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0.0 SUMMARY

Pump Loops. Dynamic corrosion data are presented for two slurry runs made in 100A pump loop CS. One test was terminated after 49 hr of 300°C operation at an average concentration of 543 g of thorium per kilogram of water, because of plugging in the loop pressurizer. The second test was terminated, as scheduled, after 300 hr operation at an average circulating concentration of 348 g of thorium per kilogram of water. In this test, thoria was charged to the system in five batch additions while operating at 300°C and 1500 psi pressure.

Calibration water runs and an attempted slurry run on the experimental in-pile slurry loop are described.

Toroids. Studies in toroids of circulating thorium oxide slurries indicate some correlation between ultimate particle size and attack rate on stainless steel. The preparation and behavior of sized fraction of thorium oxide calcined at 1200, 1400 and 1600°C are given. Generally, less attack on type 347 stainless steel and titanium was observed for the smaller original particle size, below 1 μ , while no effect of calcination temperature was evident. The effect of time of calcination at 1400°C, ranging from 2 to 96 hr is discussed. Particle characteristics affecting the degradation in size on circulation are discussed. Additions of sodium phosphate or pyrophosphate at pH values from 7 to 11, resulted in severe attack of titanium by circulating thorium oxide slurries.

1.0 PUMP LOOPS.

1.1 100A Loops. Two additional slurry tests, Runs CS-25^{1.1.a} and CS-27,^{1.1.b} were made in the 100A pump loop CS during the quarter. Each test was preceded by an operational performance test using oxygenated water at 300°C. The performance tests were designated CS-24W and CS-26W, respectively.

In the last report,^{1.1.c} ORNL-2096, a description was given concerning operational instabilities and pump cavitation which occurred in Run CS-23, a 312-hr corrosion test at 300°C with a circulating concentration of 1000 g of thorium per kilogram of water. The difficulties were attributed to excessive flow of slurry, via the mixing line, to the pressurizer where slugs of gas had been entrained in the slurry and carried to the pump. This had occurred using a 1-in. mixing line with a flow of 31 gpm and a line pressure drop of 40 psi as measured on water at room temperature. Prior to Run CS-25, the 1-in. mixing line was replaced by a 1/2-in Sch 80 pipe and flow was reduced by appropriate restrictors to 9 gpm with a corresponding line pressure drop of 46 psi.

A second modification to the system consisted in changing the bearings in the 100A centrifugal pump. Formerly the pump had been operated using No. 14 Graphitar bearings in combination with 98M2 Stellite journals. Severe wear of the front Graphitar bearings had occurred in nearly every run, even though the cavity of the pump had been purged continuously with condensate at the rate of 5 to 6 liters/hr. Front bearing wear ranged from 0.0050 in. to 0.0200 in. in run periods of 30 to 350 hr and necessitated terminating the runs before scheduled shutdown. The front Graphitar bearing was, therefore, replaced by a bearing of 98M2 Stellite in combination with a 98M2 Stellite journal.

Run CS-24W, a 49-hr performance test, was made using oxygenated water at 300°C to determine the operational characteristics of the system

with the above modifications. In general, system operation was very steady. Pump performance, which was followed by means of an oscilloscope and a microphone affixed to the pump housing, was quite satisfactory. There was no measurable bearing wear when the pump was disassembled after the test.

In Run CS-25 the three sample barrels loaded with pin-type corrosion specimens contained flow restrictors to give velocities of 11, 21 and 41 fps across the specimens with a total flow of 43 gpm, based on water flow measured at room temperature. Slurry flow through the mixing line at room temperature was approximately 8 gpm.

The system, after the usual evacuation, was charged to a concentration of 958 g of thorium per kilogram of water using 17.3 liters of slurry prepared from Batch 10-2A thorium oxide. The thorium oxide had been made at ORNL from especially pure thorium nitrate by oxalic acid precipitation and calcination at 800°C. Before charging the loop, the slurry had been passed while wet through a 200-mesh screen.

