# EROSION CORROSION OF TANKS DURING SOLID WASTE RETRIEVAL

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## ABSTRACT

Several million gallons of radioactive liquid and solid wastes are being stored in doubleshell tanks (DSTs) at the Department of Energy's Hanford Site in southeastern Washington. These wastes will be retrieved and processed to create a waste form suitable for permanent disposal. Solids in some of these tanks have been settling for many years, creating sludge layers on the tank floors, and must be resuspended in the supernatant liquids before waste retrieval can begin. The waste will be retrieved from a tank using a submerged slurry pump in combination with one or more rotating slurry jet mixer pumps. The mixer pumps generate two opposing highvolume, highvelocity jets of tank fluid and direct the jets at the settled solids. As the pump is slowly rotated, the jets sweep out arcs of fluid that suspend and mix the settled solids with the waste fluid. There is concern that the action of the jets will accelerate corrosion on the tank floor and wall. The Pacific Northwest Laboratory is performing tests to investigate this possibility. Two nonradioactive simulated wastes [neutralized cladding removal waste (NCRW) and neutralized current acid waste (NCAW)] have been tested to date. The test results are reported here. Accelerated corrosion rates due to the action of the high-velocity slurry jets have been measured on samples of the tank material during the tests, but they appear to be low enough to allow the planned retrieval operations to be conducted safely.

## INTRODUCTION

Several million gallons of radioactive, liquid, and solid wastes are being stored temporarily in 28 doubleshell tanks (DSTs) on the Hanford Site in southeastern Washington. About ten different types of such waste, most of them products of the chemical processing of nuclear fuel, are stored in varying amounts in the DSTs. Westinghouse Hanford Company (WHC), the site operations contractor, will retrieve these wastes and process them into immobile waste forms suitable for permanent disposal. However, solids in some of the tanks have been settling for many years, creating a sludge layer on the tank floor. These sludges must be resuspended in the supernatant liquid to facilitate retrieval of solids from the tank.

The current plan for suspending the solids in the DSTs uses rotating submerged slurry pumps (also referred to as mixing pumps). These pumps will create two opposing highvelocity jets of tank fluid and direct the jets at the settled solids. As the pump is slowly rotated, the jets sweep out arcs of fluid that suspend and mix the settled solids with the waste fluid. The required jet velocity will depend on the waste properties; for most wastes, the pumps will produce a jet discharge velocity of 15 m/s (50 ft/s). Fig. 1 depicts a typical equipment arrangement for retrieving DST waste.

There is a concern that the action of the jets, as they sweep across the tank wall and floor, may accelerate the rate of wall thinning by a combination of erosion and corrosion. An unacceptable erosioncorrosion rate may require a change in the retrieval strategy, with the possibility that mixing pumps may not be the best alternative.

Researchers at the Pacific Northwest Laboratory (PNL) have been studying the effects of waste fluid jets on the erosioncorrosion rates of DST steel for WHC. Two nonradioactive simulated wastes have been tested to date: neutralized cladding removal waste (NCRW) and neutralized current acid waste (NCAW). This paper discusses final results from the erosioncorrosion test using simulated NCRW and preliminary results from the test using simulated NCAW. It is planned to test at least two more waste types.

## EROSION-CORROSION

To minimize corrosion, the acid wastes produced during processing of nuclear fuel are "neutralized" to pH $>13$ before being stored in the DSTs. The corrosion rate of A-516 or A-537 carbon steel in alkaline (pH $> 13$) NCRW and NCAW is normally low, typically $<0.5$ mil/yr (1mil = 0.001in = $25.4 \times 10^{-6}$m), because the iron in the steel reacts with the solution in the tanks to form a protective passive surface film of iron oxide or hydroxide in quiescent solution (1,2,3,4). However, the action of the fluid jet, which contains abrasive resuspended solids, may affect the passive film and underlying metal as it sweeps the tank floor or impinges on a tank wall.

