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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

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ACC. NO. 139299

CC: M. H. Bacon
R. L. Folger
R. S. Ondrejcin
A. F. Riechman
TIS File (2)

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M E M O R A N D U M

TO: E. J. MAJZLIK, JR.
FROM: B. A. EBERHARD ~~DE~~

TIS FILE
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CORROSION OF TYPE 304L STAINLESS STEEL
IN OXALIC-NITRIC ACID SOLUTIONS

ABSTRACT

The applicability of 304L stainless steel as a material for containing reagents used in the destruction of oxalic acid was investigated. Samples of 304L SS in the unwelded and welded condition were exposed to varying concentrations of oxalic and nitric acid. At a test temperature of 88°C, the results indicated that no serious corrosion problems exist. The highest corrosion rates occurred with the unwelded specimens in 0.3M H₂C₂O₄. These unwelded specimens had corrosion rates of 0.91 μm/day (13.1 mils/yr) and 0.34 μm/day (4.9 mils/yr) at exposure times of 11 days and 20 days, respectively. Intergranular corrosion was not evident on the welded specimens.

INTRODUCTION

As part of the interim waste management program, radioactive waste will be transferred to new stress-relieved storage tanks. These tanks will replace the current tanks, some of which do not supply triple containment or may have cracked primaries.

The waste transfer will be a three-stage operation. First, a majority of the supernate will be removed. The remainder of the supernate will then be slurried with the sludge and the suspension pumped out. Waste that remains is an insoluble residue which will be chemically dissolved by mixing with hot oxalic acid. Spent oxalic acid will be chemically treated in waste farm pump tanks. Pump tanks are to be constructed of 304L SS with welds of 308L SS. The oxalic acid will be destroyed with nitric acid and a manganese catalyst. Reaction temperature will be about 100°C.

EXPERIMENTAL PROCEDURE

To investigate the corrosion resistance of 304L SS in the oxalic-nitric acid environment, the conditions of time, temperature, specimen condition, and solution concentration had to be defined. Test times of 11 and 20 days and temperatures of 88°C and 98°C were selected. Specimens were coupons of 304L SS 3 in. x 2 in. x 0.06 in. in dimension. Coupons in both the welded (MIG 308L SS) and as-received condition were tested for general corrosion as well as intergranular corrosion. Seven different solutions were chosen to generate corrosion data above and below

the expected concentrations. The initial concentration of the reactants in the pump tank was anticipated to be 0.15M $\text{H}_2\text{C}_2\text{O}_4$, 0.35M HNO_3 , 0.01M Fe^{3+} , and 0.005 Al^{3+} . Duplicate samples were exposed for 11 and 20 days at 88°C in the various solutions. Fifty-six coupons (28 unwelded and 28 welded) were tested.

RESULTS

After prolonged periods of exposure in oxalic-nitric acid solutions, most samples became coated with a brown stain. The stain had to be removed with an 8% HF-20% HNO_3 solution. Some specimens exposed to the 0.3M $\text{H}_2\text{C}_2\text{O}_4$ solution became covered with a greenish coating. The coating, ferrous oxalate, was associated with the increased corrosion of 304L SS.

Table I gives the seven test solutions in order of decreasing nitric acid concentration.

TABLE I

Oxalic-Nitric Acid Test Solutions

<u>Solution Number</u>	<u>Solution Concentrations</u>
1	2.5M HNO_3
2	2.5M HNO_3 ; 0.3M $\text{H}_2\text{C}_2\text{O}_4$; 0.01M Fe^{3+} ; 0.005M Al^{3+}
3	1.92M HNO_3 ; 0.002M $\text{H}_2\text{C}_2\text{O}_4$; 0.01M Fe^{3+} ; 0.005M Al^{3+}
4	1.15M HNO_3 ; 0.075M $\text{H}_2\text{C}_2\text{O}_4$; 0.01M Fe^{3+} ; 0.005M Al^{3+}
5	0.35M HNO_3 ; 0.15M $\text{H}_2\text{C}_2\text{O}_4$; 0.01M Fe^{3+} ; 0.005M, Al^{3+}
6	0.30M $\text{H}_2\text{C}_4\text{O}_4$
7	1.0M HNO_3 ; 0.6M $\text{H}_2\text{C}_2\text{O}_4$; 0.04M Fe^{3+} ; 0.04M Al^{3+} ; 0.81M Mn^{2+}

Solutions 2, 3, 4, and 5 did not contain Mn^{2+} . This was done to slow down the decomposition of the corrosion components and expose the specimens to a more consistent environment. For solutions 2, 3, 4, and 5, the corrosion rates decreased with time. It was assumed that the brown stain acted as a protective coating. Corrosion rates for the oxalic acid coupons showed the most variation for duplicates.

Tables II and III show the corrosion rates for the unwelded and welded coupons. The data are an average of duplicate test specimens.

TABLE II

Average Corrosion Rates for Unwelded 304L SS
Specimens Calculated at 88°C

Solution Number	Corrosion Rate			
	11 Days		20 Days	
	$\mu\text{m}/\text{day}$	mils/yr	$\mu\text{m}/\text{day}$	mils/yr
1	0.14	2.0	0.11	1.6
2	0.13	1.9	0.08	1.1
3	0.06	0.80	0.05	0.71
4	0.10	1.5	0.07	0.99
5	0.11	1.5	0.07	1.1
6	0.91	13.1	0.34	4.9
7*	0.01	0.13	0.01	0.12

* The 11-day column represents the 36-hour actual test time and the 20-day column, the 72-hour actual test time.

TABLE III

Average Corrosion Rates for Welded 304L SS
Specimens Calculated at 88°C

Solution Number	Corrosion Rate			
	11 Days		20 Days	
	$\mu\text{m/day}$	mils/yr	$\mu\text{m/day}$	mils/yr
1	0.08	1.1	0.08	1.1
2	0.16	2.2	0.10	1.4
3	0.05	0.75	0.06	0.91
4	0.12	1.8	0.07	1.1
5	0.15	2.2	0.08	1.2
6	0.31	4.4	0.03	0.37
7*	0.03	0.43	0.02	0.34

* The 11-day column represents the 36-hour actual test time and the 20-day column, the 72-hour actual test time.

Visual observation indicated that no intergranular corrosion occurred in the heat-affected zone of the welded specimens. Corrosion of both the welded and unwelded specimens was by uniform attack.

CONCLUSIONS

1. Corrosion rates >0.013 in./yr were not observed for either the unwelded or welded specimens.
2. Corrosion attack was uniform, intergranular corrosion was not evident on the welded specimens.
3. Exposure of 304L SS to pure oxalic acid for prolonged periods of time will produce the highest corrosion rates observed.