rates will determine the general rate of degradation of the MWF. Pitting corrosion could impact MWF performance by causing increased corrosion rates in localized regions, e.g. at phases that contain components of interest (like the long-lived fission product technetium). Oxidation behavior, including how the presence of certain alloy constituents affect oxide layer formation, will be important since oxide layers will help influence the passivity and overall corrosion of a MWF. Crevice corrosion could be relevant at areas where a waste form sits in contact with the canister, or in cases of stacking waste forms, where waste form contacts waste form. Galvanic corrosion could be possible where a waste form contacts the container, or if specific phases of an alloy corrode due to the setup of a galvanic cell with another phase. The presence of microbes may alter the environment in localized regions of the repository environment near a waste form, and as a result, the possibility of MIC of the MWF is a relevant issue to be considered. Hydrogen could be present in a repository and may affect the corrosion performance of the MWF. Radiation from surrounding canisters filled with spent fuel or vitrified waste can change the nature of the repository environment (e.g., H_2O_2 can be produced) and should therefore be taken into account when studying MWF corrosion. Since de-alloying can occur at particular phases (e.g., MnS phases), the types of phases that form in the MWF along with the stability of these phases in a repository are of interest. Changing temperature will affect the rate at which an alloy corrodes, as will the presence of certain anions in high concentrations. Very high (>10)

and very low (<2) pH levels in an aqueous environment will impact the corrosion resistance of an alloy.

A. Corrosion Testing

A variety of tests have been mentioned for studying corrosion of Yucca Mountain canister materials, and these tests are available for studying corrosion of alloy waste forms. The general types of tests that have been discussed are electrochemical tests, immersion tests, and high temperature steam tests, under a variety of conditions (e.g., pH, temperature, halide concentration, etc.). Some of these types of tests are currently being performed on the MWF.

By employing electrochemical corrosion tests, the corrosion parameters E_{corr} , E_p , and E_{prot} , for the MWF in J-13 well water, can be determined. Then, the effects of halides, radiation, temperature, pH, dissolved oxygen, inhibitors, promoters, etc. on these parameters can also be investigated. The result of this type of data is a more thorough knowledge of the general corrosion behavior (both uniform and localized) and of the passivity of the MWF alloy in potential Yucca Mountain environments that can exist over time.

Up to this point, linear polarization electrochemical tests have been performed to study uniform corrosion of the MWF in J-13 well water. As described for the testing of Yucca Mountain canister materials, this test requires measuring the current over a small range of potential using a potentiostat and associated electrochemical cell. Corrosion rates have been measured for various test samples of MWF alloys, including alloys of nominal composition and ones with noble metal additions [10,11]. Additionally, corrosion rates for candidate Yucca Mountain canister materials have been measured. At neutral values of pH (pH = 6-7) in simulated J-13 well water, 316-15 wt.% Zr MWF alloy samples corroded at a rate {on the order of hundredths of a mil-per-year (MPY)} similar to what was observed for commercial grade Types 304SS and 316SS and Incoloy 825 and about one to two orders of magnitude smaller than those for A106 low alloy steel and high-purity Cu. At pH=2, the corrosion rate for the MWF sample increased by about an order of magnitude. This rate was lower than what was observed for high-purity Cu and A106 low alloy steel and was similar to rates observed for Types 316SS and 304SS; Incoloy 825 samples exhibited lower corrosion rates (about hundredths of a MPY) compared to the MWF samples. Corrosion rates for all samples in solutions with a pH of 10 were similar to those observed for neutral pH values.

The above corrosion behavior observed for MWF alloys is similar to what has been reported for Yucca Mountain canister materials. Tsujikawa et al. [35] reported that for Type 304SS uniform corrosion is only significant at a pH value of 2, and a similar effect of pH was observed for MWF samples. Also, as discussed earlier, container materials exhibit uniform corrosion rates on the order of tenths of a micron per year in J-13 well water in independent tests [22]. These corrosion rates are similar to ones measured for the same types of materials tested in J-13 well water at ANL.

In addition, Park et al. have conducted limited pitting corrosion electrochemical tests on the MWF [75]. These tests involved anodically polarizing MWF specimens in J-13 well water and measuring charge densities during forward and reverse scans between the corrosion and vertex potentials. Results showed that adding Zr to Type 316SS increases charge density, and adding a combination of Ag-Ru-Pd in small amounts to Type 316SS increases charge density significantly in J-13 well water—this could possibly be an indication of an increased susceptibility to pitting corrosion. It will be important to look at how resistant the MWF is to pitting when it is exposed to a variety of different ions. For example, ferric ions can be present due to corrosion of the canister materials, and it will be necessary to understand whether or not these ions incite pitting in the MWF; and, dripping water, followed by evaporation, can cause waste form exposure to concentrated levels of certain species, like halides. Finally, imperfections on an ingot's surface can initiate pitting or crevice attack.