Several mechanisms for enhanced corrosion can be postulated for this scenario. The liquid flow (with or without particles) increases the mass transport of ionic species to

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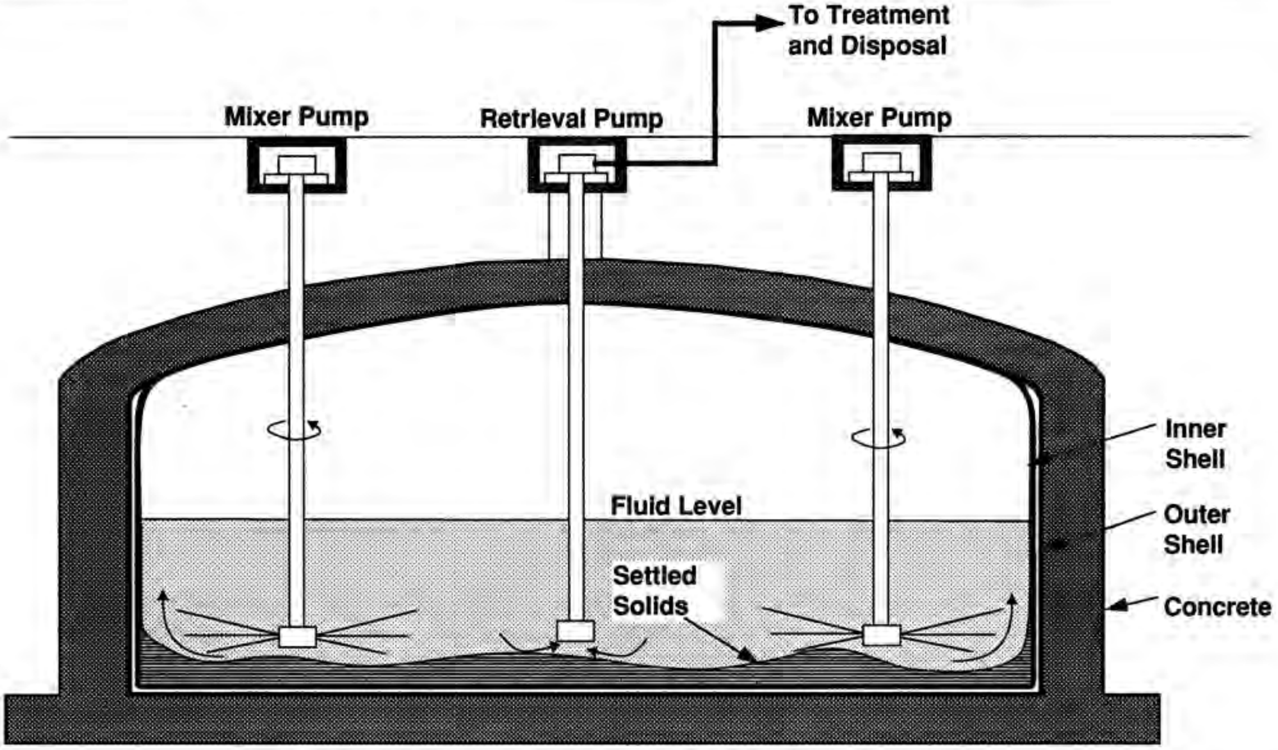

Fig. 1. Typical Equipment Arrangement for DST Waste Retrieval.

the surface and effectively changes the concentration of reactive species at the wall. As a consequence, the concentration gradient in the film increases and the corrosion rate increases until a new equilibrium value is reached. Similarly, the increased mass transport can increase the dissolution rate of the film, causing it to become thinner and thus increasing the corrosion rate. Both of these mechanisms, because they involve the transport of chemical species, are expected to follow the rules of mass transport, with the corrosion rate being a function of the Reynolds number, $Re^{(0.58)}$(5). Re is proportional to the fluid velocity past the surface.

In addition, the mechanical action of the particles entrained in the liquid may affect the concentration gradient and mass transport mechanisms. Mechanical effects of the jet can be minimal and involve the film only, or with sufficiently energetic or abrasive particles, can affect base metal. These effects would be proportional to the particle flux.

## TEST APPARATUS AND APPROACH

The objective of the erosioncorrosion testing program at PNL is to determine the effects of waste type and fluid velocity on the erosioncorrosion of DST steel. The tests are performed with a nonradioactive simulated waste that is similar to the actual waste in terms of chemical composition, weight percent solids, and abrasiveness. The concentrations of the major components of NCRW and NCAW and the simulants prepared for testing are presented in Table I.

