

Modeling Corrosion and Constituent Release
From a Metal Waste Form¹

by

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INTRODUCTION

Metallic waste forms are one end product of waste streams that result from electrometallurgical treatment of spent fuel. These waste forms are robust and well suited technically for immobilizing metallic fission products. The particular metal waste form (MWF) under study here represents materials left behind in spent fuel cladding hulls following an electrorefining process developed at Argonne National Laboratory (ANL).¹ Major constituents of the waste form were chosen to take advantage of stainless steel's high corrosion resistance and mechanical strength. The mix is (1) the stainless steel cladding, (2) 5-20 wt% zirconium (fuel constituent), (3) residual uranium (up to 10 wt%), and (4) "noble-metal" fission products (e.g., Ru, Re, Zr, Mo, Nb, Pd, and Tc). The actual waste form is created by melting and alloying the constituents together in a high-temperature inert gas furnace. Although the MWF consists mostly of stainless steel, a substantial weight fraction is made up of other metals, and it is not self-evident that the corrosion behaviors of the MWF and stainless steel should be

the same.

MEASURING METAL WASTE FORM CORROSION AND RELEASE

One of the main mechanisms proposed for long-term radioactive isotope release from a MWF is uniform aqueous corrosion. (Other potential mechanisms, including crevice corrosion, will be addressed as part of an ongoing experimental program.) This paper synthesizes results from several ongoing ANL experimental programs that measure both MWF corrosion and constituent release. The reference aqueous environment is Yucca Mountain J-13 water² and a temperature range of 20-90°C. More aggressive environments have also been studied parametrically by concentrating the dissolved J-13 constituents, varying pH, and increasing chloride concentration. Experimental methods include both electrochemical and direct immersion techniques. The goal is a quantitative, mechanistically-based model of MWF corrosion and subsequent constituent release, including all relevant corrosion mechanisms, that is applicable to the full range of aqueous environments expected at the proposed Yucca Mountain Repository.

A. Electrochemical Tests

Electrochemical tests measure corrosion rates by using external potentials to impose electric currents between a sample surface and adjacent test solution. A "polarization resistance" is the slope of applied potential versus measured current at the null current (or free corrosion) point. Polarization resistance may be used in a straightforward manner for order-of-magnitude estimates of the free corrosion rate.^{3, 4} This method has the practical advantage of simplicity and can provide relative corrosion rate data over a wide range of sample types and test environments very quickly. Its most significant limitation is insensitivity toward surface conditions that develop over time, such as

corrosion-inhibiting protective oxide layers. The ANL study reported here ⁴ was conducted on polished MWF samples. Results have been used to estimate *initial* corrosion rates over a wide parametric range: pH (2-10), chloride concentration (4-10,000 ppm), and temperature (20-90°C).

B. Immersion Tests

Immersion tests provide a technique for investigating sample corrosion and a direct measurement of constituent release. Such tests expose samples to desired environmental conditions for extended time periods. Whereas most industrial applications of this method focus on maintenance of sample structural and mechanical integrity, the MWF immersion studies reported here focus instead on the release of constituents to the environment.

One ANL study⁵ tested simulated non-radioactive MWF samples for 1 year in a test environment of concentrated (by a factor ~100) J-13 solution held at 90°C. (The simulated MWF included major constituents and surrogates for fission products but no Tc, U or other actinides.) Measurements taken at regular intervals tracked the release of MWF constituents, as found either in the test solution or on a vessel surface. (Following each measurement the sample's vessel was cleaned and the test solution was replaced.) Additionally, weight changes in the test sample were measured and overall corrosion rates were estimated by attributing all weight changes to oxidation. These results are compared with the corrosion rate determinations from electrochemical data.

A second ANL study⁶ tested samples of radioactive MWF containing prototypic amounts of both U and Tc (not present in the simulated MWF). These tests were all conducted in simulated J-13 solution at 90°C and extended over time periods of either 397 or 707 days. Only releases of Zr, U, and Tc from the test sample were measured. While measurements in this study were not as extensive,

they focused on radioactive actinide and fission products of significance to repository performance.

