

M96050429

---

# Corrosion of Mild Steel in Simulated Cesium Elution Process Solutions

M. R. Elmore

---

September 1996

Prepared for the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory  
Operated for the U.S. Department of Energy  
by Battelle



MASTER

MASTER

PNNL-11284

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

*operated by*

BATTELLE

*for the*

UNITED STATES DEPARTMENT OF ENERGY

*under Contract DE-AC06-76RLO 1830*

Printed in the United States of America

Available to DOE and DOE contractors from the  
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;  
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,  
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161



This document was printed on recycled paper.

## **Corrosion of Mild Steel in Simulated Cesium Elution Process Solutions**

M. R. Elmore

September 1996

Prepared for  
the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory  
Richland, Washington 99352

**DISCLAIMER**

**Portions of this document may be illegible  
in electronic image products. Images are  
produced from the best available original  
document.**

## Summary

The West Valley Support Project (WVSP) is being conducted by Pacific Northwest National Laboratory (PNNL) to help meet technology needs for the West Valley Demonstration Project and to provide support to the subsequent site cleanup and stabilization activities for West Valley Nuclear Services, West Valley, New York. A part of these activities involves removing residual cesium in Tank 8D-1, a carbon steel underground storage tank, after initial waste retrieval operations. In-tank oxalic acid elution of cesium-loaded zeolite is being evaluated as one approach for this process.

The work reported here involved evaluating the potential for increased corrosion of Tank 8D-1 during the cesium elution process, because oxalic acid is corrosive to carbon steel. This evaluation included laboratory-scale nonradioactive corrosion tests with mild steel (ASTM A516 Grade 55) specimens. Test parameters included temperatures ranging from 27°C to 50°C, and acid concentrations of 4 wt% and 8 wt% oxalic acid.

The tests were conducted for durations of 2, 4, and 6 days, which represent expected processing cycle times. These tests also evaluated agitation and the effects of other salts ( $\text{NaNO}_2$  and  $\text{NaNO}_3$ ) in solution on corrosion rate. The results from these tests were compared with similar results from earlier corrosion tests conducted in September 1995 (all at 50°C) for durations of 1, 2, and 3 weeks.

The results of the corrosion testing discussed here are summarized below:

- In general, the results of recent tests are in agreement with the September 1995 test results.
- Even at relatively modest temperatures (50°C), the corrosion rate of A516 Grade 55 mild steel test specimens in oxalic acid is quite high (approximately 150 mils per year, or  $\sim 3.8$  mm/y).
- Temperature had the most significant effect on corrosion of the mild steel specimens. A three- to fourfold increase in corrosion was noted with increase in temperature from ambient ( $\sim 27^\circ\text{C}$ ) to 50°C.
- Whereas earlier tests gave corrosion rates that were significantly higher in the 4 wt% acid solution than with the 8 wt% acid solution, the recent tests did not show a similar inverse dependence on acid concentration.
- Corrosion resulted in a very rough surface appearance for most conditions, indicating potential for localized corrosion such as pitting and crevice corrosion. However, the exposure times used were apparently too short to initiate and develop characteristic pitting.

- Although agitation was expected to increase steel corrosion, results of stirred vs. unstirred tests at 50°C were quite similar. The evaluation of agitation on corrosion did not include the potential for erosion by zeolite particulate, which may contribute to steel thinning due to the high velocity fluid (zeolite slurry) jets produced by the mobilization pumps.
- In addition to oxalic acid-only solutions, two of the recent tests included the addition of other salts that are expected to be present in the tank: dilute concentrations of  $\text{NaNO}_2$  and  $\text{NaNO}_3$  in the 4 wt% and 8 wt% oxalic acid solutions. At the low concentrations tested, the effect of these salts on corrosion was inconclusive.

