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**CORROSION OF DELTA PLUTONIUM IN
ROCKY FLATS TAP WATER**

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MASTER

Chemistry Research and Development
PRODUCT INTEGRITY AND SURVEILLANCE

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SUBJECT DESCRIPTORS

Corrosion

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MASTER

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CORROSION OF DELTA PLUTONIUM IN ROCKY FLATS TAP WATER

*Angelo E. Hodges, III, Joe J. Reynolds,
and John M. Haschke*

Abstract. Corrosion studies have been conducted which establish the corrosive effects of ordinary tap water at Rocky Flats on delta-stabilized plutonium. Corrosion rates were established by measuring the weight loss of a sample completely immersed in tap water for specified periods of time. Tests were conducted for periods ranging from 21 to 1824 hours at ambient temperature in sealed 125-ml containers. The weight changes observed revealed that the corrosion of delta plutonium by tap water in a closed system occurs through two separate processes. Each results in a different average corrosion rate. Initially a typical diffusion-controlled surface reaction was observed which resulted in an average corrosion rate of 0.264 mg/(cm²·hr). The second corrosion process begins when cracking and flaking of the corrosion product layer occurs. This results in an increase in the corrosion rate to 0.52 mg/(cm²·hr).

INTRODUCTION

During the last year or so, considerable interest has occurred regarding the corrosive effects of water (i.e. sea water, tap water, and distilled water) on alpha and delta plutonium contained in a closed non-circulating system. Recently, work was completed at Rocky Flats which established the corrosion rate of delta plutonium in a standard solution of sea water. As an extension of that study, corrosion tests involving delta plutonium and ordinary Rocky Flats tap water also were performed. As in the previous study, the tap water corrosion tests were conducted in accordance with the NACE Standard Method TM-0-69 for corrosion testing. Results of the tap water corrosion study are summarized in this report.

EXPERIMENTAL

The tap water corrosion tests were conducted by totally immersing delta plutonium coupons, each

**TABLE 1. Analysis of Rocky Flats Tap Water
(August 7, 1978)**

Substance	mg/l	Radioactivity	pCi/l
Dissolved Solids	49	Alpha	6
Cl ⁻	4	Beta	19
F ⁻	0.5	Ra-226	2
NO ₃	<1	U-235	0
NH ₃	0.5	Sr-90	<3
SO ₄ ²⁻	28		
CN ⁻	<0.04		
Ag	<0.0001		
As	<0.01		
B	<0.01		
Ba	0.05		
Be	<0.0001		
Ca	18		
Cd	<0.01		
Fe	0.2		
Hg	<0.005		
Mg	6.5		
Mn	0.008		
Na	2.1		
P	0.94		
Zn	0.012		

with an approximate surface area of 6.48 cm², in 125 ml of Rocky Flats tap water. An analysis of the tap water is found in Table 1. Corrosion rates were obtained by measuring the weight loss of the test coupons after a specified storage interval. Before the study was initiated, each of the plutonium coupons was cleaned of any previously accumulated oxide residues or other surface contaminants. Cleaning was conducted in the following manner: Each coupon was brushed with a fine-wire stainless steel brush, uniformly abraded with 120 grit silicon

carbide paper, solvent cleaned in 1,1,1-trichloroethane, and air dried. Following the cleaning process, each coupon was weighed to the nearest 0.1 mg and immersed in 125 ml of Rocky Flats tap water. The corrosion tests were conducted at ambient temperature in air under normal glove-box pressures (600 to 610 mm Hg). After specified intervals, the test coupons were removed from the test environment, air dried, brushed with a stainless steel brush to remove accumulated corrosion products, and reweighed to the nearest 0.1 mg.

RESULTS

Results of these corrosion tests indicate that extensive corrosion of delta plutonium can occur in relatively short periods of time when the plutonium is exposed to ordinary tap water. From the data it has been determined that the corrosion occurs through two separate processes, which run consecutively. Initially a diffusion-controlled corrosion reaction predominates. During this process, water must diffuse through a product layer (probably PuO_2) before reacting with the plutonium metal. After a period of time (about 400 hours), cracking and flaking of the corrosion layer occurs which allows free movement of the water to the unreacted plutonium surfaces.

If the initial corrosion process is controlled by the rate of diffusion of water across the product layer, it should follow the simple parabolic rate law,^{1, 2}

$$\frac{dy}{dt} = \frac{k}{y}$$

where y equals the thickness of the corrosion layer (which is directly proportional to the amount of corrosion per unit area, if the layer is of uniform thickness), t equals the elapsed time, and k is a proportionality constant.