The initial slurry sample was withdrawn from the system at run hour 3. By chemical analysis, it contained 572 g of thorium per kilogram of water. A second sample taken 20 hr later contained 496 g of thorium per kilogram of water. During the period between run hours 26 and 29.4, additional slurry was charged to the system by means of the slurry addition device^{1.1.c} in order to increase the circulating concentration to 1000 g of thorium per kilogram of water. The addition was made in two increments. The first charge contained 2785 g of thorium. The second contained 872 g of thorium.

A characteristic rise in pump power occurred during the first addition; however, during the second addition, the pump power decreased steadily. A sample taken after this addition contained only 562 g of thorium per kilogram of water. A period of erratic operation followed and a noise developed in the pump. At run hour 42.7 the auto-control on the lower pressurizer heater shut the system down because of overheating. After

circulation was resumed, the pressurizer was surveyed with a scintillometer. Scintillometer readings indicated that there was a heavy accumulation of thorium which extended from the lower pressurizer section which contained the straightening vanes up to the by-pass line inlet. The system was sampled and temporarily shut down at hour 46.

After the loop had cooled to 190°C the run was continued. An additional 2.75 liters of water and 650 ml of 0.9 N H_2SO_4 was charged to the system with a pulsafeder when circulation began. With these additions, the expanded volume at 300°C operating temperature would be sufficient to fill the pressurizer with liquid to a point above the level of solids indicated by scintillometer readings. The addition of acid was made as an aid in resuspending of the solids which adhered to the pressurizer walls. Scintillometer values remained unchanged after the addition of acid. Subsequently, 60 psi of oxygen was charged rapidly to the system to provide a sparging action.

Scintillometer readings after sparging indicated that the thorium had been dislodged from the upper section of the pressurizer but readings remained high adjacent to the heaters and around the vanes, indicating that heavy accumulations remained on the walls there. Overheating of the lower pressurizer heater continued and general operation of the system was very erratic.

An additional 350 psi of oxygen was charged to the system when the loop temperature reached 285°C but no improvement in operation resulted. Therefore, the run was terminated after 49 hr total circulation time.

The loop was cooled to room temperature and disassembled without draining or flushing. The upper section of the pressurizer was found to be free of solids; however, a heavy plug of thorium (avg density, 3.0), which extended from just above the top pressurizer heater to the bottom of the vanes, had accumulated in the lower section of the 4-in. pipe.

With the exception of a small hole, approximately 1 to 1.5 in. in diameter through the center of the plug, the pipe was filled. No other obstructions were found in the remainder of the system.

Comparative chemical analytical data and particle size analyses of samples withdrawn from the system during circulation and samples of the plug are shown in Table 1.1.

Pump components were considerably worn during the 49-hr test. The pump impeller lost 8.5 g. No localized attack was apparent, although both front and rear surfaces of the impeller were highly polished. The front bearing and journal of 98M2 Stellite wore 0.0026 in. and 0.0195 in., respectively; the back Stellite journal, 0.0005 in., and the back Graphitar bearing, 0.0002 in.

No modifications in loop geometry were made before Run CS-27; however, the pump was refitted with No. 14 Graphitar bearings and a new rotor, fabricated with a solid shaft having 98M2 Stellite journals, was used. A 30-hr performance test, Run CS-26W, at 300°C using oxygenated water was made before the following slurry test. No measurable wear of any of the pump parts was detected after the test.

For Run CS-27, a new method of charging slurry to the system was used. Initially the loop was charged with 17.3 liters of water and 120 psi of oxygen at room temperature. After circulating water in the system at 300°C for a period of 66 hr, sufficient slurry was added to the loop during operation to provide a circulating concentration of 500 g of thorium per kilogram of water. Five batch additions of a slurry prepared from lot IO-2 thoria were required to obtain the desired concentration. After each addition, the loop was sampled to determine what percentage of the added thoria was being circulated. Concentration changes were followed by withdrawing samples into special sample vials, weighing, precisely measuring the volume of the sample with a cathetometer and calculating the sample density.

After each of the first four additions the circulating concentration reached the calculated concentration level within 30 min after the charge was added, based on analyses taken at such times. The fifth charge of 1965 g of thorium oxide was injected into the loop at run hour 78 to provide a final calculated circulating concentration of 500 g of thorium per kilogram of water. A sampled concentration of 490 g of thorium per kilogram of water was obtained one hour after the addition was made. Concentration changes were then followed by sampling at 48-hr intervals for the duration of the test. A gradual downward trend to about 200 g of thorium per kilogram of water occurred over the following 222-hr period to run hour 300. A summary of sample data for Run CS-27 is shown in Table 1.2.

