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Coupon Immersion Testing in Simulated Hazardous Low Level Waste (U)

SUMMARY

AISI Type 304L (304L) stainless steel was recommended as a suitable material of construction for the new Hazardous Low Level Waste Processing Tanks (HLLWPT). This report documents the second phase of a coupon immersion test program to determine the susceptibility of 304L to localized attack in a variety of simulated wastes. The coupon test results confirmed the conclusions that were made from the first phase of the test program. First, 304L is a suitable material of construction for the new waste tanks. Second, the agreement between the cyclic polarization tests and the coupon immersion tests demonstrates that cyclic polarization can be used to predict the susceptibility of a material to localized corrosion in these wastes.

In addition to the tests performed on 304L, tests were performed on ASTM A537 carbon steel (A537) and Incoloy 825 (I825). Neither 304L nor I825 was susceptible to attack, while A537 experienced

varying degrees of attack in the different wastes. Observations on the surface attack and corrosion products on A537 were used to elucidate the mechanism by which A537 corrodes in these wastes.

INTRODUCTION

New waste tanks are to be constructed in H-area to process hazardous low level wastes.[1] The tanks will be processing wastes from Sludge Processing (SP), In-Tank Precipitation (ITP), and the Receiving Basin for Off-site Fuels (RBOF). The recommended material of construction for these tanks is AISI Type 304L (304L) stainless steel.

A corrosion testing program was proposed to investigate the susceptibility of 304L to localized attack in these waste environments.[2] The tests included cyclic polarization, coupon immersion, electrochemical impedance spectroscopy (EIS), and constant extension rate tensile (CERT) tests. An interim report on the progress of the test program was written which summarized the results of the cyclic polarization tests, the EIS tests, and the first phase of the coupon test matrix.[3] The conclusions from the initial portion of this study were that 304L is a suitable material of construction for the hazardous low level waste tanks and that good agreement between the three tests was achieved. The latter conclusion allows for greater confidence to be placed in the cyclic polarization technique for a quick assessment of the susceptibility of a material to localized corrosion in these waste solutions.

This report documents the results of the second phase of the coupon test matrix. As part of this matrix, A537 and I825 coupons were also tested to aid the interpretation of the 304L coupon test results. A537, which is similar to the carbon steel material used for the present waste tanks, has a lower corrosion resistance than 304L. The Incoloy 825, a nickel based alloy, is more resistant to halide attack and has a greater corrosion resistance than 304L. Additionally, tests were conducted on 304L and A537 coupons in which an attempt was made to maintain the solution pH by controlling the carbon dioxide level in the air above the solution. EIS tests were also performed; these results will be documented in a later report.

EXPERIMENTAL PROCEDURE

Metal coupons (2" x 1" x 0.125") were partially immersed in a simulated waste environment for approximately 100 days. Four coupons were hung by teflon string in a one liter polyethylene bottle which was half filled with solution. Waterproof epoxy was applied to the sides of two of the coupons to prevent preferential attack of the edges.

In the initial cyclic polarization tests, thirteen simulated wastes, representing a variety of compositions, were used. The solutions were representative of the types of waste generated on-site. However, they were not representative of the inhibited wastes currently stored in the carbon steel tanks. From this group five solutions solutions were selected based on either a high concentration of chloride and fluoride or a lack of inhibitor species (see Table 1).

The temperature in the bottles was controlled with a water bath for the 30° C tests and ovens for the 45° and 60° C tests. Air flow into the bottles was regulated at 100 cc/min to simulate the air flow in a waste tank. Several of the tests were conducted in which the air was passed through a flask which contained ascarite prior to entering the bottle. This procedure was done to remove carbon dioxide (CO_2) from the air so that the bulk pH could be maintained. A complete matrix of these tests is shown in Table 2.