After integration, this equation becomes

$$\frac{1}{2} y^2 = K_1 t + K_2$$

or

$$y = K_1^{\frac{1}{2}} t^{\frac{1}{2}} + K_2^{\frac{1}{2}}$$

where $K_1^{\frac{1}{2}}$ and $K_2^{\frac{1}{2}}$ are new constants. If y and t are set equal to zero, the initial conditions, then $K_1^{\frac{1}{2}}$ becomes zero. Thus, the parabolic rate equation reduces to

$$y = K_1^{\frac{1}{2}} t^{\frac{1}{2}}$$

If the initial corrosion process follows the diffusion controlled model, then a plot of the corrosion as a function of the square root of the elapsed time should yield a straight line with a slope of $K_1^{\frac{1}{2}}$. Figure 1 graphs the corrosion (in mg/cm^2) versus the square root of the elapsed time. The zero shift observed in the graph was caused by the experimental procedure which was employed to remove corrosion products from test coupons after the coupons were taken from the test environment. Although each of the plutonium coupons was wire brushed in the same manner and to approximately the same degree, the serious pitting caused by the corrosion of the coupon surfaces made it impossible to remove all of the corrosion products. However, the small amount of material remaining after the coupons were wire brushed, was not sufficient to invalidate the corrosion rates or the parabolic rate test. A least-squares linear regression of the parabolic rate data yields a correlation coefficient (R) of 0.98398.

The second corrosion process begins with the cracking and flaking of the corrosion product layer. As water moves to the unreacted plutonium, corrosion is accelerated to $0.52 \text{ mg}/(\text{cm}^2 \cdot \text{hr})$. Because the cracking continues as the corrosion products build up, the corrosion is no longer diffusion controlled. The data indicates, however, that the cracking and flaking is a continuing process that results in a constant rate of corrosion. Figure 2 graphs the corrosion as a function of the elapsed time from 400 hours to the conclusion of the experiment. Although considerable variation can be seen in the amount of corrosion as the test progresses, it is easy to discern that corrosion is constant. Table 2 provides a summary of the weight loss incurred by each of the test coupons, along with total corrosion and instantaneous corrosion rates. A graph showing all of the corrosion data and the separate corrosion regions is provided by Figure 3.

FIGURE 1. Parabolic Rate Test for Phase I Region

FIGURE 2. Partial Results for Tap Water Corrosion

TABLE 2. Results of Delta Plutonium Coupon Weight Loss in Tap Water

Coupon Weight (g)		Total Weight Loss (g)	Total Time (hrs)	Corrosion (mg/cm ²)	Corrosion Rate [mg/(cm ² ·hr)]
Initial	Final				
3.6223	3.5736	0.0487	21	7.51	0.3579
3.9801	3.9272	0.0529	21	8.16	0.3887
4.8196	4.7726	0.0470	22	7.25	0.3454
5.0698	4.9687	0.1011	44	15.60	0.3546
5.3087	5.2409	0.0678	44	10.46	0.2378
5.0713	4.9977	0.0736	44	11.36	0.2581
3.5736	3.4245	0.1491	72	23.01	0.3196
3.9272	3.7835	0.1437	72	22.18	0.3080
4.7726	4.6339	0.1387	72	21.40	0.2973
4.9977	4.8153	0.1824	122	28.15	0.2346
5.6369	5.4510	0.1859	122	28.68	0.2351
4.8791	4.6954	0.1837	122	28.35	0.2324
5.0847	4.8191	0.2656	172	41.00	0.2383
4.6288	4.3824	0.2464	172	38.02	0.2211
5.3078	5.1087	0.1991	172	30.73	0.1786
5.2409	4.9600	0.2809	220	43.35	0.1970
5.0360	4.7059	0.3301	220	50.94	0.2316
4.9687	4.6696	0.2991	220	46.16	0.2098
4.8596	4.3959	0.4637	360	71.56	0.1988
4.9717	4.3723	0.5994	360	92.50	0.2569
5.3434	4.7596	0.5838	360	90.09	0.2503
5.1497	4.3611	0.7886	624	121.70	0.1950
4.5544	3.9110	0.6434	624	99.29	0.1591
4.9478	4.2763	0.6715	625	103.63	0.1658
4.9340	4.0025	0.9315	695	143.75	0.2068
5.0887	4.3196	0.8691	695	134.12	0.1930
3.4993	2.2795	0.7698	696	118.80	0.1709
4.6620	3.3050	1.3570	836	209.41	0.2505
4.6056	2.8212	1.7838	836	275.28	0.3293
4.7470	3.6763	1.0707	836	165.23	0.1976
4.9635	3.8100	1.1535	984	178.01	0.1809
4.6451	2.9194	1.7257	984	266.31	0.2706
4.6500	2.3347	2.3153	984	357.30	0.3631
4.5334	3.6014	1.9320	1176	298.15	0.2535
4.7563	3.0293	1.7270	1176	266.51	0.2266
4.9342	2.5055	2.4287	1176	374.80	0.3187
4.2342	1.1943	3.0399	1212	469.12	0.3877
4.2229	2.0776	2.1453	1212	331.06	0.2732
5.1503	2.5537	2.5966	1212	400.71	0.3306
6.3130	2.8170	3.4960	1512	539.51	0.3568
5.2381	2.1780	3.0601	1512	472.24	0.3123
4.8081	1.9813	2.8268	1512	436.23	0.2885
5.1147	1.4079	3.7068	1824	572.04	0.3136
5.1009	1.8154	2.2855	1824	507.02	0.2780
5.0332	4.5280	4.5280	1824	698.77	0.3831

FIGURE 3. Total Results for Tap Water Corrosion.

CONCLUSION

From data gathered during this corrosion study, it is apparent that extensive corrosion of delta plutonium within a closed system containing ordinary tap water can occur in relatively short periods of time. This corrosion can cause changes in the plutonium configuration, which may result in a change in the nuclear properties of the system.

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