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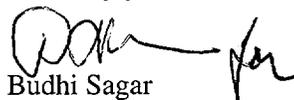
Subject: Programmatic review of Materials Research Society 25<sup>th</sup> International Symposium on the Scientific Basis for Nuclear Waste Management paper titled "Evolution of Solution Chemistry Through Interactions with Waste Package Internal Structural Components"

Dear Mrs. DeMarco:

Attached is the paper to be presented at the Material Research Society (MRS) 25<sup>th</sup> International Symposium on the Scientific Basis for Nuclear Waste Management to be held on November 26–29, 2001 in Boston. The paper is focused on the experimental investigations of changes in the solution chemistry through interactions with the proposed waste package internal structural components using a test cell that simulates the internal geometry of the waste package. High concentrations and a significant pH reduction were observed inside pits of Type 316L stainless steel. Existing agreements between the NRC and the DOE cover the path forward for resolving this subissue. Note the information presented in this paper has been abstracted from IM 01402.571.180 titled "Effect of In-Package Chemistry on the Degradation of the Vitrified High-Level Radioactive Waste and Spent Nuclear Fuel Cladding" and has been previously approved by the NRC staff.

Please contact Yi-Ming Pan at (210) 522-6640 if you have any questions regarding this paper.

Sincerely yours,



Budhi Sagar  
Technical Director

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Enclosure

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## Evolution of Solution Chemistry Through Interactions with Waste Package Internal Structural Components

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### ABSTRACT

The chemistry of the aqueous environment inside any breached waste packages is critical to the release of radionuclides from the waste packages for high-level waste disposal. A corrosion test cell that simulates some aspects of the internal geometry of the waste packages has been designed to investigate changes in the in-package solution chemistry. A series of tests was conducted to evaluate solution chemistry variations as a function of applied potential and temperature using a specimen of Type 316L stainless steel with a predrilled hole as a simulated pit. A micro-syringe was used to extract solutions from inside and outside the pit. The solutions were analyzed for cation concentrations using capillary electrophoresis, and the pH was measured using a micro-electrode. Preliminary measurements showed substantially high cation concentrations inside the pit due to anodic dissolution of Type 316L stainless steel. The solution pH became considerably acidic, reaching a value of 2.6. These results suggest that interactions of waste package internal structural components with incoming water may have significant influence on the evolution of water chemistry and the subsequent corrosion of waste forms such as spent nuclear fuel.

### INTRODUCTION

The composition of the groundwater entering breached waste packages can be influenced and modified by natural processes such as evaporation, reactions with host rock, and reactions with components of the engineered barriers such as drip shield and waste package materials. Variables such as pH, carbonate concentration, and redox potential would be influenced by interactions of groundwater with engineered barriers in any repository and could have a substantial effect on waste package and waste form corrosion. The U.S. Department of Energy (DOE) evaluation of the potential evolution of the in-package chemistry is based on calculations performed with a numerical code, EQ 3/6, that simulates the reaction of fluids with waste forms and waste package internal components after the occurrence of the thermal pulse [1]. The DOE analysis showed that the corrosion of inner waste package materials could result in relatively large changes in the fluid chemistry, and relatively low pH values can be expected as a result of corrosion of stainless steel structural components, specifically because of chromium oxidation to  $\text{Cr}^{6+}$  species.

One of the main concerns in evaluating the DOE analysis is the spatial variation in chemistry that is likely to occur inside waste packages and result in local pH values considerably more acidic than those calculated based on a volume averaged mass. Pitting and crevice corrosion are localized forms of attack that result from the breakdown of passive film caused by the evolved aggressive solution chemistry at pit and crevice areas. The evolved solutions are known to be highly concentrated mixtures of various metal-ion complexes. A few studies have

considered the speciation of solution inside pits of stainless steels [2,3]. Additionally, the pH in pits and crevices differs from bulk pH values because the anodic dissolution reactions become spatially separated from the reduction reactions. Reduction of the pH in pitting and crevice corrosion of stainless steels has been reported in a number of investigations [4-6]. The objective of this paper is to provide a summary of the preliminary results of our experimental investigations on the effect of some potential waste package internal structural components on the evolution of the in-package solution chemistry.

