

12 March 1988
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U. S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Kien:

Services Rendered on High Level Waste Repository
Performance Assessment Development 2/29/88-3/12/88

During the referenced period my efforts have been to review a substantial number of documents from NNWSI and to continue to develop the mathematical procedures that would be used to calculate the time to sensitization of 304L stainless steel using the thermodynamic model that has been advanced.

Wasteform Dissolution

The dissolution of spent fuel is receiving increased attention even though the quantity of groundwater present in a tuff repository is expected to be small. Using the composition of the water from well J-13 as representative of the groundwater that would contact the waste once a canister has been breached, Bruton and Shaw¹ have used the geochemical equilibrium code EQ3/EQ6 to simulate the equilibrium concentrations of the chemical species that would be present. This simulation assumes that equilibrium conditions have occurred, that is, that all the kinetics involved are fast compared to the time that is involved in the dissolution and transport of the elements in the spent fuel.

In addition to the limitation of validity imposed by the kinetics assumption, the thermodynamic data base use in the simulation is missing thermodynamic data for a number of chemical elements (Zr, Nb, Mo, plus others) that are present in significant quantities, and whose presence could alter the chemical balance that occurs. Nevertheless, the results are important and provide useful data on the quantity and chemical nature of the species in solution that would be available for transport.

Most of the elements considered reached a saturation limited concentration in the groundwater. This was expected, but the

¹Carol J. Bruton and Henry F. Shaw, "Geochemical Simulation of Reaction Between Spent Fuel Waste Form and J-13 Water at 25 C and 90 C, UCRL-96702 (November 1987)

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number of different species that occur was surprising. Neither Cs nor Tc reached saturation even after 100 g of fuel had reacted with 1 kg of water. The pH of the resulting solution declined to less than 7 at 90 C, but remained at 8 at 25 C.

The concentration of Pu did not exceed a molality of 10^{-12} at 90 C. The concentration of Th was even lower.

The concentration of several species is controlled by the presence of the SiO_4^{4-} ion in solution. Thus when the available SiO_4^{4-} is depleted by precipitation of insoluble compounds, the concentration of some species increased. Notable among these are U and Ni. The complexes of Am and Np are pH dependent, and their concentration increases as pH decreases.

Because radiolysis increases the Eh and decreases the pH of solutions, it is possible that this simulation has underestimated the solubility of a number of species. It would be useful to include in the simulation the concentration of oxidizing species, and effect on pH that results from radiolysis.

IGSCC of 304L Stainless Steel

A significant study of IGSCC in 304L stainless steel has been published by Westerman et al². Tests were carried out on stressed (U-bend specimens) samples of 304, and 304L for up to one year. The testing included both annealed and sensitized samples and was carried out at 50 C and 90 C for up to 25 months. The tests included exposure to both radiation and a tuff/air/groundwater environment. Specimens of 304 SS failed even at the lower temperature. Specimens of 304L SS were found to be susceptible to stress corrosion cracking at 90 C but not at 50 C after 25 months of exposure. Although the conditions were more severe than those expected in the tuff repository, it is significant that susceptibility was observed in as short a time as two years at a temperature as low as 90 C. In a nonirradiated 1-year test at 200 C 304L samples resisted failure.

It is not a simple matter to compare these results with the different scenario that would occur in the repository. In the repository scenario, the sensitized material would be subjected to temperatures in excess of 90 C (as high as 250 C) for several hundred years with minimal (presumably) groundwater interaction. During this period, sensitization could occur at which point the introduction of groundwater could lead to SCC and failure of the canister. The significance of the Westerman et al data is that it demonstrates that SCC can occur in the absence of sensitization.

²R.E. Westerman, S.G. Pitman and J.H. Haberman, "Corrosion Testing of Type 304L Stainless Steel in Tuff Groundwater Environments", UCRL-21005 (November 1987)

It is not possible to make use of this information in a predictive model as yet, but it has the potential of ruling out the use of 304L SS as a canister material. The apparent ability of irradiation to greatly accelerate the onset of SCC (or to allow SCC to occur at much higher grain boundary Cr concentrations) need to be investigated and understood before this material is selected for the canister material.