# Contents

Summary .....	iii
1.0 Introduction .....	1.1
2.0 Experimental Work .....	2.1
2.1 Test Materials .....	2.1
2.2 Test Apparatus .....	2.2
2.3 Test Procedure .....	2.2
3.0 Results/Discussion .....	3.1
4.0 Conclusions and Recommendations .....	4.1
4.1 Conclusions .....	4.1
4.2 Recommendations .....	4.2
5.0 References .....	5.1

## Figures

3.1 Corrosion Rate vs. Exposure for Mild Steel Specimens in 4 wt% and 8 wt% Oxalic Acid Tested at 27°C and 50°C .....	3.2
3.2 Corrosion Rate vs. Exposure for Mild Steel Specimens in 8 wt% Oxalic Acid at 50°C Comparing Stirred with Unstirred Tests and Added Salts with No Salts .....	3.3

## Tables

2.1 Test Matrix for Oxalic Acid Corrosion Tests, FY 1996 .....	2.1
3.1 Uniform Corrosion Rates in Mills Per Year for Duplicate Steel Specimens .....	3.2

## 1.0 Introduction

The West Valley Support Project (WVSP) being conducted by Pacific Northwest National Laboratory (PNNL)<sup>(a)</sup> is helping to meet technology needs for the West Valley Demonstration Project and is providing support to subsequent site cleanup and stabilization activities for West Valley Nuclear Services, West Valley, New York. One part of these activities involves removing residual cesium in Tank 8D-1 following initial waste retrieval operations. Tank 8D-1, a carbon steel underground storage tank, contains cesium-loaded zeolite generated by a supernatant decontamination operation involving zeolite ion-exchange. In-tank oxalic acid elution of the cesium-loaded zeolite is one approach being evaluated by PNNL to remove cesium from Tank 8D-1.

Because oxalic acid is corrosive to carbon steel, the main objective of the effort reported here was to evaluate the potential for increased corrosion of Tank 8D-1 during the cesium elution process. Laboratory-scale nonradioactive corrosion tests were conducted with mild steel specimens to determine potential corrosion rates in simulated cesium eluting solutions. Test parameters included temperatures ranging from ambient (~ 27°C) to 50°C, and acid concentrations of 4 wt% and 8 wt% oxalic acid.

Initial corrosion tests were conducted in September 1995 for durations of 1, 2, and 3 weeks. All of the initial tests were performed at 50°C. Results of those tests were reported in a combined FY 1995 summary report of cesium elution testing (Sills et al. 1996). More recently (FY 1996), tests were conducted for durations of 2, 4, and 6 days, which more closely match expected processing cycle times. These tests also evaluated agitation and the effects of other salts (NaNO<sub>2</sub> and NaNO<sub>3</sub>) in solution on corrosion rate. This report describes the results of the FY 1996 laboratory corrosion tests.

This activity was designated Impact Level II. As such, all work conducted under this activity was performed in accordance with Impact Level II quality assurance requirements as defined by PNNL QA Plan ETD-007, Rev 0.

---

(a) Operated for the U. S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

## 2.0 Experimental Work

The approach used for the oxalic acid corrosion testing involved exposing mild steel corrosion specimens to environments simulating the anticipated conditions in the waste tank(s) during cesium elution from zeolite particles. A total of seven tests were conducted. Table 2.1 summarizes the experimental conditions for each test. The two test temperatures (27°C and 50°C) were selected to bracket the expected temperature range for in-tank processing. Two oxalic acid concentrations (4 wt% and 8 wt% acid), the same concentrations used for earlier testing, were selected to bracket the anticipated processing range. The test solutions in each vessel were removed and replaced with fresh acid solution after each 2-day cycle of specimen exposure, simulating proposed multiple contacts of the zeolite with batches of oxalic acid. Following exposures ranging from 2 to 6 days, the specimens were removed from the vessels, cleaned, and examined for corrosion. General corrosion rates were calculated from weight loss measurements. The specimens were visually examined under a microscope to check for pitting. No pitting was observed on any of the specimens.

Table 2.1. Test Matrix for Oxalic Acid Corrosion Tests, FY 1996

Conditions	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
Oxalic Acid Conc.	4 wt%	4 wt%	8 wt%				
Temperature	27°C	50°C	27°C	50°C	50°C	50°C	50°C
Agitation	No	No	No	No	Yes	Yes	No
Salts Addition <sup>(a)</sup>	No	No	No	No	No	Yes	Yes

(a) Salts addition consists of 0.06 wt% NO<sub>2</sub><sup>-</sup> and 0.02 wt% NO<sub>3</sub><sup>-</sup>, added as Na salts to match salt additions used in earlier cesium elution testing.