The scheduled 300-hr test was terminated without incident. With the exception of a moderate deposit of slurry in the annulus between the specimen holder and one sample barrel in which the flow of slurry was approximately 6 gpm, no accumulations of thorium were found in the system. No measurable wear of pump parts occurred, other than the impeller, which lost a total of 11.5 g, due principally to localized erosive attack of the front hub and impeller vanes.

Loop caking and corrosion based on slurry analysis and inventory are shown in Table 1.3 for Run CS-27. Cake (i.e., non-circulating ThO_2) appeared to build up for the first 25 to 50 hr and then did not increase further until the period between hours 216 and 287, at which time the apparent amount of cake began an increase to double the original value, from about 3 to about 6 kg of thorium oxide. All of this increase, however, may not have been real, as sampling valve difficulties were encountered during this period. The pump power requirement did not decrease during the period, which indicates that there was no substantial reduction in circulating thorium oxide concentration. The loop drained readily after shutdown, and no unusual caking of the thorium was noted sufficient to account for such a quantity of "cake".

The differential corrosion rate of stainless steel and titanium was estimated for the various periods between samples. Except for the first

few hours, which showed higher values, the stainless steel corrosion rate for the loop was relatively constant for the run, averaging 1.5 mpy. Titanium appeared to be attacked at a relatively constant rate also, except for the final few hours, averaging 151 mg/hr for the run.

Corrosion rates calculated from weight losses of defilmed pin specimens exposed for 49 hr at an average concentration of 543 g of thorium per kilogram of water in Run CS-25 at 11, 21, and 41 fps, respectively, included (in mpy): gold, 0.4, 0.4, and 4; austenitic stainless steels, 2 to 4, 5 to 9, and 18 to 23; titanium and alloys, <0.1 to 1, 3 to 5, and 7 to 11; Zircaloy-2, < 0.1, 1, and 6; and mild steel, 140 to 160, 120 to 210, and 190 to 220. Generalized system corrosion averaged 4 mpy based on stainless steel products found in the slurry.

Corrosion rates observed on pin specimens exposed for 300 hr at an average concentration of 348 g of thorium per kilogram of water in Run CS-27 at 10, 22, and 41 fps, respectively, were (in mpy): gold, 0.1, 0.1, and 0.6; austenitic stainless steels, 0.7 to 1, 2 to 4, and 6 to 9; titanium and alloys, 0.2, 2, and 6; Zircaloy-2, 0.1, 0.1, and 2; mild steel, 11, 13, and 20 to 28; Incoloy, 1 and 8 at 11 and 21 fps, respectively; and nickel at 40 fps, 6. Corrosion rates of each pin-type specimen exposed in Runs CS-25 and CS-27 are presented in Table 1.4. Generalized system corrosion, as noted above, averaged 1.5 mpy for stainless steel.

For Run CS-25 the velocity was 9.5 fps in the main loop, 13 fps in the by-pass mixing line, and 0.26 fps in the pressurizer. In Run CS-27 the velocity in the main line was 9.6 fps, 14 fps in the mixing line, and 0.26 fps in the pressurizer. These values are those obtained by metering the flow of water in the loop at room temperature. System corrosion values cited above were calculated based on a gross system volume of 27.6 liters and a wetted surface area of 21,000 cm² at operating temperature.