It seems unlikely that irradiation would change the rate of the reaction that causes carbide precipitation, or the rate of diffusion of Cr along grain boundaries, but mechanisms for both effects can be postulated. In view of the use of 304L SS as fuel cladding and its use in reactor coolant systems, where intense radiation effects would be expected, these results are somewhat surprising and would lead to the possibility that some species in the groundwater, that is not present in the reactor situation, must be involved.

Modeling of IGSCC

The thermodynamic model of IGSCC must be made into a tractable form in order to be used in CONVO. This is not a straightforward process. All of the required data have been assembled and are being analyzed. These data are based on fitting various functions to experimental data that contain large uncertainties. Sensitivity analyses on some of the functions have been carried out and have indicated which independent variables have the greatest effect on model predictions.

The model involves calculations of the concentration of Cr in the grain boundary as a function of time and temperature. All of the important variables are temperature dependent. In the case of the activity coefficient of C there is a dependence on the concentration of Ni and Cr as well. Thus three of the equations involved (the Cr activity coefficient, the C activity coefficient, and the equilibrium reaction between C and Cr) are coupled and must be solved simultaneously.

Each of the relevant equations contains a number of constants that are uncertain. For example the equation for carbon activity contains 10 coefficients that were developed from fitting experimental data. Each of these coefficients has a relatively large uncertainty associated with it. These coefficients were originally derived by Natesan and Kassner³ from their own experimental data and other earlier data. They did not provide a statistical analysis of the data.

Their data for the activity coefficient of carbon results in an equation having five terms. Each term has a temperature

³K. Natesan and T.F. Kassner, "Thermodynamics of Carbon in Nickel, Iron-Nickel and Iron-Chromium-Nickel Alloys", *Metallurgical Trans.*, 4 (2557-2566) 1973

dependent constant of the form $a \pm b/T$. The data for each of these five constants were provided in the Natesan and Kassner paper. They have been used in a simple linear regression analysis to compute the variances in the intercepts (a) and slopes (b) for each of the five constants. The relative standard deviation of each of the five slope values is greater than 0.2. The relative standard deviation of each of the intercepts is large as well, but at 250 C or less have a smaller effect on the value of carbon activity than does the slope.

The carbon activity equation also involves the independent variables carbon concentration, temperature, Ni concentration and Cr concentration. It is not practical to carry out Monte Carlo calculations repeatedly on a system that has 13 random variables to sample. Fortunately it appears possible to reduce the number of random variables by using the response surface approach. This would involve Monte Carlo analysis to generate a five dimensional surface that represents the carbon activity as a function of the four independent variables, at least to first order.

The sensitivity of the carbon activity to Ni concentration is not large compared to other variables. The greatest sensitivity is in Cr concentration, where a 1% change in Cr concentration results in a 30% change in carbon activity. Obviously it is not possible to calculate the carbon activity and Cr concentration independently.

The carbon activity enters into the calculation of Cr concentration as the 6/23 root, hence a 30% change in carbon activity (not caused by a change in Cr concentration) results in a 7% change in Cr concentration. This points out the sensitivity of IGSCC to the carbon concentration in the alloy and emphasizes the fact that relatively large changes in carbon concentration are required in order to produce a major impact on IGSCC. Interesting the temperature sensitivity of the carbon activity is not great; a 1% change in temperature resulting in a 0.6% change in carbon activity.

Other temperature dependent constants are the equilibrium constant K, and the Cr diffusion coefficient D. These involve an additional 4 uncertain coefficients. In all there are 28 coefficients whose uncertainties must be accounted for in the Monte Carlo analysis.

Obviously, some simplifications must be achieved if these uncertainties are to be reflected in the predictions of the model. In all the calculations on time to sensitization that have been published the experimental uncertainties have not been accounted for. These calculations only provide the mean value of the time and give no indication of the spread in the time to sensitization that is a highly significant factor for a probabilistic analysis.

Both the anticipated variations in composition and the

uncertainties in the data must be part of any acceptable analysis. This does not include the variations in heat treatment. In general, the heat treatment will be very variable and not amenable to quantitative assessment, consequently it is possible that model calculations will predict a time to sensitization that is longer than will occur in practice. There seems to be no remedy for this problem other than to invoke a conservative criterion.

Other Information

I am enclosing three (3) copies of the Voucher for Professional Services for your approval.

As of 12 March 1988 I have charged 90 days of the 130 authorized.

If you have any questions please feel free to call me.

Sincerely,

Robert B Moler

Robert B. Moler

enc: vouchers