### 2.1 Test Materials

The materials used for this testing included the oxalic acid solutions and ASTM A516 Grade 55 mild steel corrosion specimens (taken from the same batch of specimens used in previous tests). The samples were procured from Metal Samples Co., Munford, Alabama, and all were prepared from the same "heat" of steel. The chemical composition of the steel was given as follows: C (0.12 wt%), Mn (0.63 wt%), P (0.01 wt%), S (0.026 wt%), Si (0.26 wt%), and Fe (balance). The oxalic acid solutions were prepared by dissolving crystalline oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) in deionized water. Fresh 4 wt% and 8 wt% acid solutions were prepared for each changeout, replacing the previous cycle's test solutions. Also, NaNO<sub>2</sub> and NaNO<sub>3</sub> salts were added to the acid solutions for Tests 6 and 7.

The corrosion specimens were flat, rectangular-shaped with a mounting hole drilled through the center. The dimensions of each specimen were measured with digital calipers to the nearest 0.001 in. (1 mil), or 0.0254 mm. Typical specimen dimensions were 2.0 in. x 0.75 in. x 0.13 in. (~ 50.8 mm x 19.0 mm x 3.3 mm). An initial thorough cleaning of the specimens was performed by brushing them with a soft bristle brush in soap and water, followed by deionized water rinse, acetone rinse, and air dry. The specimens were then weighed on a four-place analytical balance to the nearest 0.0001 g. Typical initial weight of the specimens was ~23 g.

## 2.2 Test Apparatus

The test apparatus used for the static tests consisted of four ~4-L Teflon-lined vessels with removable lids. These vessels were partially immersed in and heated by a controlled temperature oil bath and were fitted with reflux condensers to minimize evaporation. The vessel temperatures were monitored with thermocouples inserted through ports in the lids of the vessels. The vessels used for the stirred tests were slightly smaller to fit better under the stirring apparatus and were heated by resistance-type heating mantles. The stirring mechanism was a Bird-Phipps multiple stirrer apparatus that permitted several vessels to be stirred simultaneously (in this case, 200 RPM). The steel specimens were fastened horizontally to Teflon stir shafts, and suspended and rotated in the acid solutions by the stirring apparatus.

## 2.3 Test Procedure

Once the specimens were cleaned and weighed, they were suspended on Teflon rods in the test vessels. The vessels were assembled and sealed; oxalic acid solution was added; and the oil bath was adjusted to maintain the vessels at 27°C or 50°C. Throughout the test, the vessels were monitored to ensure that the solution temperature was constant and that the solution did not evaporate.

One set of specimens was removed from each vessel after 2 days exposure. The removed set of specimens was replaced with new specimens, and the test continued for 4 more days. In this manner, one set of specimens was exposed for 2 days; a second set was exposed for 4 days; and a third set was exposed for the entire 6 days of the test. Acid solutions were replaced following 2 and 4 days of exposure. Solutions were replaced to simulate possible multiple cycles of acid contact and decant during actual processing, which would represent worst-case conditions in terms of tank corrosion.

The examination of the corrosion specimens included 1) observing the general appearance of the specimens as they were removed from the vessels, 2) cleaning the specimens in an inhibited acid cleaning solution to remove corrosion products, 3) weighing the cleaned specimens to then calculate corrosion rate from the weight loss, and 4) visually examining the specimens with the aid of a microscope for any localized corrosion. Because pitting was not observed, no pit depth measurements were made.

### 3.0 Results/Discussion

All specimens removed from the tests had accumulations of yellow precipitate on their surfaces. This precipitate had previously been identified by x-ray diffraction (XRD) analysis as Humboldtine, a common crystalline form of iron oxalate (Sills et al. 1996). No additional XRD analyses of the precipitates were performed for these tests. In addition to accumulations on the specimens, precipitate was also observed in the bottoms of the vessels at the end of each of the 2-day intervals. The accumulation of iron oxalate on the specimens did not vary noticeably with acid concentration as it had in earlier testing, nor was there a noticeable difference in precipitate accumulation as a function of temperature between 27°C and 50°C.

In previous corrosion testing at 8 wt% oxalic acid and at 50°C, there was an accumulation of a crystallized material at the liquid interface, which was identified later by XRD as oxalic acid crystals. Apparently the solubility of the oxalic acid had been affected during the test. Solubility data for oxalic acid gives a solubility limit of ~12 wt% at 25°C (Dean 1985). No information was found to suggest the solubility changes inversely with temperature. Therefore, especially at 50°C, the solubility of oxalic acid should have been at least 8 wt%. The buildup of iron oxalate in solution has been considered as a possible explanation. No precipitation of oxalic acid was noted in any of the recent tests at 8 wt% acid and 50°C.