The abrasiveness of the simulated and actual wastes is determined by a slightly modified version of the ASTM Miller Number procedure (ASTM G-75-82). The Miller Number scale ranges from 1 for nonabrasive slurries to 1000 for very abrasive slurries. Measured Miller Numbers for both actual wastes and both simulants were at the low end of the scale, from 1 to 30. Simulated NCRW Erosion-Corrosion Test The erosioncorrosion test apparatus, shown in Fig. 2, consists of a carbon steel vessel containing about 150 liters (40 gal) of slurry, a recirculation pump, tank heaters, magnetic flow meters, three stationary jet nozzles, three circular impingement coupons, and three rectangular "non-impingement" coupons (control coupons). The test coupons were fabricated from an archived piece of actual DST (ID No. H 1470). The circular coupons [1.9cm dia (0.75in. dia)] were loaded into holders that allowed only one flat surface to be exposed to the impact of the jet (see Fig. 3). The other flat surface, and the circumference of the coupon, were exposed to essentially quiescent fluid. The three rectangular coupons were placed in a stagnant region in the tank.

During testing, the waste in the tank was heated to the temperature expected during *actual retrieval* operations (80°C) and pumped through the three nozzles onto the circular coupons. The flow was adjusted through each nozzle to achieve a range of velocities expected during actual operations. For the tests using simulated NCRW, the velocity of the jets at each of the coupons was 1.1, 4.4, and

TABLE I
Major Components of Actual and Simulated NCRW and NCAW

| | ACTUAL NCRW | | NCRW SIMULANT | | ACTUAL NCAW | | NCAW SIMULANT | |
|---|---|---|---|---|---|---|---|---|
| | LIQUID | SOLIDS | LIQUID | SOLIDS | LIQUID | SOLIDS | LIQUID | SOLIDS |
| | (M) | (mg/g) | (M) | (mg/g) | (M) | (mg/g) | (M) | (mg/g) |
| Al | | | | | 0.49 | 40 | 0.39 | 147 |
| Fe | | | | | | 80 | | 159 |
| Na | 1.8 | 82 | 2.16 | 98 | 4.95 | | 6.26 | |
| Zr | | 116 | | 116 | | | | |
| F | 0.62 | 75 | 0.62 | 75 | 0.09 | 1 | 0.08 | |
| OH | 0.76 | 11 | 0.16 | 11 | 1.10 | | 1.45 | |
| $NO_3$ | 0.48 | 25 | 0.48 | 25 | 1.77 | 72.5 | 3.01 | |
| $NO_2$ | 0.12 | 5 | 0.12 | 5 | | | | |
| $CO_3$ | 0.87 | 63 | 0.34 | 63 | | | | |
| Cl | 0.11 | 2 | 0.11 | 2 | | | | |
| $SO_4$ | | | | | 0.15 | 9.8 | 0.25 | |
| pH | 13.2 | | 13.2 | | 13 | | 13.1 | |

16.6 m/s (3.6, 14.4, and 57.4 ft/s). The test was run for 107 days.

Periodically, the test was shut down for about 24 h to examine the coupons and measure the weight loss. The coupons were washed in deionized water before weighing. The weight loss data from the coupons in the noflow region were used to determine the corrosion rate of the steel. The weight loss data from the impingement coupons were used to determine whether the corrosion rate of the steel was accelerated by the action of the jet.

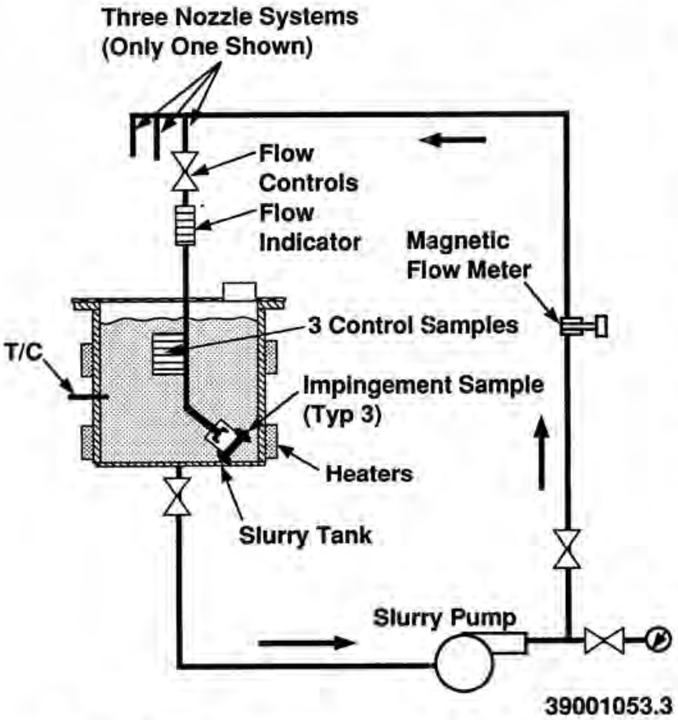

Fig. 2. NCRW Erosion-Corrosion Test Apparatus.

