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CORROSIVENESS OF PUREX
HIGH-LEVEL WASTE SOLUTIONS

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UC-70, Waste Disposal
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CORROSIVENESS OF PUREX HIGH-LEVEL WASTE SOLUTIONS

By

R. F. Maness

Chemistry Research Department
Chemistry and Metallurgy Division

November 1969

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CORROSIVENESS OF PUREX HIGH-LEVEL WASTE SOLUTIONS

R. F. Maness

INTRODUCTION

Several Purex plant flowsheet changes which would permit improved strontium recovery during B-Plant processing are currently under consideration. These changes would reduce the Fe(III) and Al(III) content of waste solution to 25 to 80 percent and the sulfate content to 75 to 100 percent of the current flowsheet values. These changes would apply to waste solutions produced during the processing of both aluminum-clad fuels (IWW solution) and Zircaloy-clad fuels (ZWW solution). The composition of high-level waste solutions after sugar denitration (PAW and ZAW solutions) would also be affected by the proposed flowsheet changes. The effect of these compositional changes on the corrosion of 304L stainless steel and Uranus S alloy is the subject of this report.

SUMMARY AND CONCLUSIONS

Corrosion of 304L in IWW solution was not affected greatly by the proposed compositional changes. The most corrosive composition evaluated [no sulfate and 50 percent of the flowsheet value of Fe(III)] was only 50 percent more corrosive (9.5 vs 6.4 mils/mo) than the current composition. All proposed compositional changes adversely affected 304L corrosion in PAW solution. However, the most corrosive composition evaluated [no sulfate and 50 percent Fe(III)] corroded 304L at a rate of only 1.8 mils/mo. Current ZWW solution corroded 304L at a rate of 13 mils/mo, whereas the corrosion rate in solutions containing no sulfate, 20 percent of the flowsheet value of Fe(III) and 0.0 and 20 percent Al(III) was only one mil/mo. The decrease in corrosion was the result of a decrease in nitrate concentration. The corrosion rate of 304L in current ZAW solution was 1.7 mils/mo. Decreasing the total nitrate concentration by reducing the ferric nitrate and/or aluminum nitrate concentration decreased corrosion. The corrosion rate in the solution containing no sulfate, 20 percent Fe(III) and 20 percent Al(III) was only 0.3 mil/mo.

Limited data indicate corrosion of Uranus S alloy responded to the compositional changes in the same manner as that observed for 304L. However, the magnitude of the corrosion rates was somewhat lower,

EXPERIMENTAL AND DISCUSSION

Compositions of the IWW, PAW, ZWW and ZAW solutions evaluated are given in Tables I through IV. All solutions were prepared from reagent grade chemicals (with the exception of ruthenium nitrate) and distilled water. A ten percent $\text{Ru}(\text{NO}_3)_3$ solution in 5.5M HNO_3 (obtained from Engelhard Ind.) was used as the source of $\text{Ru}(\text{II})$. All test solutions were maintained at the boiling point under complete reflux. Fluoride-bearing solutions were contained in Teflon containers equipped with Teflon condensers, whereas the fluoride-free solutions were contained in glass equipment. All evaluations of 304L were made with sensitized (one hour at 675C, water quenched) coupons. Specimens were exposed to the liquid and to the vapor phase in all cases. Evaluations with Uranus S alloy used weldments in the as-welded condition in the liquid phase and sensitized coupons in the vapor phase. The specimens were removed from test, cleaned, dried, inspected and weighed at one week intervals.

The corrosion rates obtained with 304L and Uranus S alloy specimens, as determined by weight loss, are given in Tables V through VII. Summary data are given in Table VIII. It is apparent that the corrosiveness of IWW solution was not affected greatly by the compositional changes evaluated. A reduction in sulfate content was somewhat detrimental to 304L corrosion, whereas a reduction in $\text{Fe}(\text{III})$ content was beneficial. Based upon the average rate for the last three exposure periods, the 304L corrosion rate varied from a minimum of 5.1 mils/mo in the solution containing no sulfate, 20 percent $\text{Fe}(\text{III})$ and no $\text{Al}(\text{III})$ to a maximum of 9.5 mils/mo in the solution containing no sulfate and 50 percent $\text{Fe}(\text{III})$. The corrosiveness of PAW solution increased when the sulfate content was eliminated. However, the magnitude of corrosion, even for the most corrosive composition, was relatively small, about 1.8 mils/mo. In all cases, attack of 304L specimens was predominately intergranular, whereas attack on Uranus S was uniform. However, Uranus S weldments exposed to IWW solution were preferentially attacked in the area of the heat affected zone.

