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CORROSION STUDIES IN
PLUTONIUM-NITRIC-HYDROFLUORIC SOLUTIONS

Kazuji Terada

James M. Macki

Marston R. Dringman

David L. Cash

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

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Research and Ecology

PRODUCT AND HEALTH PHYSICS RESEARCH

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Corrosion
Plutonium
Nitric Acid
Hydrofluoric Acid
Process Solution

MASTER

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CORROSION STUDIES IN PLUTONIUM-NITRIC-HYDROFLUORIC SOLUTIONS

Kazuji Terada, James M. Macki, Marston R. Dringman, and David L. Cash

Abstract. Several alloys were evaluated as possible construction material in chemical processing equipment for plutonium at Rocky Flats. Corrosion studies were made of these alloys in solutions obtained from a production storage tank. The principal components of these solutions were nitric acid, hydrofluoric acid, and plutonium. Results showed relative concentrations of these components can significantly affect corrosion rates. Of the alloys tested, Inconel 690 exhibited the lowest corrosion rates in the process solutions. E-Brite 26-1 also showed corrosion resistance greater than 304L stainless steel.

INTRODUCTION

In the chemical processing of plutonium for weapons and fuels applications, plutonium as metal, oxide, or fluoride is dissolved in boiling HNO_3 -HF solutions. This acid combination is very corrosive to metals and presents a containment problem regarding the highly radioactive process solution. A number of reports on corrosion rates of different alloys in HNO_3 -HF solutions have been published.¹⁻⁵

Alloys having the greatest resistance to corrosion are high nickel-chromium alloys such as HAPO 20 (56 wt % nickel - 36 wt % chromium) and Corronel 230 (50 wt % nickel - 25 wt % chromium). Corrosion rates of unwelded HAPO 20 and Corronel 230 in boiling 13M HNO_3 -HF solution after 24 hours were 32 and 17 mil/month, respectively.¹ These corrosion rates are normally considered too high. In addition, HAPO 20 and Corronel 230 are experimental alloys and are not commercially available.

Plastics can sometimes be used in place of metals, but there are many situations where plastics are

not suitable. Some of the reasons are flammability, low heat-exchange properties, and low temperature tolerance compared to metal.

At Rocky Flats, 304L stainless steel has been used in the processing of plutonium in HNO_3 -HF solutions. The steel has corrosion rates significantly lower than 17 mils/month. This lower rate is due to (1) generally lower concentration of fluoride in the process stream, (2) lower overall temperature of the solute, and (3) the presence of plutonium in the solution. Corrosion rates are known to be highly dependent on the HF concentration.^{2, 5} The fluoride-ion concentration in Rocky Flats solutions can vary considerably, but it is generally about 0.05 molar. Solutions are kept at boiling temperature during actual dissolution, but during most other processing steps involving the solution, the temperature varies down to room temperature. Plutonium, like the aluminum ion, complexes quite strongly with fluoride ions and decreases the effective concentration of hydrofluoric acid. This in turn lowers the solution's corrosive effect on 304L stainless steel.

Previous to this work, no corrosion studies have been made under Rocky Flats process conditions to determine actual corrosion rates. In this work, tests were made to obtain this information. In addition, several new and old alloys were tested to seek a suitable replacement for 304L stainless steel to contain process solutions.

SUMMARY AND CONCLUSIONS

Test results show the relative concentrations of HNO_3 -HF-Pu in process solutions greatly affect

the corrosion rates of process equipment. By carefully controlling these concentrations, corrosion rates can be lowered, thereby increasing equipment life by years. Where it is necessary to use solutions that are highly corrosive to 304L stainless steel, use of more expensive Inconel 690 would ultimately result in greater economy. E-Brite 26-1, having a cost between that for 304L stainless steel and Inconel 690, could also be useful in HNO_3 -HF environments. However, it should be remembered that E-Brite 26-1 requires heat treatment after welding and this is not always possible in the process lines.

EXPERIMENTAL

Corrosion tests were conducted in Teflon®* pots 6 in. in diameter and 12 in. high. Each pot was covered with a tight fitting Teflon lid that had openings for an immersion heater, reflux condenser, and a thermometer. The immersion heater was made with an external quartz jacket, and the quartz was protected from the HF by Teflon tape. Teflon was also used for constructing "wetted" parts of the water-cooled reflux condenser whereas glass or plastic was used for the outer cooling jacket. Intermittent temperature measurements were made by passing a mercury thermometer through a hole in the lid of the reaction pot and into the solution. For most of the test duration, the hole was stoppered with a Teflon plug to prevent vapor leakage.