To obtain the erosioncorrosion rate of the impingement coupons, the weight loss data were adjusted to compensate for the regions not directly exposed to the jet. It was assumed that the areas not directly exposed to the jet would corrode at the same rate as the coupons exposed to the quiescent fluid. The plot of adjusted weight loss data versus time for the impingement coupons is presented in the Results section.

## Simulated NCAW Erosion-Corrosion Test

The erosion-corrosion test using simulated NCAW was similar to the simulated NCRW test described above with two exceptions: 1) the jet velocity at each of the coupons was 1.2, 2.4, and 4.6 m/s (4, 8, and 15 ft/s); and 2) two impingement coupons were used for each velocity. A photograph of the test coupons used in the simulated NCAW test is presented in Fig. 4. The impingement coupons were set up so that while one of the coupons was being impinged by the jet, the other was not. Modifications to the test apparatus required for this setup is illustrated by Fig. 5. An air-actuated lever arm was used to rotate the coupon holders into and out of the jets.

One set of the coupons was exposed to the direct impact of the jet for 0.5 min, then rotated to a "stagnant" condition for 4.5 min (giving a jet exposure time of ~ 1/10th of the total test time. The 0.5-min:4.5-min ratio simulates conditions in the tank during the intended operation of the rotating mixing pump. As the pump rotates a portion of the tank wall, floor or other structure in the tank will be exposed to the slurry jet for approximately 1/10th of the time. The other set of coupons has the opposite exposure (0.5 min in stag-

Fig. 3. Impingement Coupon Mounted Near Jet.

Fig. 4. NCAW Test Coupons.

nant fluid and 4.5 min exposed to the jet). The simulated NCAW erosioncorrosion test has operated for about 53 days and will continue for about 60 more. Weight loss data from the first 53 days are presented in the Results section.

## RESULTS

### Simulated NCRW Erosion-Corrosion Test Results

The weight loss data for the NCRW test are plotted in Figs. 6 and 7. Weight losses for the impingement coupons at intervals throughout the test are shown in Fig. 6 along with erosioncorrosion rates, calculated in mil/yr, based on the slopes of the curves at various times during the test. The sample areas used in the calculations are for the faces of the erosion samples exposed to the slurry jets. The weight changes of the control samples that were not in the slurry flow are shown in Fig. 7. A photograph of the samples after 53 days of testing is included as Fig. 8. After two to four weeks, a substantial difference in the erosioncorrosion rates at the three velocities was noted, as shown in Fig. 6. The maximum erosioncorrosion rate occurred in the 16.6 m/s velocity jet. Erosioncorrosion is often typified by a weight loss versus time curve that shows an incubation period followed by a region of maximum erosioncorrosion rate and then a decline in erosioncorrosion rate. This type of response is suggested by the weight loss curves shown in Fig. 6.

The plot of weight loss versus time for the control coupons (Fig. 7) shows that the amount of corrosion under more static conditions was small. Initially, the indicated

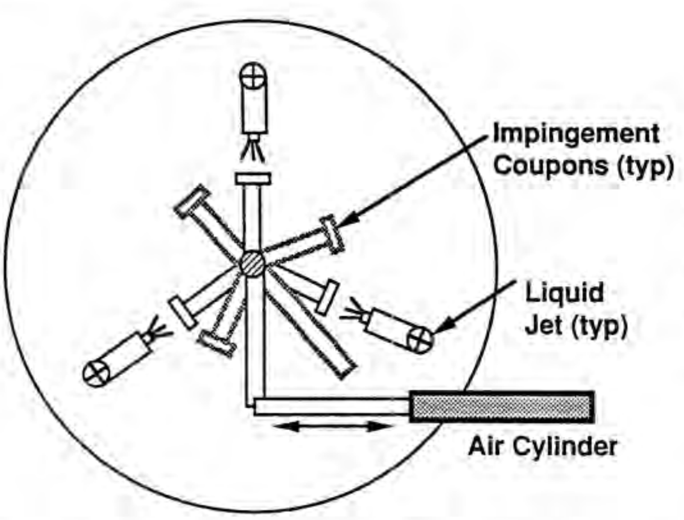

Fig. 5. Top View of the NCAW Test Vessel (Control Coupons-Not Shown-Are Located in the Stagnant Region of the Tank).