The use of different sources for the oxalic acid was suspected as a possible reason for differences between the two sets of tests. However, samples of the crystalline oxalic acid from both sources were analyzed and found to be ~98% pure oxalic acid with no apparent impurities. (The crystalline oxalic acid is very hygroscopic, and the other ~2% appeared to be absorbed water for both sources.)

After the specimens were cleaned in inhibited hydrochloric acid to remove the corrosion products, the final specimen weights were recorded. Overall corrosion rates were calculated from weight loss determinations. Table 3.1 summarizes the results of the weight loss-derived uniform corrosion rates, showing calculated corrosion rates for duplicate specimens for each test. Corrosion rates are given in mils per year, along with accompanying SI units (mm/y).

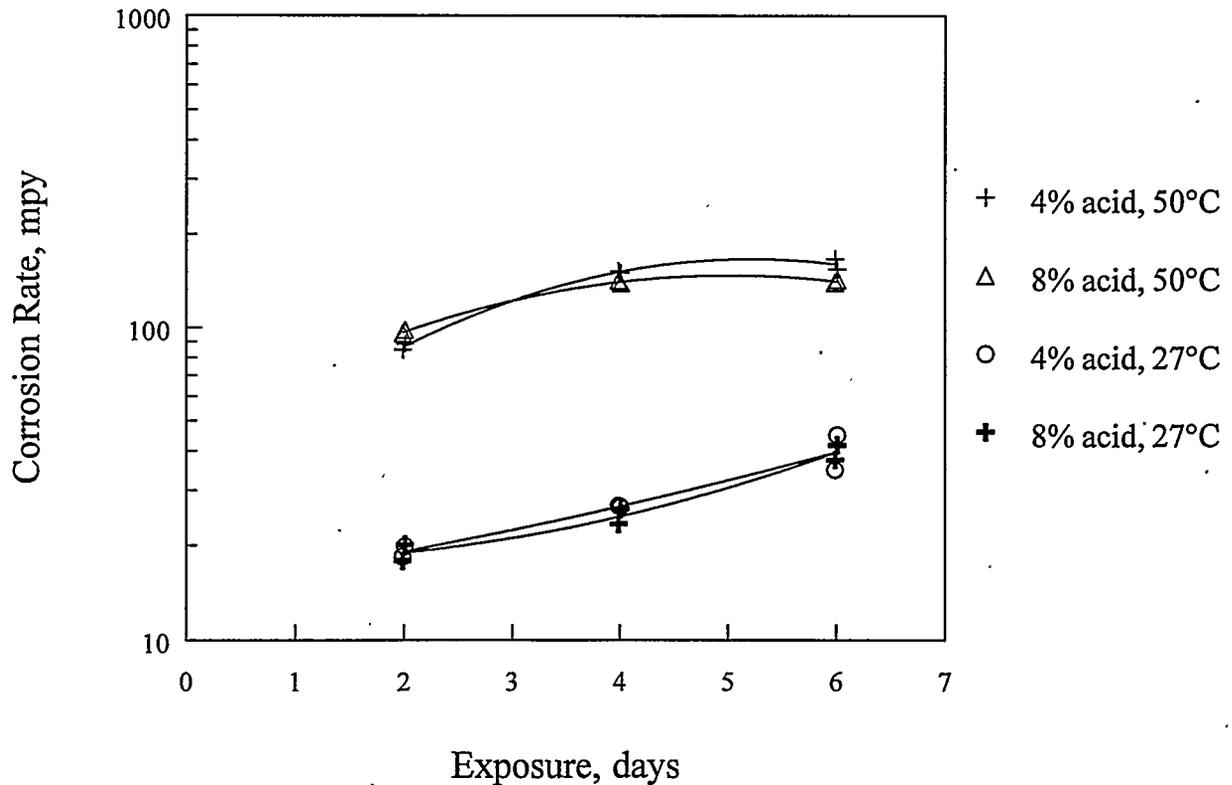
Figures 3.1 and 3.2 show plots of corrosion rate vs. exposure time for the tested conditions. Figure 3.1 shows the effects of temperature and acid concentration on corrosion rate.

Temperature had a very significant effect on corrosion with the rate increasing by a factor of about 3 to 4 as temperature increased from 27°C to 50°C. Doubling the acid concentration, on the other hand, had no significant effect on corrosion (in contrast to earlier tests). The reason for this result has not been identified.