C. Test Results

Figure 1 compares selected corrosion and release rate deduced from the three MWF studies at 90°C. For purpose of comparison, the "normalized" constituent release rates reported here were obtained by dividing a measured release rate by the constituent's weight fraction in the MWF. With this choice of normalization all release and corrosion rates are the same if corroded material is promptly released to solution.

Electrochemical measurements of initial corrosion rate are shown on Fig. 1 by small circles. The pH of the test solutions is indicated along the abscissa, and chloride concentrations are labeled. The solid and dashed lines indicate a least-square fit to a model functional form described in the following section (dashed lines indicate the standard deviation of the measurements). It is useful to note that these electrochemical corrosion rate determinations on MWF samples are generally similar to those of 316 stainless steel.

Corrosion and release rates deduced from the immersion tests yield both initial values and time-dependence for the J-13 and concentrated J-13 test environments. Test data clearly indicates that, in general, corrosion and release rates are not the same. Immersion test results shown in Fig. 2 illustrates that initial normalized release rates of all fission product elements and major MWF constituents are consistently 1-2 orders of magnitude lower than initial corrosion rates. However, all measured corrosion and release rates exhibit a similar time dependence, i.e., fall off in time by ~1 order of magnitude over 100 days, and level off thereafter. Some of the same normalized release rate data, plus U and Tc results, are included on Fig. 1 as initial and long-term corrosion rates (at pH locations

appropriate to J-13 and concentrated J-13 test solutions). The approximate timing of each long-term measurement is indicated.

It is instructive to evaluate the consistency of the corrosion and release rate measurements compared on Fig. 1. Considering the order-of-magnitude nature of the electrochemical technique and data scatter, it is significant that both electrochemical and immersion weight-gain techniques result in consistent magnitudes of *initial* corrosion rates; i.e., the point where a passivating oxide layer could begin to form. Also, both immersion test studies yield reasonably consistent results for initial- and long-term release rates of fission product elements. In fact, the immersion studies indicate that similar normalized release rates apply also to major MWF constituents (Fe). By contrast, the measured initial- and long-term normalized uranium release rate is higher than for fission products but still below measurements of overall corrosion rate.

The following rough picture of aqueous corrosion in simulated (and concentrated) J-13 solution at 90°C emerges from these test results. The initial corrosion process associated with the measured sample weight gain appears to build up a protective or barrier layer(s) that reduces the underlying corrosion rate and holds up most release of major constituents and principal fission products. We also infer that the time dependence observed in Fig. 2 for all release rate and weight gain measurements (~1 order of magnitude drop in 100 days) reflects the actual time-dependence of the underlying corrosion rate. The observed release rate of uranium is sufficiently high to suggest that uranium may not be tied up in the barrier layer and that its measured release rate may serve instead to "mark" the progress of the underlying corrosion process. Considering that the postulated barrier layer can eventually dissolve or otherwise break down, release of formerly trapped MWF constituents would be signaled by an

increase of the release-to-corrosion rate ratio with time. Such trends are neither evident nor ruled out by the present test data covering ~1-2 year exposures.

A PRELIMINARY CORROSION AND RELEASE RATE MODEL

The above results have been incorporated into a simple corrosion and release rate model, limited to the uniform aqueous corrosion mechanism, and suitable for preliminary application to the Yucca Mountain Repository environment.⁷ This model and its successors will support inclusion of the MWF of the in the forthcoming license application.