The corrosiveness of the fluoride-bearing ZWW solution was highly dependent upon the total nitrate concentration. Decreasing the aluminum nitrate concentration to 20 percent of the flowsheet value decreased corrosion of 304L by a factor of three. Decreasing both the aluminum

nitrate and ferric nitrate content to 20 percent (total nitrate from 8.4 to 6.2M) decreased corrosion by a factor of about 13. Corrosion of 304L was also evaluated in boiling ZWW solutions containing 0.0, 1.0, 2.0, 3.0 and 4.0M NH_4NO_3 (no aluminum nitrate present). The total nitrate concentration varied from 5.56 to 9.56M. The results of these tests, given in Table IX, indicated that the total nitrate concentration should not be allowed to exceed seven molar. Corrosion of 304L in ZAW solution was also dependent upon the total nitrate concentration. The corrosion rate in current ZAW solution was 1.7 mils/mo, whereas in the solution containing 20 percent of the flowsheet value of aluminum nitrate the corrosion rate was 0.7 mil/mo. The solution containing no sulfate, no aluminum nitrate and 20 percent ferric nitrate corroded 304L at a rate of only 0.1 mil/mo. As with the non-fluoride bearing solutions attack of 304L coupons was predominately intergranular, whereas Uranus S was attacked uniformly. However, Uranus S weldments exposed to ZWW solutions were preferentially attacked in the area of the heat affected zone. It is to be noted that the Zr(IV) concentration of the fluoride-bearing test solutions was nearly equal to the fluoride concentration (0.15 vs 0.18M). Zr(IV) is known to form a strong complex with fluoride ion, thus extrapolation of the corrosion data obtained with ZWW and ZAW solutions to systems with significantly lower Zr(IV)/F mole ratio would not be justified.

TABLE I
Composition of IWW Solutions
Moles/Liter

	Solution Number					
	1	2	3	4	5	6
HNO ₃	5.8	5.8	5.8	5.8	5.8	5.8
NaNO ₃	.07	.15	.47	.47	.47	.47
Fe ₂ (SO ₄) ₃	.15	-	-	-	-	-
Fe(NO ₃) ₃	-	.15	.15	.06	.06	.06
Al(NO ₃) ₃	.30	.30	.30	.30	.06	-
Na ₂ SO ₄	.20	.16	-	-	-	-
ZrO(NO ₃) ₂	.004	.004	.004	.004	.004	.004
Na ₃ PO ₄	.01	.01	.01	.01	.01	.01
Cr(NO ₃) ₃	.02	.02	.02	.02	.02	.02
Ni(NO ₃) ₂	.01	.01	.01	.01	.01	.01
Na ₂ SiO ₃	.01	.01	.01	.01	.01	.01
Ru(NO ₃) ₃	.002	.002	.002	.002	.002	.002
Total NO ₃ ⁻	6.9	7.4	7.7	7.5	6.7	6.6

TABLE II
Composition of PAW Solutions
Moles/Liter

	<u>Solution Number</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
HNO ₃	1.0	1.0	1.0	1.0	1.0	1.0
NaNO ₃	.07	.15	.47	.47	.47	.47
Fe ₂ (SO ₄) ₃	.15	-	-	-	-	-
Fe(NO ₃) ₃	-	.15	.15	.06	.06	.06
Al(NO ₃) ₃	.30	.30	.30	.30	.06	-
Na ₂ SO ₄	.20	.16	-	-	-	-
ZrO(NO ₃) ₂	.004	.004	.004	.004	.004	.004
Na ₃ PO ₄	.01	.01	.01	.01	.01	.01
Cr(NO ₃) ₃	.02	.02	.02	.02	.02	.02
Ni(NO ₃) ₂	.01	.01	.01	.01	.01	.01
Na ₂ SiO ₃	.01	.01	.01	.01	.01	.01
Ru(NO ₃) ₃	.002	.002	.002	.002	.002	.002
Total NO ₃ ⁻	2.1	2.6	2.9	2.6	1.9	1.8

