**CORROSION TESTS OF CARBON STEEL EXPOSED TO A
SIMULATED DWPF RECYCLE STREAM (U)**

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INTER-OFFICE MEMORANDUM

September 30, 1993

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CORROSION TESTS OF CARBON STEEL
EXPOSED TO A SIMULATED DWPF RECYCLE STREAM(U)

SUMMARY

Coupon immersion tests of ASTM A537 Class 1 carbon steel in simulated DWPF recycle solutions did not generate shock-sensitive deposits, consistent with two previous tests at SRTC. The results of the three sets of tests indicate that the formation of detectable amounts of shock-sensitive deposits is not possible under the test conditions.

The solutions used in the present tests included the increased nitrate concentration (0.05 M vs. the 0.01 M used previously) that reflects the introduction of ammonia scrubbing in the DWPF. The nitrite and hydroxide concentrations were 0.042 M and 0.5 M, respectively, which are the current Process Requirement concentrations for the DWPF Recycle Collection Tank. As a result of the increased nitrate level, the coupon showed superficial uniform corrosion at a rate ≤ 0.4 mils per year (0.0004 in. per year) and pitting corrosion with a maximum depth of 0.7 mils (0.0007 in.).

Electrochemical corrosion tests to revise the nitrite concentration limit to accommodate the higher nitrate concentration will be completed in October, 1993.

INTRODUCTION

Contaminated waste water generated in the Defense Waste Processing Facility (DWPF) will be collected in the DWPF recycle collection tank where it will be made alkaline, and then transferred to Tank 43 in H-Area. Tank 43, a Type III waste tank, serves additionally as an 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 not be corrosive to Tank 43.

Corrosion testing of waste tank steel, ASTM A537 class 1 carbon steel (A537), in simulated recycle solutions has been conducted several times since the mid-1980s as calculated compositions changed. The test objective was to establish 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 ETC coupon tests developed deposits of small (≤ 0.004 in. diameter) particles which detonated upon mechanical shock. A series of coupon immersion tests has been conducted at SRS to try to confirm the formation of shock-sensitive deposits and produce sufficient quantity of the deposits to enable a complete characterization.

The deposits seen in the ETC tests were numerous and covered Teflon™ washers and string, and type 316 stainless steel hardware, as well as the wetted portions of the partially immersed A537 coupons.⁴ They were not precisely characterized, but apparently contained mercury. The first SRTC coupon tests to investigate the formation of shock-sensitive deposits were conducted in 1992.⁵ 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.

A second set of coupon tests was completed in March, 1993. No deposits of any kind were seen in these tests. This report describes the results of a third and final effort to reproduce the shock-sensitive deposits.

EXPERIMENTAL PROCEDURE

The test solution was prepared with reagent grade chemicals and distilled water according to the concentrations shown in Table 1. The nitrate concentration reflects the change in the recycle composition due to the planned ammonia scrubbing in the DWPF vent system. The small concentration of ammonium hydroxide added to the solution reflects ammonia scrubbing. The nitrite and hydroxide concentrations were the same as previously tested, 0.042 M and 0.5 M, respectively.

The coupons used in this study were fabricated from ASTM A537 class 1 carbon steel and supplied by Metal Samples, Inc., Munford, Ala. Their sizes were 0.75 in. by 2 in. by 0.12 in., 0.75 in. by 3 in. by 0.12 in., and 1 in. by 3 in. by 0.12 in. The first two sizes were polished to a 600 grit finish; the third was ground to 120 grit. The coupons were tested in 500 mL of solution. The 3-in.-long 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. The 2-in.-long

coupons were fully immersed.

Table 2 lists test conditions. Bottles 93-90A and 93-90B were maintained at $90^{\circ} \pm 2^{\circ}\text{C}$ for 123 days, and bottles 93-90C and 93-80D were maintained at $90^{\circ} \pm 2^{\circ}\text{C}$ and $80^{\circ} \pm 2^{\circ}\text{C}$, respectively, for 101 days in constant temperature baths. With the exception of bottle 93-90B, the bottles had air passed through the vapor space at 50 - 100 mL/min. Bottle 93-80D was the only bottle equipped with a condenser. The two other bottles with air flow had about 1 m of plastic tubing for an exhaust path. Solution losses by evaporation were restored with additions of distilled water, when the level had dropped 0.2 to 0.3 in. The frequency of water addition varied. Water was added to bottle 93-90A twice per week, to bottle 93-90C three times per week, and to bottles 93-90B and 93-80D once every 10 to 14 days.