The presence of plutonium in the test solution necessitated enclosing the equipment in a glovebox; also separating the pots to prevent any possibility of creating a critical mass. The pots were kept apart by placing each in the middle of a 24-in.-diameter spacer ring.

Process solutions were used for the test media. These were obtained from the holding tanks into which solutions from the cascade dissolvers were stored for processing. They were regarded as typical of the process solutions and their analyses are listed in Tables 1, 2, and 3.

Table 1. First Series of Planned-Interval Tests.

Specimen	Corrosion Rates (mpy)*		Concentration of Solution
	in Solution	in Vapor	
After First 24 Hours			
304L	167	161	39.3 g/liter Pu 12.0 molar H ⁺ 1.02 g/liter F ⁻
	178	165	
309	136	109	
	126	112	
Carpenter 20 Cb-3	191	240	38.7 g/liter Pu 12.2 molar H ⁺ 1.1 g/liter F ⁻
	194	112	
Inconel 690	38	38	
	39	38	
E-Brite 26-1	70	65	38.9 g/liter Pu 12.2 molar H ⁺ 1.08 g/liter F ⁻
	70	61	
E-Brite 26-1 Welded and Heat Treated	71	71	
	70		
After Additional 46 Hours			
304L**	212	191	39.3 g/liter Pu 12.6 molar H ⁺ 1.10 g/liter F ⁻
	174	200	
309**	139	137	
	135	136	
Carpenter 20 Cb-3	321	269	40.5 g/liter Pu 12.7 molar H ⁺ 1.14 g/liter F ⁻
	378	265	
Inconel 690	45	40	
	44	39	
E-Brite 26-1	151	106	40.8 g/liter Pu 12.8 molar H ⁺ 1.00 g/liter F ⁻
	151	101	
E-Brite 26-1 Welded and Heat Treated	62	61	
	64		
After Final 24 Hours			
Carpenter 20 Cb-3	487	272	40.8 g/liter Pu 13.6 molar H ⁺ 1.14 g/liter F ⁻
	363	262	
Inconel 690	38	38	
	39	38	
E-Brite 26-1	199	133	41.6 g/liter Pu 13.08 molar H ⁺ 1.12 g/liter F ⁻
	197	127	
E-Brite 26-1 Welded and Heat Treated	49	48	

* mils per year

** Terminated after only 22 additional hours due to leak in the reflux condenser

* Trademark of E. I. duPont deNemours and Company.

Table 2. Second Series of Planned-Interval Tests.

Specimen	Corrosion Rates (mpy)*		Concentration of Solution
	in Solution	in Vapor	
After First 24 Hours			
304L	21	16	46.8 g/liter Pu 10.2 molar H ⁺ 0.66 g/liter F ⁻
	19	17	
309	14	15	
	14	15	
E-Brite 26-1	10	9	47.9 g/liter Pu 9.9 molar H ⁺ 0.70 g/liter F ⁻
	7	7	
E-Brite 26-1	8	9	
	7	10	
Inconel 690	9	15	47.5 g/liter Pu 10.9 molar H ⁺ 0.66 g/liter F ⁻
	8	12	
Inconel 690	12	16	
	16	11	
After Additional 42 Hours			
304L	23	22	47.9 g/liter Pu 9.0 molar H ⁺ 0.74 g/liter F ⁻
	23	22	
309	16	17	
	16	18	
E-Brite 26-1	11	15	49.6 g/liter Pu 9.4 molar H ⁺ 0.80 g/liter F ⁻
	11	17	
E-Brite 26-1	12	17	
	13	15	
Inconel 690	22	27	48.0 g/liter Pu 9.2 molar H ⁺ 0.82 molar F ⁻
	23	25	
Inconel 690	28	29	
	29	25	
After Final 24 Hours			
304L	33	26	47.4 g/liter Pu 9.4 molar H ⁺ 0.66 g/liter F ⁻
	36	27	
309	18	18	
	19	18	
E-Brite 26-1	19	28	57.4 g/liter Pu 10.8 molar H ⁺ 0.88 g/liter F ⁻
	18	31	
E-Brite 26-1	20	28	
	21	30	
Inconel 690	25	26	48.8 g/liter Pu 9.5 molar H ⁺ 0.79 g/liter F ⁻
	27	27	
Inconel 690	30	25	
	31	25	
* mils per year			

* mills per year

Table 3. Third Series of Planned-Interval Tests.