The 304L coupons used in the test were either solution annealed or heat treated. The heat treatment for the 304L was performed to simulate weld heat affected zones. The maximum degree of sensitization, as determined by electrochemical potentiokinetic reactivation (EPR), was obtained after heat treating the sample at 650° C for six hours. Welded coupons of 304L were also tested. The A537 and I825 coupon were tested in the as-received condition. The compositions of these materials are listed in Table 3.

After the samples were removed, they were cleaned according to ASTM standard G 1-88. The same standard was used to determine the corrosion rate. The coupons were weighed before the test and after they had been cleaned. Given the weight loss, the following equation was used to determine the corrosion rate in mil per year (mpy):

$$\text{Corrosion rate} = K\,\Delta W/(ATD) \qquad (1)$$

where K is a constant, ΔW is the weight loss, A is the area of the coupon, T is the immersion time, and D is the density. Optical light and scanning electron microscopy were used to evaluate the coupons for pit size, density, and location. Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD) were used to identify corrosion products or precipitated layers on the surface. The waste solutions were analyzed prior to and after the test to detect any changes in the molar anion concentrations. The results of these tests are recorded laboratory notebooks WSRC-NB-90-107, WSRC-NB-90-312, and WSRC-91-43.

RESULTS AND DISCUSSION

The coupon immersion test results confirmed the previous conclusions that 304L is a suitable material of construction for the HLLWPT and that the cyclic polarization technique is a useful tool for predicting the localized corrosion susceptibility of the tank. Table 4 provides a summary of the results of the second coupon test. For comparison results from the first phase of the coupon test are also included in the table. Both the 304L and I825 coupons showed no susceptibility to localized attack in any of the tested solutions. The A537 coupons, however, underwent severe attack in solutions #8 and 13 and very light attack in solutions #1, 4, and 11. For coupons in solutions #8 and 13 the severity of attack increased with solution temperature. The heaviest attack generally occurred in the non-immersed area of the coupon, although at the higher temperatures coupons immersed in solution #13 were attacked in both the immersed and non-immersed areas. Coupons which were coated with epoxy corroded more severely around the edges than those that were not coated. This attack occurs due to a crevice which formed as the epoxy de-adhered.

The morphology of the corrosion products and the attacked surface on the A537 coupons immersed in solutions #8 and 13 was investigated. There appeared to be two layers of corrosion products: a black layer next to the metal covered by a reddish brown layer. The morphology of the black layer was flake-like, while the reddish brown layer was tubular. The corrosion products were identified by

XRD to be goethite (α-FeO(OH)), magnetite (Fe_3O_4), and lepidocrocite (γ-FeO(OH)). The black layer is probably magnetite, while the reddish brown layer is most likely the iron hydroxides. Beneath the corrosion products broad, shallow pits between 0.6 and 1 mil deep were coalesced together to give the surface a crater like appearance. The attack on the coupons in the three remaining solutions was similar, but was confined to sporadic sites in the non-immersed area.

Corrosion rate measurements, determined by weight losses, were a good indicator of the severity of attack on the A537 coupons. Table 5 shows that the corrosion rates in solutions #8 and 13 (0.6-1.2 mpy) are one to two orders of magnitude greater than those for the other solutions. The rate was also observed to increase with temperature. No significant corrosion rate was determined for either the 304L or I825 coupons.

In addition to the cyclic polarization tests, the results of the coupon tests correlate well with observations of present tank walls. The non-immersed area of Tank #23, which contained an uninhibited RBOF waste, was covered with reddish-brown corrosion products while only precipitate layers were observed in the immersed area.[4] Upon cleaning the non-immersed area, shallow coalesced attack was seen.

The corrosion mechanism for the tank walls and the severe attack observed on the A537 coupons immersed in solutions #8 and 13 are similar. In the previous coupon tests, significant precipitation of gibbsite (α-$Al_2O_3 \cdot 3\ H_2O$) and silicate compounds occurred. These precipitates form as the solution evaporates and condenses back on the coupon. The precipitate layer serves as a crevice into which the condensed solution may seep. The crevice creates a depleted oxygen region which, when combined with a condensed solution that is probably more aggressive than the bulk solution, results in the corrosive attack. As the corrosion products form, they provide additional crevices for attack. In order to alleviate the corrosion problems, the bulk solution must be sufficiently inhibited or a more resistant material such as 304L must be utilized.