TABLE III

Composition of ZWW Solutions
Moles/Liter

	Solution Number						
	1	2	3	4	5	6	7
HNO ₃	5.0	5.0	5.0	5.0	5.0	5.0	5.0
NaNO ₃	-	-	.14	.14	-	.14	.14
Fe ₂ (SO ₄) ₃	.075	-	-	-	.075	-	-
Fe(NO ₃) ₃	-	.075	.075	.03	-	.03	.03
Al(NO ₃) ₃	1.0	1.0	1.0	1.0	.20	.20	-
NH ₄ F	.18	.18	.18	.18	.18	.18	.18
Na ₂ SO ₄	.075	.075	-	-	.075	-	-
ZrO(NO ₃) ₂	.15	.15	.15	.15	.15	.15	.15
Na ₃ PO ₄	.01	.01	.01	.01	.01	.01	.01
Cr(NO ₃) ₃	.02	.02	.02	.02	.02	.02	.02
Ni(NO ₃) ₂	.01	.01	.01	.01	.01	.01	.01
Na ₂ SiO ₃	.01	.01	.01	.01	.01	.01	.01
Ru(NO ₃) ₃	.002	.002	.002	.002	.002	.002	.002
Total NO ₃ ⁻	8.4	8.6	8.8	8.6	6.0	6.2	5.6

TABLE IV
Composition of ZAW Solutions
Moles/Liter

	<u>Solution Number</u>						
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
HNO ₃	1.0	1.0	1.0	1.0	1.0	1.0	1.0
NaNO ₃	-	-	.14	.14	-	.14	.14
Fe ₂ (SO ₄) ₃	.075	-	-	-	.075	-	-
Fe(NO ₃) ₃	-	.075	.075	.03	-	.03	.03
Al(NO ₃) ₃	1.0	1.0	1.0	1.0	.20	.20	-
NH ₄ F	.18	.18	.18	.18	.18	.18	.18
Na ₂ SO ₄	.075	.075	-	-	.075	-	-
ZrO(NO ₃) ₂	.15	.15	.15	.15	.15	.15	.15
Na ₃ PO ₄	.01	.01	.01	.01	.01	.01	.01
Cr(NO ₃) ₃	.02	.02	.02	.02	.02	.02	.02
Ni(NO ₃) ₂	.01	.01	.01	.01	.01	.01	.01
Na ₂ SiO ₃	.01	.01	.01	.01	.01	.01	.01
Ru(NO ₃) ₃	.002	.002	.002	.002	.002	.002	.002
Total NO ₃ ⁻	4.4	4.6	4.8	4.6	2.0	2.2	1.6

TABLE V

Corrosion of 304L in Fluoride-Free High-Level Waste Solutions

Conditions: Six one-week exposures to boiling solutions.
Specimens exposed to liquid (L) and vapor (V) phases.