## EXPERIMENTAL

The in-package chemistry tests were conducted in an electrochemical cell, shown schematically in figure 1, equipped with a platinum counter electrode and a Luggin probe connected to a saturated calomel electrode (SCE). Test specimens were machined from mill-annealed Type 316L stainless steel (Fe-18Cr-12Ni-2.5Mo) plates, having a 33.0-mm diameter well and a 0.4-mm diameter, 6.35-mm deep hole as an artificial pit that simulates some aspects of the internal geometry of the proposed waste packages. The initial solution used for the experiments was 0.028 M  $\text{Cl}^-$  (as KCl). The chloride concentration of the initial solution is similar to that obtained from the evaporation experiments of synthetic J-13 Well water conducted by the DOE [7]. Initially, 4 mL of solution was added to the well, resulting in an exposed surface area of the specimen to the test solution of approximately  $11 \text{ cm}^2$ . The solution was heated using two cartridge heaters inserted into drilled holes in the specimen, and the temperature was monitored by a resistance temperature detector connected to a temperature controller.

In initial tests, specimens were held potentiostatically at various potentials for 0.5 hour at temperatures of 20, 60, and 90 °C while the current density was recorded. From the current density data a range of potentials was selected for additional experiments in which solution extractions were made to study solution chemistry variations. These tests were performed at 20 °C at different potentials for a period of 24 hours. At the end of each test, a micro-syringe was used to extract approximately 5  $\mu\text{L}$  of solution from inside the pit, followed by a second extraction of 25  $\mu\text{L}$  of solution from outside the pit. The cation concentration of the solutions was analyzed using capillary electrophoresis, and the pH was measured using a silver-silver chloride microelectrode (Model MI402, Microelectrodes Inc.). Ionic speciation in capillary electrophoresis was determined based on differences in the ionic migration time of the species present in the solution under an applied electric field, in this case 20 kV. Quantitative analysis was performed by comparison of peak areas to those measured on samples of known concentration. All cations were analyzed using the method described by Krol, et al. [8]. For pH measurements, the microelectrode was connected to a pH/selective ion meter and calibrated using standard buffer solutions before and after the measurements to verify the accuracy of the results.

## RESULTS

**Electrochemical Tests** — Anodic current densities for the dissolution of Type 316L stainless steel were measured potentiostatically in 0.028 M  $\text{Cl}^-$  solution at temperatures of 20, 60, and 90 °C, respectively. A representative plot of the current density-versus-time curves for the 60 °C tests is shown in figure 2. As seen in the plotted current density changes with time,

two different types of current evolution behavior were observed. In the first type, the anodic current density decreased with time during the initial potentiostatic step from the open circuit potential and then rapidly reached a steady state of constant current density. This type of current response, as observed for all tests at 20 °C, is characteristic of anodic passivity. The steady-state current density was in the range of  $4 \times 10^{-7}$  to  $3 \times 10^{-6}$  A/cm<sup>2</sup>. The second type of current response was an increase of current density with time as a result of breakdown of the passive film and enhanced anodic dissolution. This behavior is illustrated by the current curves for the 60 °C tests at potentials of 150 and 200 mV<sub>SCE</sub> in figure 2 and also for the 90 °C tests at potentials of 0 and 100 mV<sub>SCE</sub>. High anodic dissolution current densities were observed in all these cases at the conclusion of the tests. In the 60 °C test at 200 mV<sub>SCE</sub>, the final current density was as high as  $1 \times 10^{-2}$  A/cm<sup>2</sup>. Tests at 60 °C applying 100 mV<sub>SCE</sub> (figure 2) and 90 °C applying -100 mV<sub>SCE</sub> showed predominantly the first type of current response; however, several large current spikes were observed, suggesting periodic events of passivity breakdown and repassivation without an increase in the mean value of the current density.