The effect of controlling the CO_2 level in the air above the solution was studied. A hypothesis was made that the precipitates may form as a result of absorption of CO_2 in the solution and the consequent reduction in pH[5]. Table 6 summarizes the periodic pH measurements that were taken for solutions with controlled and uncontrolled CO_2 levels. These results indicate that pH changes were similar whether CO_2 was controlled or uncontrolled. Additionally, there were no observable changes in the morphology or amount of precipitate formed on the coupons. Post-test analysis of the solution composition showed that for both cases the carbonate concentration had significantly increased while the hydroxide concentration had decreased slightly. CO_2 absorption in the controlled case may have occurred due to the need to replenish evaporated solution, particularly at the higher temperatures.

A relationship between the solution pH and the severity of attack on the A537 coupons was observed. Solutions #8 and 13 experienced a pH reduction of approximately two units, the pH for solutions #1 and 4 remained nearly constant. Attack of A537 coupons was inhibited in solutions #1 and 4 due to the maintenance of a relatively high hydroxide concentration with respect to the the nitrate concentration. The pH reduction was greater as the temperature increased. The pH in solution #11 also decreased. However, this solution contained no hydroxide to maintain the solution pH or nitrate which would aggressively attack the surface.

CONCLUSIONS

The second phase of the coupon test confirmed the conclusions made from the first coupon tests. Type 304L stainless steel is a suitable material for the Hazardous Low Level Waste Processing Tanks. Furthermore, the agreement between the cyclic polarization tests and the coupon immersion tests allows for one to utilize cyclic polarization as a predictive tool for the susceptibility of a material to localized corrosion in these waste environments.

Additional information on the corrosion of A537 was obtained. The corrosion products were identified as goethite, magnetite and lepidocrocite. The results agreed with observations of the present tank walls and substantiate the present understanding of the corrosion mechanisms which occur. A relationship exists between the severity of attack and both a significant drop in solution pH and an increase in solution temperature. However, controlling the CO_2 level of the air above the solution did not affect either the attack or the formation of precipitate layers.

FUTURE CORROSION TESTS

As part of the corrosion testing program, Constant Extension Rate Tensile (CERT) tests were to be performed to determine the susceptibility of a material to stress corrosion cracking. CERT tests are currently being performed on 304L, in both the solution annealed and heat treated conditions, and A537. The same solutions which were used to conduct the coupon tests will be used for these tests.

REFERENCES

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2. J. I. Mickalonis to D.T. Hobbs, "Corrosion Study of Replacement Materials for Hazardous Low Level Waste Processing Tanks", WSRC-TR-90-74-1, January 31, 1990.

3. B. J. Wiersma and J. I. Mickalonis, "Corrosion Study of Replacement Materials for Hazardous Low Level Waste Processing Tanks", WSRC-TR-91-138, March 28,1991.

4. Private communication with F.G. McNatt, March 6,1991.

5. Private communication with Waste Tank Corrosion Working Group, February 1991.

Table 1.
Molar Anion Compositions of Low Level Hazardous Waste

Solution Number	ESP 1	ITP 4	RR 8	TTC 11	CD 13
pH	13.7	13.5	12.7	12.4	12.5
OH^-	2.1	1.3	0.15	-	-
$CO_3^=$	0.1	0.16	0.098	-	-
NO_2^-	1.1	0.6	0.07	-	-
NO_3^-	1.4	2.0	0.7	-	4.6
Cl^-	0.022	0.022	0.0013	-	-
F^-	0.011	0.015	-	-	0.039
$SO_4^=$	0.095	0.14	0.0079	-	-
$Al(OH)_4^-$	0.3	0.31	0.007	-	0.26
$C_2O_4^=$	0.0051	0.014	-	-	-
$CrO_4^=$	0.0021	0.0033	0.00084	0.013	-
$MoO_4^=$	0.00027	0.00043	-	-	-
$SiO_3^=$	0.0021	0.0038	0.00058	-	-
PO_4^{-3}	0.0058	0.0085	0.014	0.22	-