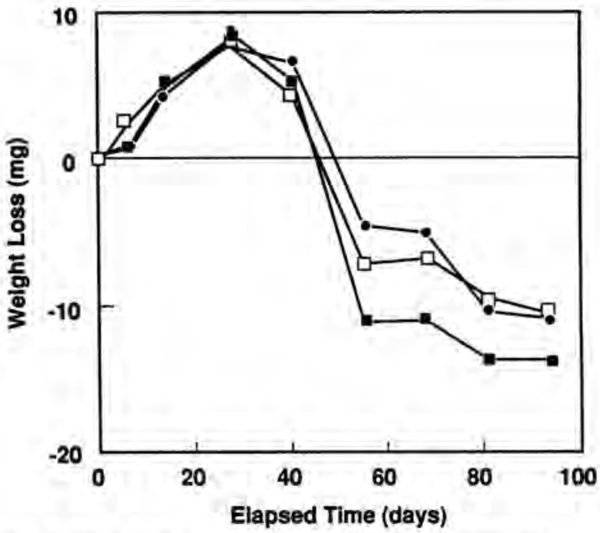

Fig. 7. Weight Loss Data from Simulated NCRW Erosion-Corrosion Testing (107 Days at 80°C-Control Coupons).

corrosion rates, calculated without stripping the corrosion products from the sample surfaces, were about 0.1 mil/yr. At the conclusion of testing, the surface films on all the control and flow samples were stripped off for final weighing to provide an accurate measure of the total metal loss, which is the true average corrosion rate. The more accurately determined corrosion rates for the control samples were found to be 0.3 mil/yr as shown in Table II.

For the impingement specimens, the total weight loss was largest for the specimen exposed to the jet with the highest velocity, as would be expected (Fig. 6). However, final average corrosion rates for all specimens exposed to NCRW jets ranged only from 2 to 4.5 mil/yr (Table II). The similar slopes near the end of the test indicate that the weight loss was primarily caused by corrosion and that the slurry jet apparently acted to remove some of the surface oxide film, rather than to abrade the base metal as by an abrasive slurry. There are two possible explanations for this behavior:

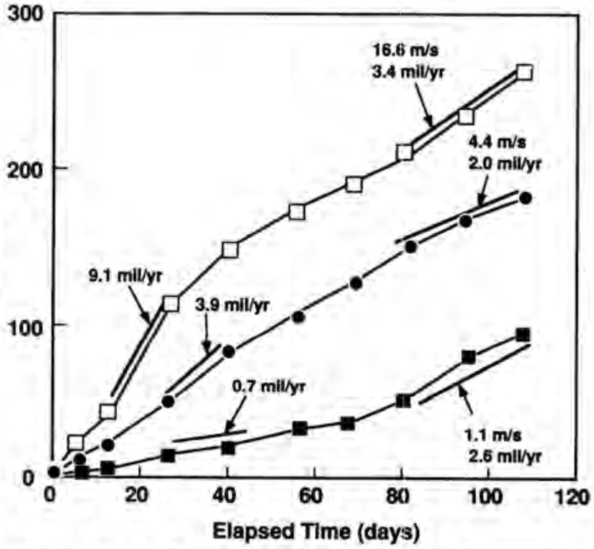

Fig. 6. Weight Loss Data From Simulated NCRW Erosion-Corrosion Testing (107 Days at 80°C-Impingment Coupns).

1. The slurry may have been "worn down" and become less abrasive with time. However, a determination of the Miller Number abrasive index at the end of the test showed the simulant had similar abrasivities at the beginning and end of the test.
2. A thin rate-controlling iron oxide film may have developed at all velocities and controlled the corrosion rate by diffusion through the film, independent of the velocity near the end of the test. This is often seen in corrosion processes where the rate-controlling chemical reaction occurs under the oxide film at the metal-oxide interface and is therefore isolated from the flow.