All the steady-state and final anodic current densities (depending on the type of current response) are shown in figure 3 as a function of potential at the various temperatures for all the tests conducted. As is evident in figure 3, passive corrosion was observed at all temperatures when the applied potential was not greater than a critical value that depends on temperature. Critical potentials at which the current density increases significantly were observed in both 60 and 90 °C tests, indicating the onset of enhanced anodic dissolution. A significant decrease in the critical potential can be seen as the temperature increases from 60 to 90 °C. However, at 20 °C, current density gradually increased with increasing potential and no critical potential was observed. Integration of the current with time gives a total charge, which is a reliable measure of the total dissolution of the specimen. The plots of the effects of temperature and potential on total charge also exhibit a temperature-dependent critical potential similar to that observed for the current density variations in figure 3.

**In-Package Solution Chemistry Measurements** — In-package chemistry tests aimed at evaluating solution chemistry variations were performed at 20 °C by holding the specimen at different potentials for 24 hours. Capillary electrophoresis analyses of the solutions extracted from both inside and outside the pit did not detect the presence of any species released from the test specimen except for the test at 200 mV<sub>SCE</sub>. The measured cation concentrations from the anodic dissolution of Type 316L stainless steel at 200 mV<sub>SCE</sub> and 20 °C are listed in table 1. It is clearly seen in table 1 that metal concentrations inside the artificial pit are much higher than those outside the pit. Preferential dissolution of Type 316L stainless steel was observed for such conditions. The measured concentrations of chromium and nickel were much lower than the alloying contents in Type 316L stainless steel, particularly the chromium species. Because the characteristic peak of Cr<sup>3+</sup> is overlapping with that of Fe<sup>2+</sup> in the capillary electrophoresis spectrum, the chromium concentration could be underestimated, even though a series of solution dilutions was attempted.

The extent of preferential dissolution was evaluated using a selectivity coefficient, Z(M), as discussed by Cavanaugh et al. [5]. In case of Type 316L stainless steel, Z(M) is defined as the ion concentration ratio of component M and iron in solution divided by the weight percent ratio of component M and iron in the alloy. The calculated Z(M) values are also listed in table 1. It is interesting to note that while the solution is more concentrated inside the pit (than outside), the Z values for nickel remain almost constant, suggesting a similar dissolution behavior inside and

Table I. Cation concentrations from anodic dissolution and selectivity coefficient (Z) for Type 316L stainless steel tested at 200 mV <sub>SCE</sub> in 0.028 M Cl <sup>-</sup> solution at 20 °C				
Cation	5 μL Inside Pit Solution		25 μL Outside Pit Solution	
	Concentration (ppm)	Z (M <sub>i</sub> )*	Concentration (ppm)	Z (M <sub>i</sub> )
Fe <sup>2+</sup>	12,900	1.00	550	1.00
Ni <sup>2+</sup>	270	0.12	10	0.10
Cr <sup>3+</sup>	100	0.03	—	—

\*Z(M<sub>i</sub>) = [ppm M<sub>i</sub> / ppm Fe] / [wt.% M<sub>i</sub> / wt.% Fe]

outside the pit. Preferential dissolution measured in this study is contrary to the results reported by Suzuki, et al. [4] and Brossia and Kelly [3], in which no preferential dissolution was observed in either pitting or crevice corrosion of stainless steels. This discrepancy may be attributed to formation of chromium- and nickel-rich corrosion products and surface deposit films.