At the end of their exposure the coupons were removed, rinsed in distilled water, and dried at ambient temperature or at 60°C for about 24 hours. 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. Pit depths were determined with a measuring microscope. The coupons were weighed to determine weight loss and a uniform corrosion rate.

DISCUSSION

None of the coupons showed evidence of the shock-sensitive deposits reported in the ETC tests. There also was no evidence of the soft, stable deposits seen in earlier SRTC recycle corrosion tests.⁵

The immersed coupons and the wetted portions of the partially immersed coupons that were exposed to solutions with air flow showed a slight uniform corrosion. The unwetted portions had a slight tarnish. The wetted portions of the coupons exposed in bottle 93-90B (without air flow) were free of corrosion, reflecting the high pH that persisted in that bottle. The unwetted portions of that bottle's coupons also showed a slight tarnish.

Weight loss measurements made after cleaning in Clarke's solution for about 30 seconds are listed in Table 2. Corrosion rates were calculated from these measurements under the assumption that the entire coupon was corroding in a uniform manner. Since the totally immersed coupon in bottle 93-90B appeared in microscopic examination to be free of corrosion, its 0.13-mils-per-year rate is concluded to have resulted from the cleaning step. The maximum uniform corrosion rate shown in Table 2 is the highest value, from among the rates for each of the four coupons in a test bottle, less 0.13 mils per year (mpy). The maximum uniform corrosion rate seen in the 90°C tests is 0.36 mpy mils per year. The maximum uniform corrosion rate for the 80°C coupons is 0.26 mpy. The 80°C -rate may be overstated, as result of the inadvertent dilution of the test solution by air-borne moisture drained into the test bottle by a too-cool condenser. This over-filled condition persisted for about 10 days until evaporation brought the solution back to its proper

volume.

The microscopic examination of the coupons showed that uniform corrosion and pitting were both present. In this situation it becomes somewhat subjective to distinguish pitting from irregular uniform corrosion. (This distinction is important in assessing the likelihood for localized failure of a structure.) The pits were quite numerous and rather evenly distributed on the coupon faces at and above the liquid level. Pits were shallow, with depths typically in the range 0.3 mils (0.0003 in.) to 0.7 mils (0.0007), which is below the threshold of 1 mil (0.001 in.) used to identify significant pitting. Although the present test solution contained a five-fold higher nitrate concentration than that of the previous coupon test, the present range of pit depths was far below a 3-mil (0.003 in.) depth seen in a single instance in that previous test. It is clear that the recycle solution is not very aggressive, due to the high (0.5 M) hydroxide concentration. Protection by this level of hydroxide is consistent with waste tank experience, in which pitting has not been detected where carbon steel is exposed to solutions with > 1 M hydroxide.

CONCLUSIONS

Shock-sensitive deposits were not detected on coupons immersed at 90°C in simulants of the DWPF recycle solution. Based on this result and the negative results from two previous SRTC recycle corrosion tests, the primary conclusion is that the formation of detectable amounts of shock-sensitive deposits is not possible during the storage of the recycle stream in carbon steel waste tanks.

The higher nitrate concentration had little effect on the corrosivity of the recycle stream. Many small pits were evident, compared with previous recycle coupon tests, but the pits were shallower than those seen previously. This level of corrosion can be inhibited with higher nitrite concentrations. Electrochemical corrosion tests are in progress to establish minimum effective nitrite concentrations for DWPF recycle streams which contain nitrate in the range 0.01 to 0.1 M and hydroxide at 0.5 M. These tests will be complete in October, 1993.

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Table 1
Composition of Coupon Test Solutions

<u>Compound</u>	<u>Concentration (M)</u>
Sodium Nitrate	5.01E-02
Sodium Oxalate	1.57E-02
Sodium Sulfate	2.24E-04
Sodium Chloride	1.60E-03
Sodium Fluoride	3.00E-04
Sodium Tetraborate	1.70E-04
Sodium Phosphate Dibasic Heptahydrate	4.66E-05
Potassium monoxide	5.16E-05
Mercuric Oxide	1.87E-04
Ammonium Hydroxide	2.04E-03
Sodium Hydroxide	5.00E-01
Potassium Hydroxide	5.19E-04
Sodium Nitrite	4.20E-02

Table 2
Test Conditions and Uniform Corrosion Results

<u>Bottle</u>	<u>Temperature</u>	<u>Air Flow</u>	<u>Duration</u>	<u>Max. Uniform Corrosion Rate</u>
93-90A	90°C	Yes	123 days	0.35 mpy*
93-90B	90°C	No	123	0.23
93-90C	90°C	Yes	101	0.36
93-80D	80°C	Yes	101	0.26

*mpy = mils (0.001in.) per year

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