Specimen	Corrosion Rates (mpy)* in Solution	in Vapor	Concentration of Solution
After First 24 Hours			
304L	133	161	14.9 g/liter Pu 13.4 molar H ⁺ 0.41 g/liter F ⁻
	165	172	
309	168	174	15.0 g/liter Pu 12.9 molar H ⁺ 0.48 g/liter F ⁻
	121	117	
E-Brite 26-1	68	66	15.0 g/liter Pu 12.9 molar H ⁺ 0.48 g/liter F ⁻
Welded and Heat Treated	75	74	
E-Brite 26-1	75	68	15.16 g/liter Pu 13.8 molar H ⁺ 0.49 g/liter F ⁻
Heat Treated	76	70	
Inconel 690	65	53	15.16 g/liter Pu 13.8 molar H ⁺ 0.49 g/liter F ⁻
Welded	69	66	
Inconel 690	55	50	15.16 g/liter Pu 13.8 molar H ⁺ 0.49 g/liter F ⁻
Welded	46	42	
After Additional 46 Hours			
304L	168	187	14.5 g/liter Pu 12.4 molar H ⁺ 0.41 g/liter F ⁻
	270	203	
309	171	147	14.5 g/liter Pu 12.4 molar H ⁺ 0.41 g/liter F ⁻
	149	148	
E-Brite 26-1	50	52	16.8 g/liter Pu 13.0 molar H ⁺ 0.49 g/liter F ⁻
Welded and Heat Treated	51	49	
E-Brite 26-1	49	53	16.8 g/liter Pu 13.0 molar H ⁺ 0.49 g/liter F ⁻
Heat Treated	52	53	
Inconel 690	50	35	16.4 g/liter Pu 12.8 molar H ⁺ 0.53 g/liter F ⁻
Welded	50	40	
Inconel 690	44	37	16.4 g/liter Pu 12.8 molar H ⁺ 0.53 g/liter F ⁻
Welded	44	31	
After Final 24 Hours			
304L	167	206	14.46 g/liter Pu 11.2 molar H ⁺ 0.48 g/liter F ⁻
	162	224	
309	223	167	14.46 g/liter Pu 11.2 molar H ⁺ 0.48 g/liter F ⁻
	153	170	
E-Brite 26-1	38	29	40.6**g/liter Pu 9.6 molar H ⁺ 0.38 g/liter F ⁻
Welded and Heat Treated	35	40	
E-Brite 26-1	35	40	40.6**g/liter Pu 9.6 molar H ⁺ 0.38 g/liter F ⁻
Heat Treated	36	40	
Inconel 690	40	29	15.1 g/liter Pu 10.8 molar H ⁺ 0.5 g/liter F ⁻
Welded	40	30	
Inconel 690	39	30	15.1 g/liter Pu 10.8 molar H ⁺ 0.5 g/liter F ⁻
Welded	37	27	

* mils per year

** Probable analytical error

* mills per year

** Probable analytical error

Samples of E-Brite 26-1®* and Inconel 690®** alloys were obtained from the manufacturers. The remaining steel samples were commercial, 2-in. disks designed for corrosion tests. These disks were quartered to reduce each specimen's surface area. To obtain good corrosion data it is recommended that 250 ml of corrosion solution be used for every square inch of surface area⁶. Because of nuclear criticality considerations, the volume of solution had to be greatly reduced and a volume-to-area ratio of 100 ml of solution to 1 sq. in. of surface area was used in the tests.

With the exception of E-Brite 26-1 and Inconel 690, the alloy samples as received were simply cleaned in 65% HNO₃ before testing. Some of the E-Brite 26-1 and Inconel 690 samples were subjected to welding and heat treatment prior to testing. The types of welds were open air TIG weld, "inert" chamber TIG weld, and electron beam weld. The heat treatment of E-Brite 26-1 involved annealing for 1 hour at 1400°F and then water quenching. Inconel 690 was annealed at 2150°F for 1 hour and water quenched. Duplicate samples were immersed in the test solutions and suspended in the hot vapors.

Most of the corrosion studies utilized a modified "Planned-Interval Test" method⁷ in which corrosion rates were determined after three time intervals with the first and third time interval being 24 hours. It was hoped the maximum amount of information could be obtained by this procedure rather than extensive experimentation for prolonged periods.

The "Planned-Interval Test" was modified because nuclear criticality considerations precluded using large volumes and necessitated smaller pots separated by at least 2 feet. The availability of glovebox space for only a limited time also contributed to the decision to modify the "Planned-Interval Test."

RESULTS AND DISCUSSION

Results of the three series of tests are summarized in Tables 1, 2, and 3. Just a cursory glance through

the tables provides an indication that the process solutions can be highly corrosive. Table 1 shows the austenitic stainless steels (304L, 309, and Carpenter 20 Cb-3) have significantly lower corrosion resistance than the ferritic stainless steel (E-Brite 26-1) and nickel-chromium-iron alloy (Inconel 690). Only Inconel 690 had corrosion rates under 50 mils per year.