Other types of electrochemical corrosion tests that may prove useful in determining MWF corrosion behavior include: open circuit electrochemical potential (ECP) measurements, potentiodynamic (or potentiostatic) anodic polarization scans, fixed-potential passive current density tests, or cyclic polarization, staircase polarization, stepwise repassivation, and scratch repassivation methods which can be utilized for studying initiation, propagation, and repassivation of pitting for the MWF. Voltammetric and *ac* impedance techniques, which have been mentioned for investigating passive film formation on stainless steel, may be applicable to the MWF.

Immersion tests are another type of test available for corrosion testing of a MWF. These tests give a corrosion rate, in mm/yr or mg/dm²/day, which is determined by calculating weight loss of the sample after a period of time. These tests can be employed to investigate uniform and localized corrosion of samples exposed to solutions of varying aggressiveness (pH, temperature, halide concentrations, etc.). Tests can be run as static tests, or as flowby tests, where flowing solutions are used. Samples can also be exposed to gaseous environments

(e.g., air), instead of solutions, at varying temperatures, and an oxidation rate can be determined. By varying the humidity of the air, as in an air/steam test, corrosion due to the presence of thin surface films can be investigated.

Immersion tests have been used by Park and co-workers to determine the uniform corrosion rates for the MWF in J-13 well water at pH=6-8, 90°C, and 1 atmosphere pressure [75]. Tests were interrupted after 10,000 hours, at which time, weight loss, leaching of elements, and pitting corrosion were measured. Samples reportedly came out of the test solution exhibiting negligible signs of corrosion [75]. As a result, it is very difficult to quantify corrosion of the MWF when there is such little evidence of corrosion. Mass changes were reportedly insignificant and within the error of the precision of the measurements (± 0.1 mg). The corrosion rates were determined to be <0.003 MPY, which is an order of magnitude smaller than those measured using the linear polarization method.

The immersion test results discussed above compare favorably to those reported for immersion tests of Yucca Mountain canister materials. Corrosion rates on the order of tenths of a micron per year have been reported for Types 304L and 316L stainless steel specimens tested in J-13 well water at 50, 70, 80, 90, and 100°C for exposure times of 3,548 and 5,000 hours [22]. When including tests run at 7,500 hours, the corrosion rates were around 0.15 microns per year. The total range of corrosion rates was 0.025 to 0.36 $\mu\text{m}/\text{year}$ and the corrosion rates for the MWF have been reported to be around 0.01 $\mu\text{m}/\text{year}$. The fact that corrosion rates for MWF immersion test samples are an order of magnitude lower than corrosion rates for linear polarization test samples is consistent with the research of Glass et al. [22] described earlier, who observed similar results for tested stainless steel specimens. Glass et al. attributed corrosion rate differences to be due to differences in the two methods used to determine the corrosion rates.

The last common testing technique for studying corrosion behavior is an air/steam exposure test. A type of air/steam exposure test is currently being conducted on MWF samples [76]. In this particular test, dime-sized specimens are polished to 600 grit, notched, and suspended in stainless-steel containers where they are exposed to water-saturated vapor at 200°C for various time periods. Any corrosion products that appear on the surface are then analyzed using scanning electron microscopy, X-ray diffraction, and Raman Imaging/Spectroscopy techniques. Based on reported results for similar tests on Yucca Mountain canister materials, it will be important to determine for tested MWF samples the nature of the oxide(s) that form on samples layers (are they stable, adherent, continuous, protective, etc., ?), the effects of alloy

composition variations on the nature of the oxide(s), and the test temperature effects on oxide layer development (Lutton et al. found that notable corrosion may occur at some test temperatures and not at others [38]). Furthermore, it should be kept in mind that variations in corrosion behavior can be observed depending on whether the test environment is "wet" or "dry" steam [37]. For example, for AISI 1020 carbon steel tested in air at varying levels of humidity, a transition in corrosion rate has been reported for a relative humidity level of 75-85%, with Fe_3O_4 and Fe_2O_3 being the most commonly observed corrosion products [30]. For stainless steels, $\text{Cr}_2\text{O}_3 \cdot \text{FeO}_3$ is the commonly observed corrosion product [41].

As has been the case for researchers testing Yucca Mountain canister materials, a modeling component is required for projecting how well a MWF alloy will perform in a Yucca Mountain environment over a long period of time. Efforts to model MWF performance are currently underway at ANL [77]. Laboratory testing will also be required to validate these types of models, and some tests will have to be long-term tests. It will be important to understand degradation mechanisms of the waste form, since extrapolation of short laboratory tests will have to be made if waste form performance is to be projected for long time periods. If mechanisms are not determined to remain the same for 10,000 years, then extrapolations can not be made.

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