The current density and total charge as a function of time for the dissolution of Type 316L stainless steel at 20 °C at an applied potential of 200 mV<sub>SCE</sub> is shown in figure 4. Unlike the steady-state current density observed in the 0.5-hour test, the current density increased initially with time, reached a stable high value of  $\sim 1 \times 10^{-5}$  A/cm<sup>2</sup> for a period of 6 hours, and decreased afterward. The high anodic current period resulted in a total anodic charge of 3.38 coulombs at the end of the test. The total charge values were calculated for all the 24-hour tests. Assuming congruent dissolution of the major alloying elements such as Fe<sup>2+</sup>, Cr<sup>3+</sup>, and Ni<sup>2+</sup>, the equivalent weight for Type 316L stainless steel is 25.29 g/equivalent. The total metal ion concentration from electrochemical reactions can be computed by Faraday's law, which states that one Faraday (or 96,489 coulombs) is the quantity of electrical charge required to produce one equivalent. Thus, the total metal ion concentration for the 4-mL solution of the test at 200 mV<sub>SCE</sub> as a result of Type 316L stainless steel anodic dissolution should be 221 ppm, with 155 ppm Fe, 40 ppm Cr, and 26 ppm Ni. Comparison with the measured concentrations in table 1, clearly shows that the measured metal cation concentrations within the pit are much higher than the calculated values, with different orders of magnitude for each species. While the high cation concentrations measured inside the pit are attributed to the spatial variation of the anodic dissolution, the Fe<sup>2+</sup> concentration of 550 ppm measured outside the pit, which is higher than the calculated bulk value, is probably due to mixing of the pit and bulk solutions during the solution extraction process. Given a detection limit of 100 ppb or better for capillary electrophoresis analysis of cations, the absence of metal cations in the solutions extracted from the tests at potentials less than 200 mV<sub>SCE</sub> is unexpected, in contradiction with the calculations using the total charges measured for each of the tests.

The pH values of the solutions extracted from inside the pit were measured using a silver-silver chloride microelectrode. The pH of the pit solutions remained almost the same during the electrochemical tests ( $\sim 5.6$ ) except for the test at 200 mV<sub>SCE</sub>. The solution pH became considerably acidic reaching a value of 2.61. Solution pH was also calculated by hydrolysis reactions based on the measured ion concentrations from capillary electrophoresis analysis. A minimum value of 2.51 was calculated using the Cr<sup>3+</sup> concentration and the associated full hydrolysis reaction, in good agreement with the microelectrode measurements. It is apparent

that dissolution of the metal in the pit generates the metal cations that then hydrolyze and acidify the pit solution. As reported by Suzuki, et al. [4], analyses of pH changes in corroding cavities of stainless steels have shown a significant pH reduction in solution within the cavities mainly due to  $\text{Cr}^{3+}$  hydrolysis.

## DISCUSSION AND CONCLUSIONS

Preliminary in-package chemistry studies indicate that because the internal geometry of any waste packages may have many tightly packed regions, interactions of waste package internal structural components with the incoming water may have significant influence on the evolution of water chemistry and the subsequent corrosion of waste forms such as spent nuclear fuel. High cation concentrations and a pH of 2.6 were measured in the pit solution using an initial solution of 0.028 M  $\text{Cl}^-$  and holding the potential of the Type 316L stainless steel specimen at 200 mV<sub>SCE</sub> for 24 hours. In contrast with the results of the DOE calculations that attribute the pH decreases to chromium oxidation, the acidification within the pit in the present experiments is dominated by the hydrolysis of chromic ions.

It is important to notice the potential consequences of the evolved in-package chemistry environments. Pitting corrosion of Zircaloy is known to occur in chloride solutions above a critical potential. This potential, equivalent to the repassivation potential, is attained in the presence of reducible species such as  $\text{Fe}^{3+}$ . It is anticipated that  $\text{Fe}^{2+}$  generated by corrosion of stainless steel components can be oxidized to  $\text{Fe}^{3+}$  in solution by oxidizing radicals or  $\text{H}_2\text{O}_2$  as the stable product of the  $\gamma$ -radiolysis of water. The combined process of migration of chloride ions and hydrolysis of the dissolved metal ions within a pit will result in a decrease of the pH and an increase of the chloride ion concentration. Pitting of spent nuclear fuel cladding may occur during such environmental conditions. The contribution of cladding as an additional metallic barrier to the release of radionuclides to the near-field environment could be, therefore, substantially diminished.

Premature cladding failure could increase the quantity of commercial spent nuclear fuel exposed to water and available for dissolution. Local decrease of pH may affect the dissolution rate of the irradiated  $\text{UO}_2$  matrix locally and, hence, the local release rate of highly soluble radionuclides such as Tc-99. From this investigation, it is recommended that additional work, both theoretical and experimental, be conducted to determine the ranges of solution chemistry that could exist inside waste packages and the consequences of such evolved environmental conditions. Alternative models taking into account electrochemical reactions coupled to transport processes also should be considered in the process level analyses and included, if needed, in the model abstraction. As part of the issue resolution process, DOE has agreed to provide additional analyses and documentation to address these questions regarding potential in-package chemistry to produce an adequate basis for the U.S. Nuclear Regulatory Commission (NRC) to conduct any licensing review for a proposed high-level waste repository.

