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DWPF RECYCLE STREAM CORROSION TESTS (U)

by

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MASTER

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INTER-OFFICE MEMORANDUM

April 21, 1993

TO: G. T. Chandler, 773-A

FROM: P. E. Zapp, 773-A *P.E. Zapp*

Approved by:

N. C. Iyer, Acting Manager

Materials Application and Corrosion Technology Group

Technical Reviewer

Authorized Derivative Classifier

DWPF RECYCLE STREAM CORROSION TESTS (U)

SUMMARY

Coupon immersion tests were performed on ASTM A537 Class 1 carbon steel in simulated DWPF recycle solutions at $90 \pm 2^\circ\text{C}$, as part of the continuing effort to investigate the formation of shock-sensitive deposits. Coupons were partially immersed for four months in solutions of the same composition used previously at SRTC and at the DuPont Engineering Test Center (a salt solution containing 0.5 M hydroxide and 0.043 M nitrite). Shock-sensitive deposits were not seen on the coupons from this test. There was considerable general corrosion above the water line due to condensate and distilled water contact of the steel. New immersion tests are being planned for completion by September, 1993. The new test solution will reflect the recycle stream chemistry changes brought about by planned ammonia scrubbing in the DWPF.

BACKGROUND

Contaminated waste water generated in the Defense Waste Processing Facility (DWPF) will be collected in the DWPF recycle collection tank (fabricated from alloy C276), where it will be made alkaline, and then pumped to Tank 43 in H-Area. Tank 43, a Type III waste tank, serves additionally as the 1H evaporator feed tank and a fresh canyon waste receipt tank. The alkaline recycle stream, amounting to several million gallons per year, will likely be the major input to tank 43. Necessary corrosion inhibitors will be added to the recycle collection tank so that the recycle stream will neither be corrosive to Tank 43 nor depend upon inhibitors already in that tank for protection.

Corrosion testing of waste tank steel, ASTM A537 class 1 carbon steel (A537), in

simulated recycle solutions has been conducted since the mid-1980s, with the objective of establishing minimum concentrations of the hydroxide and nitrite corrosion inhibitors. Coupon immersion tests of susceptibility to general and localized corrosion were conducted by the DuPont Co. at the Engineering Test Center (ETC), Newark DE.^{1,2} Electrochemical tests for localized corrosion were conducted at SRS in 1988.³ The simulants used in both sets of tests were based conservatively on the recycle stream's originating entirely from DWPF melter off-gas concentrate, the most concentrated among the available sources. The composition of one particular simulant (identified as 'Matrix C' solution) thought to be the best estimate of the off-gas concentrate is shown in Table 1. Tests using this simulant were conducted with varied levels of nitrite and hydroxide (and carbonate/bicarbonate in the electrochemical tests).

In the ETC coupon tests, as-received, 600-grit polished A537 coupons were partially immersed in test solution for periods of one month and four months at temperatures of 70 and 90°C. It was found that 1.7% hydroxide (1 M hydroxide) combined with 0.2% nitrite inhibited pitting corrosion at 90°C. Some slight (<0.001 in.) crevice corrosion was found with these inhibitor concentrations, and the overall general corrosion rate was determined to be approximately 0.0005 in. per year. At 0.85% hydroxide (0.5 M) and 2000 ppm nitrite crevice corrosion was observed. Slightly less crevice and general corrosion were seen on A537 coupons which had been pre-soaked in caustic or stress-relief heat-treated in air prior to immersion.

In the SRS electrochemical corrosion tests, cyclic potentiodynamic polarization scans were conducted at temperatures up to 80°C. The hydroxide content in these tests was lowered from the ETC solution concentrations to a steady-state value representative of an aqueous film on the tank wall which is saturated with atmospheric carbon dioxide (which depletes hydroxide in the film faster than it can be replenished from the bulk solution). The results of these tests agreed with the ETC coupon results. Localized attack was absent in solutions with a steady-state pH of 10.18 (which results from an initial hydroxide concentration of 1.7%) and with nitrite concentrations of 0.1% and 0.2%.

In the course of analyzing the four-month ETC coupon immersion tests, shock-sensitive deposits were found at and below the liquid-air interface on the coupons, as well as on Teflon™ washers and string and type 316 stainless steel hardware attached to the coupons.⁴ Generally more deposits formed on the 90°C coupons than on the 70°C coupons. The deposits were 50 to 100 µm in diameter and were determined to be a mercury-based compound, but to this date they have not been precisely characterized. Nor have the precise conditions under which the deposits form been established. The small quantity of deposits produced on the coupons has made analyses difficult.