Solution (1)	Corrosion Rate, Mils/Month											
	Period											
	1		2		3		4		5		6	
	L	V	L	V	L	V	L	V	L	V	L	V
1) IWW, Current	3.05	.55	3.31	.09	4.77	.03	6.84	.13	6.33	.03	6.16	.73
2) IWW, 25% SO ₄ , 50% Fe	3.80	.84	4.53	.18	7.46	.24	8.28	.11	7.74	.15	7.38	.24
3) IWW, 0.0% SO ₄ , 50% Fe	3.68	.92	5.08	.78	6.80	.28	9.28	.39	8.34	.38	10.9	1.87
4) IWW, 0.0% SO ₄ , 20% Fe	2.91	.52	2.81	.14	3	.23	5.49	.42	5.49	.24	5.93	.51
5) IWW, 0.0% SO ₄ , 20% Fe, 20% Al	3.70	.53	5.16	.33	5.55	.29	7.10	.29	5.56	.07	6.58	.71
6) IWW, 0.0% SO ₄ , 20% Fe, 0.0% Al	2.48	1.30	2.99	.68	3.94	.39	5.88	.51	4.61	.29	4.76	1.10
1) PAW, Current	.15	.02	.28	.01	.26	.01	.25	.01	.29	.01	.45	.03
2) PAW, 25% SO ₄ , 50% Fe	.77	.01	.88	.01	1.18	.01	.87	.01	1.68	.04	1.29	.04
3) PAW, 0.0% SO ₄ , 50% Fe	1.27	.01	1.47	.31	2.03	.01	2.63	.32	1.35	.03	1.56	.01
4) PAW, 0.0% SO ₄ , 20% Fe	.87	.01	.75	.02	.72	.01	1.18	.04	.99	.01	1.29	.33
5) PAW, 0.0% SO ₄ , 20% Fe, 20% Al	1.04	.02	.95	.01	.87	.01	.96	.04	1.49	.01	.63	.01
6) PAW, 0.0% SO ₄ , 20% Fe, 0.0% Al	1.04	.04	.73	.03	1.02	.01	.83	.04	.35	.01	.49	.01

Note: (1) Percent values are percent of amount present in current solutions.

TABLE VI

Corrosion of 304L in Fluoride-Containing High-Level Waste Solutions

Conditions: Six one-week exposures to boiling solutions.
Specimens exposed to liquid (L) and vapor (V) phases.

Solution ⁽¹⁾	Corrosion Rate, Mils/Month											
	Period											
	1	2	3	4	5	6	7	8	9	10	11	12
	L	V	L	V	L	V	L	V	L	V	L	V
1) ZWW, Current	4.73	.95	7.38	.29	10.3	.25	13.3	5.20	12.3	.21	13.8	.50
2) ZWW, 25% SO ₄ , 50% Fe	4.42	.91	10.6	.34	20.9	.32	36.1	1.30	24.0	7.48	27.5	.16
3) ZWW, 0.0% SO ₄ , 50% Fe	3.98	2.63	7.14	1.28	10.5	1.56	13.0	.40	16.1	.62	19.9	.58
4) ZWW, 0.0% SO ₄ , 20% Fe	4.72	1.13	8.31	.24	12.5	.22	16.8	.27	16.3	.68	24.6	.35
5) ZWW, 20% Al	2.26	1.75	2.32	.52	3.05	.34	3.78	7.54	3.85	.44	4.46	.40
6) ZWW, 0.0% SO ₄ , 20% Fe, 20% Al	1.00	.41	.67	.10	.74	.34	.85	.42	1.02	.50	1.27	.04
7) ZWW, 0.0% SO ₄ , 20% Fe, 0.0% Al	1.02	.52	.55	.18	.74	.07	.71	.23	.92	.43	1.06	.08
1) ZWW , Current	1.46	.04	1.05	.04	1.20	.02	1.32	.45	1.72	.02	2.07	.01
2) ZWW , 25% SO ₄ , 50% Fe	1.26	.03	1.24	.03	1.47	.05	1.66	.31	2.08	.02	2.55	.02
3) ZWW , 0.0% SO ₄ , 50% Fe	1.00	.22	1.02	.03	1.24	.04	1.47	.37	1.94	.02	2.36	.01
4) ZWW , 0.0% SO ₄ , 20% Fe	1.01	.08	.83	.08	.98	.04	1.16	.14	1.43	.07	1.60	.01
5) ZWW , 20% Al	.76	.22	.65	.16	.66	.13	.58	.25	.76	.02	.77	.01
6) ZWW , 0.0% SO ₄ , 20% Fe, 20% Al	.61	.01	.42	.01	.28	.01	.28	.06	.30	.01	.31	.01
7) ZWW , 0.0% SO ₄ , 20% Fe, 0.0% Al	.48	.01	.26	.01	.12	.01	.11	.08	.13	.01	.13	.01

Note: (1) Percent values are percent of amount present in current solutions

TABLE VII

Corrosion of Uranus S Alloy in High-Level Waste SolutionsConditions: Four one-week exposures to boiling solutions