In contrast, the results of the second series of tests, listed in Table 2, show all the specimens had corrosion rates of less than 50 mils per year. Test solutions in the first series started with about 40 gm/liter Pu, 12 molar in HNO₃ and 1.1 gm/liter F⁻. The concentration of the solution for the second series was about 47 gm/liter Pu, 10 molar in HNO₃, and 0.7 gm/liter F⁻. The concentrations do not differ greatly, but the corrosion rates show significant differences.

Results of the third series of tests are listed in Table 3. Corrosion rates are generally quite high although the fluoride ion concentrations are relatively low. The high rates are due probably to the comparatively low plutonium and high acid concentrations.

Where corrosion rates are low, the difference in corrosion resistance of the alloy decreases. Table 2 shows the E-Brite 26-1 has lower corrosion rates than Inconel 690, and the corrosion resistance of 304L stainless steel is comparable to that of Inconel 690.

The modified "Planned-Interval Tests" were conducted to determine whether the metals become more susceptible to corrosion with time. For example, all three tables show that some metals exhibited higher corrosion rates during the final 24 hours than the initial 24-hour test period. This was due either to the increased corrosion susceptibility of the metal or the increased corrosivity of the liquids. The corrosivity of the liquid arises from the HNO₃-HF combination in solution, and during the tests, some of the acid and water is lost. From the binary azeotropic data on the H₂O-HNO₃ and H₂O-HF systems, proportionately more water than acid would be expected to vaporize. The acid concentration of the solution should therefore be increased.

* Trademark of the Airco Vacuum Metals Company.

** Trademark of the International Nickel Company.

Table 4. Concentration of the Three Test Solutions.

Solution	Analytical Results (moles/liter)			Calculated Results (moles/liter)			
	Pu	F	HNO ₃	PuF ⁺³	Pu ⁺⁴	HF	F ⁻
I	0.17	0.058	12	0.057	0.11	1.4×10^{-3}	8.5×10^{-8}
II	0.20	0.037	10	0.036	0.16	5.3×10^{-4}	3.9×10^{-8}
III	0.062	0.024	13	0.022	0.040	1.7×10^{-3}	9.0×10^{-8}

At the same time, the concentration of plutonium is increased to a greater degree than the acid, because of its nonvolatility.

The overall effect is that the corrosivity of the solution is decreased. This statement is based on corrosion tests made in a solution of initially 12M HNO₃, 0.5M HF, and 0.5M AL(NO₃)₃. Aluminum nitrate was used as a fluoride complexing agent in place of plutonium. Half of the solution was boiled off and the tests were repeated in the remaining liquid. Results of 24-hour corrosion tests showed the original and concentrated solutions were 117 and 65 mpy, respectively. Therefore, corrosivity of the test solution at boiling temperatures decreased with time. Any increase in corrosion rate must be attributed to increased corrosion susceptibility of the alloys and not to the solution.

Table 4 shows the analyzed concentrations of H⁺, F⁻, and Pu⁺⁴ of the three test solutions and the calculated concentrations of other chemical species in the solutions.

These concentrations are based on representative analytical results of the three solutions. A computer was used in making the calculations, and it was assumed that under the test conditions only one plutonium complex, PuF⁺³, was formed. According to McLane⁸ the difluoride complex is not formed until the HF/Pu ratio reaches about 6 and this ratio was not approached in any of the test solutions. The stability constant used for PuF⁺³ was 5.9×10^6 and for the dissociation

constant of HF, 7.2×10^{-4} was used. The stability constant for PuF₂⁺² is not known.

The calculated values in Table 4 are in agreement with the experimental results. Table 4 shows that HF, one of the key corrosive reagents, is lowest in solution II and results from corrosion tests showed solution II was less corrosive than the other two solutions although it contained about 50% more fluoride than solution III. This difference was due to the complexing of the F⁻ by Pu⁺⁴ which had a higher Pu concentration in solution II than solution III and offset the higher total fluoride concentration in the former solution. The effective HF and HNO₃ concentrations in solutions I and III are comparable according to the calculations, and their corrosion rates as shown in Tables 1 and 2 are also comparable.

Solution II was the least corrosive of the three test solutions by a significant factor. Its HNO₃ concentration, while lower than the other two, does not appear to be significantly different at first glance. This indicates that within the range of concentrations of the process solutions, there is considerable variation in corrosivity. By carefully controlling the relative concentrations of Pu-HNO₃-HF in the solutions, corrosion rates can be reduced to an acceptable level—even for 304L stainless steel. Although Table 2 shows the corrosion rates of 304L stainless steel to be of marginal utility, it must be recognized that the tests were conducted at boiling temperatures while the actual processes, for the most part, are performed at lower temperatures.

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