**TABLE II**

Average ErosionCorrosion Rates in Simulated NCRW Before and After Stripping the Oxide Films on the Coupons

| | Calculated Erosion-Corrosion Rates | |
|---|---|---|
| Jet Impact Velocity m/s | Before mil/yr | After mil/yr |
| 16.6 | 4.0 | 4.5 |
| 4.4 | 2.8 | 3.4 |
| 1.1 | 1.4 | 2.1 |
| 0 | -0.06(a) | 0.29 |
| 0 | -0.03 | 0.31 |
| 0 | -0.04 | 0.30 |

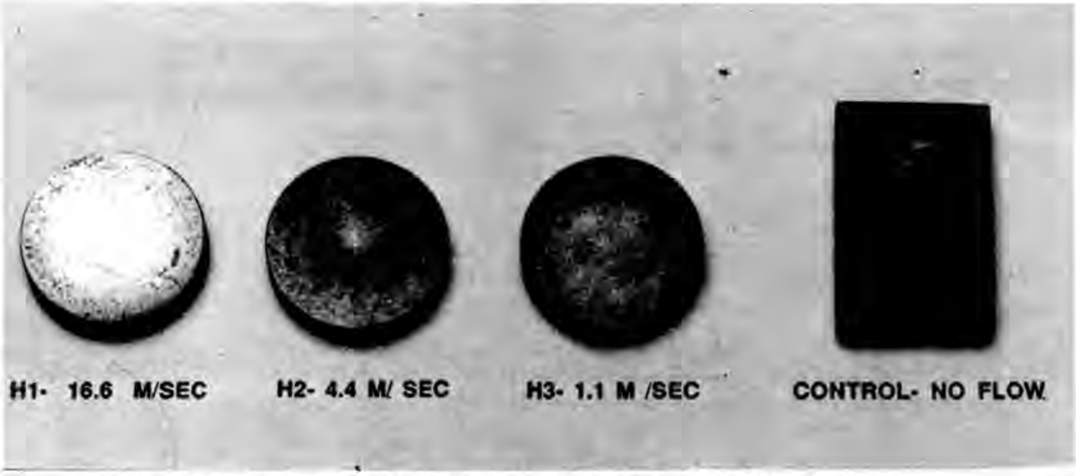

Fig. 8. Photograph of Test Samples After 55.3 Days of Testing.

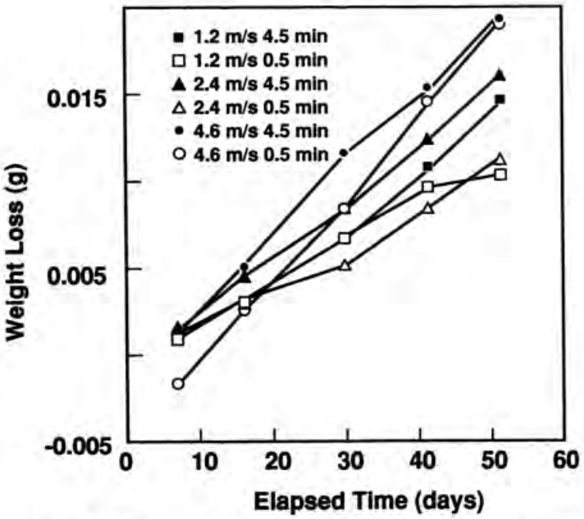

Fig. 9. Weight Loss Data from Simulated NCAW Erosion-Corrosion Testing (53 Days at 80°C-Impingement Coupons).

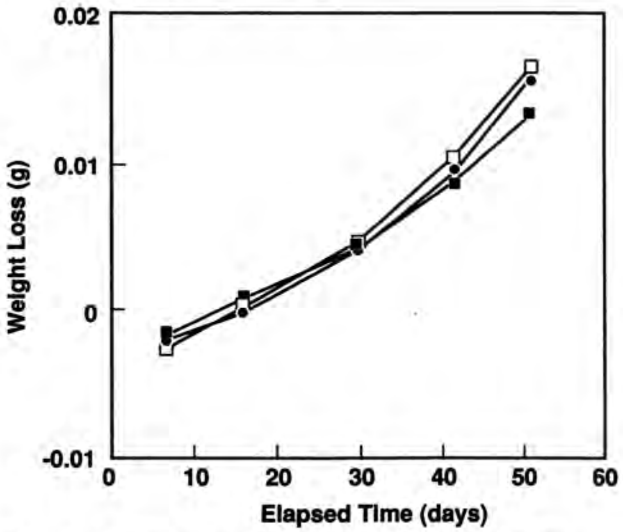

Fig. 10. Weight Loss Data from Simulated NCAW Erosion-Corrosion Testing (53 Days at 80°C-Control Coupons).