Solution	Corrosion Rate, Mils/Month							
	Period							
	1		2		3		4	
	L	V	L	V	L	V	L	V
1) IWW, Current	2.14	.60	2.27	.58	1.97	.57	2.00	.55
5) IWW, 0.0% SO ₄ , 20% Fe, 20% Al	2.00	.94	1.69	.31	2.15	.46	2.08	.26
1) PAW, Current	.64	.02	.58	.03	.61	.04	.52	.02
5) PAW, 0.0% SO ₄ , 20% Fe, 20% Al	.37	.01	.37	.04	.43	.01	.23	.01
1) ZWW, Current	1.75	2.31	1.86	.50	1.99	.90	2.00	.89
4) ZWW, 0.0% SO ₄ , 20% Fe	1.01	.95	.69	1.34	1.62	1.94	2.17	1.74
6) ZWW, 0.0% SO ₄ , 20% Fe, 20% Al	.56	.84	.29	.19	.23	.68	.27	1.05
1) ZAW, Current	.59	.40	.39	.04	.36	.06	.38	.03
4) ZAW, 0.0% SO ₄ , 20% Fe	.25	.11	.08	.10	.06	.06	.07	.04
6) ZAW, 0.0% SO ₄ , 20% Fe, 20% Al	.17	.01	.06	.01	.03	.01	.02	.00

TABLE VIII

Corrosion of 304L and Uranus S in High-Level Waste Solutions -
Summary of Liquid Phase Corrosion Data

Solution	Corrosion Rate, Mils/Month	
	304L ⁽¹⁾	Uranus S ⁽²⁾
1) IWW, Current	6.4	2.0
2) IWW, 25% SO ₄ , 50% Fe	8.0	-
3) IWW, 0.0% SO ₄ , 50% Fe	3.5	
4) IWW, 0.0% SO ₄ , 20% Fe	5.6	-
5) IWW, 0.0% SO ₄ , 20% Fe, 20 % Al	6.4	2.1
6) IWW, 0.0% SO ₄ , 20% Fe, 0.0% Al	5.1	-
1) PAW, Current	0.3	0.5
2) PAW, 25% SO ₄ , 50% Fe	1.3	-
3) PAW, 3.0% SO ₄ , 50% Fe	1.8	-
4) PAW, 0.0% SO ₄ , 20% Fe	1.2	-
5) PAW, 0.0% SO ₄ , 20% Fe, 20% Al	1.0	0.2
6) PAW, 0.0% SO ₄ , 20% Fe, 0.3% Al	0.6	-
1) ZWW, Current	13	2.0
2) ZWW, 25% SO ₄ , 50% Fe	29	-
3) ZWW, 0.0% SO ₄ , 50% Fe	16	-
4) ZWW, 0.0% SO ₄ , 20% Fe	19	2.2
5) ZWW, 20% Al	4.0	-
6) ZWW, 0.0% SO ₄ , 20% Fe, 20% Al	1.0	0.3
7) ZWW, 0.0% SO ₄ , 20% Fe, 0.0% Al	0.9	
1) ZAW, Current	1.7	0.4
2) ZAW, 25% SO ₄ , 50% Fe	2.1	-
3) ZAW, 0.0% SO ₄ , 50% Fe	1.9	-
4) ZAW, 0.0% SO ₄ , 20% Fe	1.4	0.07
5) ZAW, 20% Al	0.7	-
6) ZAW, 0.0% SO ₄ , 20% Fe, 20% Al	0.3	0.02
7) ZAW, 0.0% SO ₄ , 20% Fe, 0.0% Al	0.1	-

Notes: (1) Average rate during last three exposure weeks.
(2) Average rate during fourth exposure week.

TABLE IXCorrosiveness of ZWW Solution as a Function of Nitrate Concentration

Conditions: Current ZWW solution containing no aluminum nitrate butted to given total nitrate concentrations with ammonium nitrate. Three one-week exposures to boiling solutions. Sensitized 304L specimens.

<u>Total NO₃⁻, M</u>	<u>Corrosion Rate, Mils/Month</u>		
	<u>Period</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
5.56	0.59	1.00	1.27
6.66	0.54	1.15	1.35
7.66	0.92	2.29	3.50
8.66	1.48	5.21	7.28
9.66	2.63	13.8	28.0

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