The following equation represents the least-square fit to the electrochemical determinations of initial corrosion rate. The ranges of pH, chloride concentration, and temperature covered in the fitted data are indicated.

$$\log_{10} CR = 1.52 + 2.07 \times 10^{-3} T + 4.15 \times 10^{-2} \text{pH} - 3.35 \text{pH}/T + 1.82 \times 10^{-7} [\text{Cl}^-] T$$

where

| | | |
|------|---|---|
| CR | = | electrochemical uniform corrosion rate in gm m ² y ⁻¹ |
| T | = | temperature in °C (20°C ≤ T ≤ 90°C) |
| pH | = | pH of the bulk solution (2 ≤ pH ≤ 12) |
| [Cl] | = | the halide or chloride ion concentration in ppm or mg/L, |

and the standard deviation of log₁₀CR data points is 0.36.

The model assumes the release rate of each constituent is proportional to the corrosion rate, CR. Release rate dependence on pH, chloride concentration, and temperature is thus assumed to be the same as for the fitted corrosion rate. The constant of proportionality is determined by choosing an appropriate bounding release rate from the immersion test data. Constants have been determined

separately for fission products (represented by Tc) and actinides (represented by U). Additional “upper” and “lower” bound determinations represent initial and long-term measurements, respectively.

The current estimated values are given in Table I.

| Table I Preliminary Fission Product and Actinide Release Model | | |
|--|--------------------------------|--------------------------------|
| | Fission Products | Actinides |
| Upper Bound | $2.7 \times 10^{-2} \times CR$ | $4.7 \times 10^{-1} \times CR$ |
| Lower Bound | $2.7 \times 10^{-3} \times CR$ | $2.5 \times 10^{-2} \times CR$ |

CONCLUSIONS AND FUTURE WORK

Several ANL ongoing experimental programs have measured MWF corrosion and constituent release. Analysis of this data has initiated development of a consistent and quantitative phenomenology of uniform aqueous MWF corrosion. The effort so far has produced a preliminary fission product and actinide release model based on measured corrosion rates and calibrated by immersion test data for a 90°C J-13 and concentrated J-13 solution environment over 1-2 year exposure times.

Ongoing immersion tests of irradiated and unirradiated MWF samples using more aggressive test conditions and improved tracking of actinides will serve to further validate, modify, and expand the application base of the preliminary model- including effects of other corrosion mechanisms. Sample examination using both mechanical and spectrographic techniques will better define both the nature and durability of the protective barrier layer. It is particularly important to assess whether the observations made with J-13 solution at 90°C persist under more aggressive conditions. For example, all the multiplicative factors in Table I implicitly assume the presence of protective barriers. Under sufficiently aggressive test conditions, such protective barriers may very well be altered or even eliminated.

ACKNOWLEDGMENT

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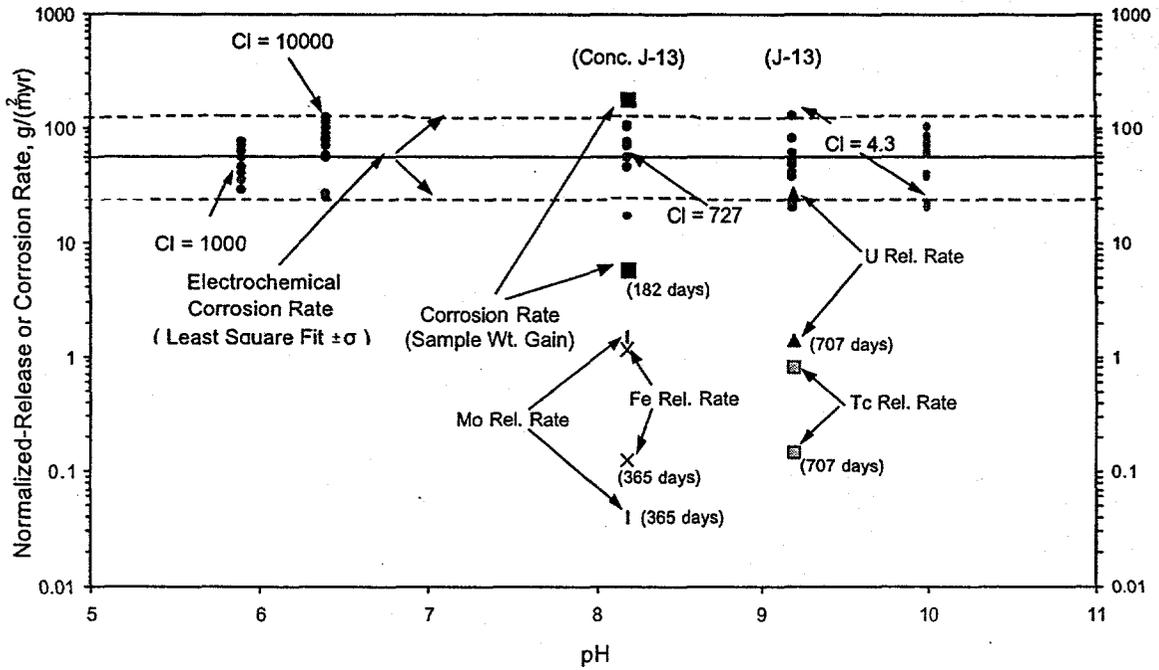