The issue of shock-sensitive deposits remains important. Coupon immersion tests were conducted at SRTC in 1992 to verify the ETC test results.⁵ A537 coupons were partially immersed for four months in solutions identical to the ETC solution which

yielded shock-sensitive deposits. Soft, solid particulate deposits were observed on wetted surfaces of the A537 coupons, but the deposits were smaller (1 - 2 mils across) and less numerous compared with those reported in the ETC tests. These deposits however were not shock sensitive. Liquid mercury drops were also observed.

EXPERIMENTAL PROCEDURE

The first SRTC coupon immersion tests were conducted by placing test bottles in Blue M™ ovens. Rapid evaporation of the test solutions required replenishment with distilled water every 2 days. The present tests used different a heating apparatus in an effort to reduce the need for such frequent replacement of evaporated water. The new arrangement used individual water baths made from specially modified 2-liter round flasks, into which were placed a single 1-liter Teflon™ test bottle and sufficient water to cover half of the bottle. The bath was placed in a heating mantle. Both the bath and the test bottle were equipped with condensers operated in reflux and cooled with recirculated chilled water. Three test set-ups were run at 90°C and one set-up at 80°C. The bath water required only infrequent replenishment, but the solution in the 90°C test bottles (which had a 100 mL/min. air purge) required 2 to 3 additions of distilled water per week. The bath temperatures were maintained within 2°C of the set point, except for two excursions to 100°C, lasting about 18 hours each, in the 80°C bath due to failure of the temperature controller.

The solution composition was identical to that used in the previous SRTC immersion test and the 'C-4' ETC solution composition and is shown in Table 1. As before, the coupons used in this study were fabricated from ASTM A537 class 1 carbon steel and supplied by Metal Samples, Inc., Munford, Ala. All specimens were tested with a 600-grit surface finish. One set of four A537 specimens tested at 90°C was heat-treated in air for one hour at 1100°F to simulate the stress-relieving heat treatment applied to fabricated waste tanks. The coupons were suspended by Teflon™ - insulated wires so that one half of each coupon was immersed in the test solution and the other half exposed to the vapor above the solution.

At the end of their 4-month exposure the coupons were removed, rinsed in acetone and distilled water, and dried at 60°C for about 24 hours. (This was the practice used for some of the ETC test coupons which did have shock-sensitive deposits.) The coupons were microscopically examined for pitting corrosion and for solid deposits. The coupons were then cleaned of much of their corrosion products in Clarke's solution (complexed hydrochloric acid) for further pitting evaluation.

DISCUSSION

The coupons were generally characterized by the absence of any corrosion below the liquid line and by patches of general corrosion above the liquid line. The patches of general corrosion appeared to originate from exposure of the steel to condensate or to distilled water which had inadvertently splashed onto the coupons during the periodic replacement of evaporated solution. None of the coupons showed shock-sensitive deposits or deposits of the kind seen in the previous SRTC coupon immersion test, although liquid mercury drops were seen on one coupon. Corrosion

products and salt deposits were analyzed by x-ray diffraction. The corrosion products were Fe_3O_4 magnetite, Fe_2O_3 hematite, and $\alpha\text{FeO-OH}$ goethite, which are all typical of corroded steel. The salt was sodium carbonate monohydrate.

Nearly all of the coupons were free of distinct pitting corrosion. There were deeper penetrations in the patches of general corrosion described above, but these were characterized by a relatively low aspect ratio (depth divided by diameter) and so not described as pitting. One coupon in one of the sets exposed at 90°C did have an area of pitting about 0.6 in. above the liquid level. Several pits were clustered together in this area, with the deepest being 0.003 in. (3 mils) deep. This is the first observation of apparent pitting on a coupon exposed to the Table 1 solution. The presence of nearby general corrosion on the same coupon, however, precludes a clear conclusion that the Table 1 solution promotes pitting corrosion in carbon steel. This question will be resolved in the additional testing described below.

FUTURE WORK

The DWPF plan to scrub equipment to prevent the build-up of ammonia nitrate will alter the composition of the recycle stream. Additional coupon tests in solutions with a composition revised to account for ammonia scrubbing will be performed beginning in April, 1993. They are scheduled for completion in September, 1993. The objectives of these tests will be to study the potential for shock-sensitive deposit formation and to establish of inhibitor levels for the revised recycle composition.

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4. J. J. Kvochak to M. K. Carlson, "Corrosion Testing - Tank Farm Recycle Solutions," June 16, 1988.
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Table 1
Composition of Aqueous Phase of Coupon Test Solutions (ppm)

<u>Ionic Species</u>	<u>Concentration</u>
Sulfate	250
Fluoride	50
Chloride	500
Iodide	20
Nitrate*	600
Nitrite	2000
Mercuric**	400
Hydroxide	0.5 M

* Nitrate added as sodium nitrate and mercuric nitrate.

** Mercuric added as the nitrate salt. Recipe concentration is before precipitation as the hydroxide.

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