**Table 3.1. Uniform Corrosion Rates in Mills Per Year for Duplicate Steel Specimens<sup>(a)</sup>**

Duration, Days	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
	4 wt%, 27°C Unstirred, No Salts	4 wt%, 50°C Unstirred, No Salts	8 wt%, 27°C Unstirred, No Salts	8 wt%, 50°C Unstirred, No Salts	8 wt%, 50°C Stirred, No Salts	8 wt%, 50°C Stirred, w/Salts	8 wt%, 50°C Unstirred, w/salts
2	18.4 (0.47)	84.8 (2.15)	17.9 (0.45)	95.6 (2.43)	39.1 (0.99)	101.4 (2.57)	43.9 (1.12)
	19.8 (0.50)	88.6 (2.25)	20.1 (0.51)	97.9 (2.49)	38.2 (0.97)	96.1 (2.44)	48.1 (1.22)
4	26.7 (0.68)	151.9 (3.86)	23.4 (0.59)	141.4 (3.59)	56.7 (1.44)	85.8 (2.18)	69.1 (1.76)
	26.5 (0.67)	150.0 (3.81)	26.0 (0.66)	138.9 (3.53)	53.7 (1.36)	81.7 (2.08)	74.2 (1.88)
6	34.8 (0.88)	165.8 (4.21)	37.5 (0.95)	139.3 (3.54)	44.1 (1.12)	80.5 (2.04)	55.0 (1.40)
	45.0 (1.14)	153.8 (3.91)	41.8 (1.06)	142.2 (3.61)	40.9 (1.04)	79.9 (2.03)	58.8 (1.49)

(a) Corrosion rates are shown with accompanying SI units in parentheses (mm/y).



**Figure 3.1. Corrosion Rate vs. Exposure for Mild Steel Specimens in 4 wt% and 8 wt% Oxalic Acid Tested at 27°C and 50°C**