Notes:

- Solution Designation
  - ESP- Extended Sludge Processing slurry
  - ITP- In-Tank Precipitation slurry
  - RBOF- Receiving Basin for Off-site Fuels wastes:
    - RR- Resin Regeneration waste
    - TTC- Tritium Target Cleaning waste
    - CD- Cask Decontamination waste

- pH determined at 30° C

Table 2.
Test Matrix for the Coupon Tests

Solution	1	4	8	11	13
Metal					
304L solution annealed (ascarite)	xx	x	x		
304L heat treated (ascarite)	xx	x	x		
304L welded (ascarite)		x	x		
A537 (ascarite)	x	x	x		
A537		x		x	x
I825		x		x	x

Notes:

x- tests performed at 30, 45, and 60 °C
xx- tests performed at 30 °C

Table 3.
Analysis of Materials Tested (wt. %)

	C	Mn	Si	P	S	Cr	Ni	Mo	Ti	Al	Fe	Cu
304L	.02	1.90	.85	.032	.02	19.4	8.9	--	--	--	bal.	--
A537	0.22	1.01	.032	.033	.031	.2	.21	.06	--		bal.	.22
I825	.02	.44	.23	--	.01	20.5	41.2	2.3	.85	.08	28.9	2.2

Table 4.
Summary of Coupon Test Results

Solution / Material	ESP 1	ITP 4	RR 8	TTC 11	C D 13
304L	NO	NO	NO	NO	NO
A537	light	light	severe	light	severe
I825	NO	NO	NO	NO	NO

Notes:

NO- No corrosion products or pits observed
light- Sporadic shallow etching in the non-immersed area
severe- Black and reddish brown corrosion product covering shallow pits

Table 5.
Corrosion Rates of A537 Determined From Coupon Immersion Tests

Solution	T (°C)	Δ w (g)	Corrosion Rate (mpy)
1	30	.0097	0.067
1	45	.0049	0.034
1	60	.0085	0.059
4	30	.0168	0.117
4	45	.0137	0.095
4	60	.0034	0.024
4	30	.0132	0.092
4	45	.0092	0.064
4	60	.0083	0.057
8	30	.0849	0.627
8	45	.1601	1.17
8	60	.1482	1.08
11	30	.0033	.024
11	45	.0032	.024
11	60	.0033	.024
13	30	.1247	.902
13	45	.1490	1.078
13	60	.1598	1.156

Table 6.
Bulk pH in Simulated Wastes During Coupon Immersion Tests.

Solution	T (°C)	Ascarite	Dates 3/6	3/26	4/23	5/20
1	30	yes	13.15	13.08	13.30	13.42
1	30	yes	13.18	13.06	13.32	13.38
1	45	no	12.41	12.69	12.79	12.89
1	60	no	12.37	12.44	12.48	12.50
4	30	yes	13.06	13.04	13.16	13.29
4	60	yes	12.25	12.35	12.39	12.40
4	30	no	-	13.08	13.28	13.34
4	60	no	-	12.33	12.23	12.25
8	30	yes	12.49	12.36	12.20	12.32
8	60	yes	11.51	10.59	9.96	9.87
8	30	no	12.1	11.76	10.32	10.17
8	60	no	11.21	9.88	9.86	9.79
11	30	no	11.83	11.54	10.96	10.72
11	60	no	11.19	10.46	9.98	9.87
13	30	no	12.41	12.29	12.15	12.11
13	60	no	11.35	9.99	9.51	9.37