## ACKNOWLEDGMENTS

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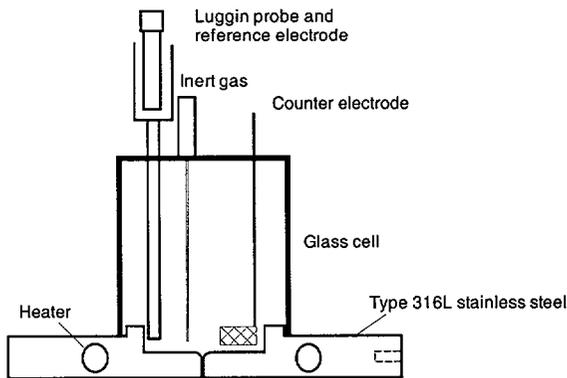


Figure 1. Schematic of the electrochemical test cell that simulates aspects of the internal waste package geometry

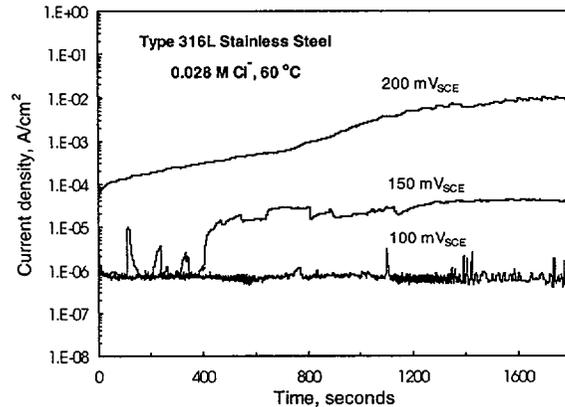


Figure 2. Anodic current density for Type 316 L stainless steel under potentiostatic conditions in 0.0028 M Cl<sup>-</sup> solution at 60 °C

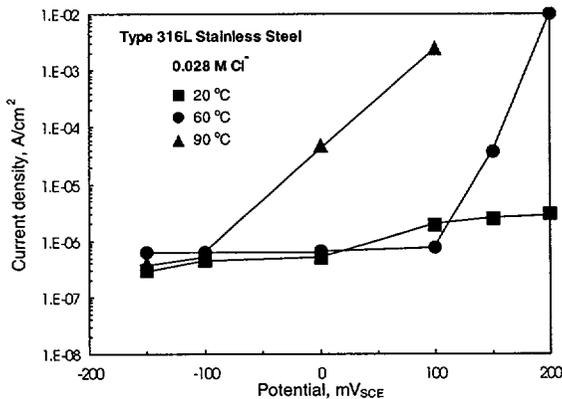


Figure 3. Anodic current density for Type 316 L stainless steel in 0.0028 M Cl<sup>-</sup> solution for 1800 seconds at various temperatures

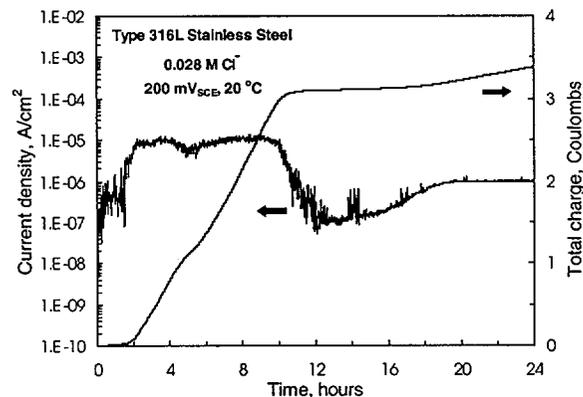


Figure 4. Anodic current density and total charge for Type 316 L stainless steel at 200 mV<sub>SCE</sub> in 0.0028 M Cl<sup>-</sup> solution at 20 °C