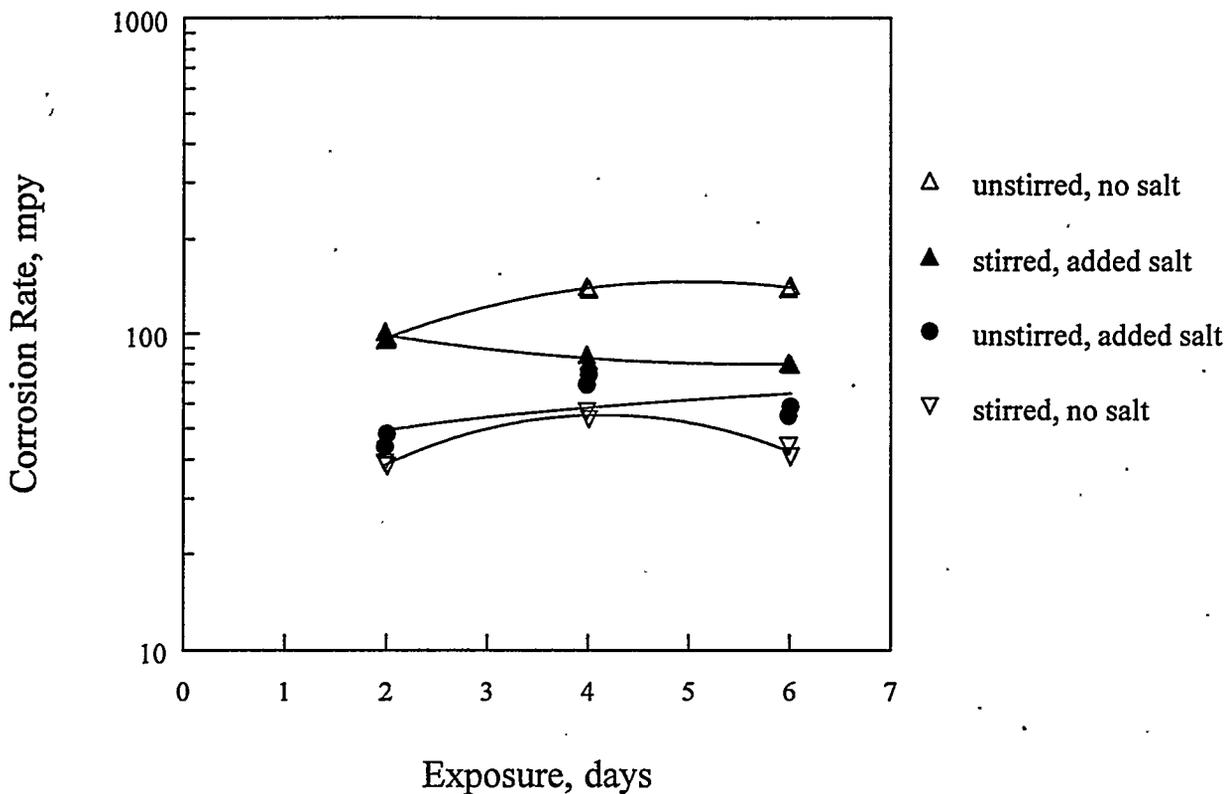


Figure 3.2. Corrosion Rate vs. Exposure for Mild Steel Specimens in 8 wt% Oxalic Acid at 50°C Comparing Stirred with Unstirred Tests and Added Salts with No Salts

Figure 3.2 shows the relative effects of agitation and the presence of low concentrations of other salts on corrosion rate in 8 wt% oxalic acid. Based on the appearance of specimens from earlier unstirred tests, agitation was expected to increase the corrosion rate by increasing diffusion of reactants through the accumulated layer of iron oxalate. Results comparing stirred and unstirred tests in solutions with the added salts appear to confirm the expected behavior. However, for the corresponding tests with no added salts, the results are contrary to the expected behavior. The added salts consisted of 0.06 wt%  $\text{NO}_2^-$  and 0.02 wt%  $\text{NO}_3^-$ , added as Na salts to match salt additions used in earlier cesium elution testing (Sills et al. 1996). Similarly, by comparing the effects of added salts for the stirred tests, corrosion rates are higher with added salts than for no salts. The opposite is true for unstirred tests. This anomalous behavior may mean that the reactions involved in the corrosion of steel in oxalic acid solutions are highly variable in the beginning stages and do not exhibit readily reproducible behavior until after some period of initiation. The short durations of these tests might then accentuate these variations.

It may also be possible that the interdependent solubilities of the various species present in these solutions are responsible for the differences in observed corrosion rates. For instance, oxalic acid readily dissolves iron, but the solubility of iron in oxalic acid is quite low. Therefore, as iron dissolution proceeds, the solubility of iron is quickly exceeded and solid iron oxalate precipitates from solution. If the precipitation occurs immediately at the iron surface, the precipitated iron oxalate may partially mask the surface of the steel and inhibit further corrosion. If the dissolved ferrous ion is able to move farther out into the bulk solution before the precipitate forms, the precipitated iron oxalate may not interfere with subsequent steel corrosion in the same manner. It is possible that, for the given test conditions, some factor or combination of conditions (i.e., very slight differences in solution composition, temperature, oxygen availability, etc.) may significantly affect the solubilities of these species. This possibility has not yet been proven.

The actual tank waste (simulated in these tests with oxalic acid solutions) also includes zeolite particulate, which was not added to the simulated waste solutions. Although the zeolite should not interact chemically with corrosion of the steel, the particulates may contribute to steel thinning due to the high velocity fluid (zeolite slurry) jets produced by the mobilization pumps in Tank 8D-1. The evaluation of agitation on corrosion did not include the potential for erosion by zeolite particulate.

The results of these and earlier tests, along with the unexplained differences, illustrate the importance of adopting a conservative approach in future plans to use in-tank oxalic acid processing to elute cesium from remaining zeolite in Tank 8D-1:

- Perform the processing at as low a temperature as practicable. Temperature has a significant effect on corrosion rate.
- Expect the higher observed corrosion rates (~150 mils per year, or ~3.8 mm/y) to occur during processing. Very short contact times should not present a problem to tank integrity. However, the capability to quickly neutralize the tank contents (e.g., caustic addition) should be immediately available in the event of unforeseen shutdowns, where the tank contents would remain in the tank for an extended period of time.

## 4.0 Conclusions and Recommendations

The following conclusions and recommendations are based on results from continued laboratory-scale testing of oxalic acid corrosion of mild steel.