Fig. 1 Selected Corrosion and Release Data at 90 deg-C

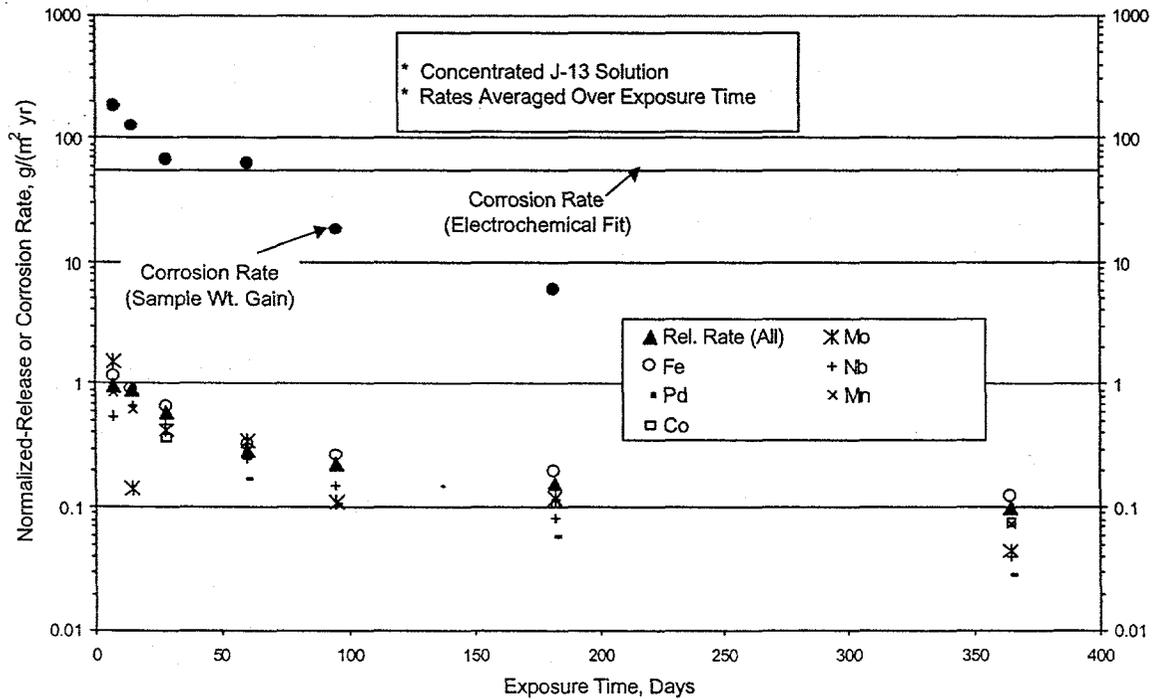


Fig. 2 Average Normalized Release and Corrosion Rates Vs. Exposure Time