(a)Negative values indicate film formation caused weight gain

Simulated NCAW ErosionCorrosion Test Results To date, eight weeks of testing in simulated NCAW have been conducted. Preliminary weight losses were determined like those done for NCRW coupons. Weight losses indicate a nearly linear response with time, although graphs of weight loss vs time for some of the lowvelocity specimens appear to be developing some curvature (Figs. 9 and 10) as was noted in the NCRW test.

The effect of impingement time is not clear. At this stage in the testing, the 0.5min exposure time results in slightly lower total weight losses than the corresponding 4.5min exposure time samples, although the erosioncorrosion rates are generally similar (Fig. 9). This also tends to support the idea that erosioncorrosion of the samples is not a result of abrasion, since one would expect greater differences between the two impingement times if actual abrasion of the coupons was occurring. Also, based on optical microscope observations of the test specimens, the base metal does not appear to be directly affected; therefore, the particle energy or abrasiveness is apparently low enough that the jet is apparently only affecting the protective film on the steel surface.

Averaging the erosion-corrosion rates for the two sets of impingement times and plotting them against flow rate yields Fig. 11. The results demonstrate a reasonable fit to a curve proportional to $Re^{(0.58)}$, *again suggesting* that the mechanism involves transport of chemical species to or away from the specimen surface.

In general, weight loss rates for the impingement coupons in both of the simulated waste slurries and at all slurry velocities were higher than weight loss rates for the coupons

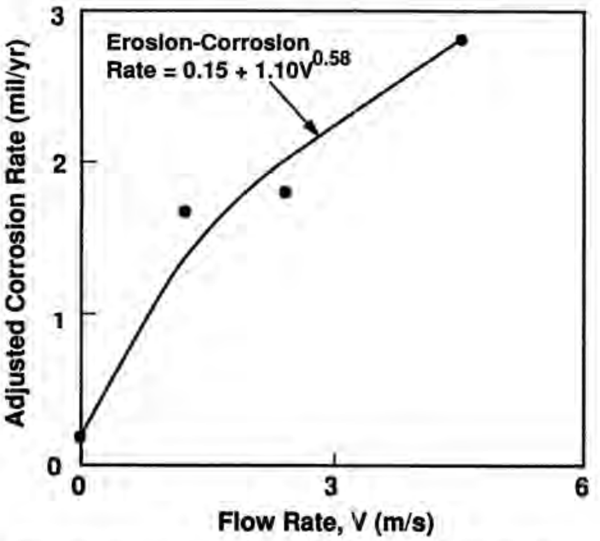

Fig. 11. Corrosion Rate as a Function of Velocity.

in the quiescent region of the test tank. Thus, corrosion of the DST steel is being accelerated as a result of the action of the impinging jets. However, if erosion is defined as a wearing away of the steel or its protective film, the evidence to date does not prove that erosion is in fact responsible for the higher weight losses. The results also may be explained by a transport- or diffusion-controlled phenomenon.

Results of testing in NCAW are expected to be similar to the results of the NCRW test. Corrosion rates of this magnitude (1 to 2.5 mil/yr) during waste retrieval operations are well within the corrosion allowance provided by the tank design. Therefore, in terms of tank integrity the currently proposed method for waste retrieval, using slurry jet mixer pumps for solids suspension, appears to be acceptable.

## CONCLUSIONS

- Corrosion of the DST steel is being accelerated as a result of the action of the impinging jets. Erosion of the steel or its protective film may account for the higher weight losses. However, the results can also be explained as a transport- or diffusioncontrolled phenomenon.
- The accelerated corrosion rate in NCAW appears to depend on the slurry flow rate (Reynolds Number) to the 0.58th power.
- Average corrosion rates for carbon steel samples exposed to jets of simulated NCRW slurry were 2 to 4 mil/yr and were somewhat independent of velocity.
- Based on current data using simulated NCAW, the accelerated corrosion rate anticipated in the waste tanks due to the impact of fluid from a jet nozzle is approximately the same as that found from testing with simulated NCRW, approximately 1.5 to 2.5 mil/yr.
- Additional data are required to clearly define the impact of different impingement times on accelerated corrosion rates in simulated NCAW. The trend for the lower two flow rates appears to be that the corrosion rate increases with the impingement time.
- Based on accelerated corrosion rates seen in each of the simulated wastes, higher corrosion rates anticipated during waste retrieval should still be within the corrosion allowance originally designed into the tanks.

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