### 4.1 Conclusions

With some exceptions, the results of tests conducted in FY 1996 are in agreement with the results of similar tests conducted in September 1995. Highest overall corrosion rates were approximately the same for both sets of tests (~150 mils per year, or ~3.8 mm/y). Whereas earlier tests gave corrosion rates that were consistently higher in the 4 wt% acid solution than with 8 wt% acid, this effect was not observed in the recent tests. The reason for this difference between the earlier and recent tests has not been determined. Solubility changes for some of the species in this system (possibly linked to the precipitation of iron oxalate) may be responsible for the apparent differences in steel corrosion rates, but the combination of factors ultimately affecting those solubilities to produce the observed results has not been identified.

Temperature had the most significant effect on corrosion of the mild steel specimens: For the unstirred tests, a three- to fourfold increase in corrosion was noted with increase in temperature from ambient (~27°C) to 50°C. Even at relatively modest temperatures (50°C), the corrosion rate of A516 Grade 55 mild steel test specimens in the oxalic acid solutions is quite high. The highest rates observed were approximately 150 mils per year.

Corrosion resulted in a very rough surface appearance for most conditions, indicating there is some potential for localized corrosion such as pitting and crevice corrosion. The surface roughness of the specimens was even more pronounced in the previous longer duration tests. Some of the nonuniform corrosion was characterized as pitting on specimens from the previous tests, but no pitting was observed on the recent test specimens, probably because of the shorter durations used for the recent tests.

Although agitation was expected to increase steel corrosion, this effect was not observed. The corrosion rate is apparently limited by kinetics rather than by diffusion of reactants through the precipitate layer that accumulates on the surfaces of the specimens.

Besides oxalic acid-only solutions, tests were conducted to evaluate the effects of other salts expected to be present in Tank 8D-1. The low concentrations of  $\text{NaNO}_2$  and  $\text{NaNO}_3$  tested did not appear to increase corrosion of the steel. Consequently, the presence of these other salts in the actual waste solutions should not significantly affect corrosion of the tank.

It is uncertain how closely results of these tests predict the effects oxalic acid would have on Tank 8D-1, since the present condition of the tank has not been well characterized. However, the tank

is expected to have moderate to severe corrosion on the inside and outside surfaces, whereas the test specimens initially had clean bright metal surfaces. Oxalic acid is expected to dissolve corrosion products on the tank surface, depending on the conditions of the contact (Sills et al. 1996). Therefore, the rate of oxalic acid dissolution of the already corroded tank wall may differ from the rates observed on the initially smooth, clean test specimens.

## 4.2 Recommendations

Certain unexpected differences in the results of the two sets of tests discussed here have not yet been explained. Therefore, it is recommended that a corrosion rate of ~150 mils per year (~3.8 mm/y) be assumed for planning the implementation of oxalic acid processing of cesium-loaded zeolite remaining in Tank 8D-1.

As processing parameters become better defined, the conditions used for these tests may no longer represent expected processing conditions. Final confirmatory corrosion testing should be performed at the selected process conditions (i.e., maximum expected processing temperature, acid concentration, presence of other minor chemical components, longest expected contact duration, and number of process cycles).

## 5.0 References

Dean, J. A. (ed.) 1985. *Lange's Handbook of Chemistry*. 13th edition. McGraw-Hill Book Company, New York.

Sills, J. A., et al. 1996. *Fiscal Year 1995 Laboratory Scale Studies of Cs Elution in Tank 8D-1 and Sludge Dissolution in Tank 8D-2*. PNNL-10945, Pacific Northwest National Laboratory, Richland, Washington.

## Distribution

No. of Copies		No. of Copies	
<b>Offsite</b>		<b>2</b>	<b>Westinghouse Hanford Company</b>
<b>3</b>	West Valley Nuclear Services Co., Inc. P.O. Box 191/10282 Rock Springs Rd. West Valley, NY 14171-0191 C. S. King D. C. Meess J. Y. Chang		J. L. Nelson R1-30 J. A. Voogd H5-03
		<b>24</b>	<b>Pacific Northwest National Laboratory</b>
			E. G. Baker P8-38 J. L. Buelte P7-41 M. L. Elliott (3) P7-41 M. R. Elmore (7) K3-75 S. R. Gano K3-75 A. L. Lund P8-15 G. K. Patello P7-28 R. L. Russell P7-28 H. D. Smith P7-28 Information Release (7)
<b>Onsite</b>			
	<b>DOE/Richland Operations Office</b>		
	R. A. Gilbert K6-51		