TABLE 1.1

SUMMARY OF SAMPLE DATA - RUN CS-25

Run Time, hr	0	3.0	23.2	29.4 ^a	46.0 ^b	49.0	Solids Removed From Pressurizer After Shutdown	
							Center of Plug	Adjacent to Wall
Slurry Conc'n								
g Th/kg H ₂ O	958	572	496	580	506	562	2700 (Den.-3.12)	2340 (Den.-2.85)
mg Th/g slurry	458	345-347	317-319	348-350	322-321	339-343	660-665	638-640
H ₂ O, mg/g slurry							229	252
Solid Phase								
Fe, mg/g slurry	0.016	0.037	0.142	0.133	0.172	0.235	0.480	0.470
Cr, " "	0.003	0.036	0.054	0.119	0.116	0.102	0.199	0.185
Ni, " "	0.006	0.017	0.024	0.037	0.095	0.030	0.062	0.074
Ti, " "	0.002	0.027	0.071	0.059	0.099	0.078	0.146	0.132
Co, " "	0.005	0.005	0.005	0.16	0.21	0.05	0.005	0.005
Cl, " "	0.015	0.015	0.01	0.01	0.01	0.01	0.01	0.01
Si, " "	0.01	0.01	0.01	0.01	0.01	0.03	0.07	0.07
SO ₄ , " "	0.01	0.01	0.01	0.01	0.01	2.49	4.90	3.93
Mg, " "	0.010	0.020	0.011	0.020	0.013	0.016	0.020	0.023
Al, " "	0.010	0.015						
Average Sedimentation Particle Size ^c								
Over 10 μ , (% by wt)	28	0	1	2	0	0	1	0
3 to 10 μ , " " "	20	8	7	3	3	2	16	3
1 to 3 μ , " " "	27	25	19	21	23	30	20	20
< 1 μ , " " "	25	67	73	74	73	68	63	77
X-Ray Crystallite Size, Å	240	245	240	245	255	245		
Surface Area, N ₂ (m ² /g)	16.5			21.1		21.5		

a. Slurry addition made at run hour 26 - 29.5.

b. 650 ml 0.9 N H₂SO₄ added at hour 46.c. Determined by neutron activation analysis using 0.001 M Na₄P₂O₇.

TABLE 1:2

RUN CS-27: ANALYTICAL AND PARTICLE SIZE DATA ON SAMPLES

Slurry Cir. Hr.	Charge ⁱ 0	7.9 ^e	23.9 ^e	29.5 ^e	48.3 ^e (b)	53.5 ^e (c)	119.3 (c)	167.3 (c)	215.8 ^d	287.2 ^d (f)	289.4 ^e (f)	291.4 ^d (f)	293.4 ^e (f)	294.3 ^e (f)	CS-27 Drain 300.9
Slurry Concentration															
g Th/kg H ₂ O (dens) _b	-	360	-	400	400	490	460	460	410	285	370	285	355	200	UNCLASSIFIED (Avg) ^j (348) 532
g Th/kg H ₂ O (anal) _b	958	339	-	338	-	381	403	435	390	254	318	166	212	188	
mg Th/g slurry (anal)	(458)	245	-	244	(b)	266 ^c	276 ^c	291 ^c	270	197	233	144	168	153	
mg H ₂ O/g slurry (anal)	-	-	-	-	-	-	-	-	-	716	730	831	808	822	
Fe, µg/g slurry	16	67	-	124	-	172	349	344	427	425	513	326	249	338	
Cr, " " "	3	23	-	33	-	30	56	65	97	44	54	29	41	32	869
Ni, " " "	6	9	-	19	-	32	71	72	76	82	98	63	47	66	154
Ti, " " "	< 20	20	-	40	-	78	71	162	246	50	265	384	297	406	137
Co, " " "	< 5	-	-	< 10	-	< 10	< 10	< 10	< 10	< 5	< 5	< 5	40	5	880
pH of slurry	-	8.4	-	7.8	-	7.8	7.2	7.0	7.0	5.8	6.8	6.9	6.7	6.7	< 5
Gas Analysis	(Al, 10 SO ₄ , < 100 Si, < 10 Mg, 10 Ca, < 50)														
Oxygen (ppm)			984												
CO ₂ (ppm)			13												
Particle Size ^a															
Over 10 µ (wt.%)		1		1	1	1	1	1	1	1					
3 to 10 µ "		6		6	5	4	7	4	4	2					
1 to 3 µ "		25		20	20	20	36	27	37	34					
Under 1 µ "		69		76	75	76	56	69	58	64					
Avg. Particle Size, µ		0.7		0.7	0.7	0.7	0.95	0.75	0.91	0.85					

a. By gravitational sedimentation in 0.005 Na₄P₂O₇ using neutron activation analysis.

b. Sample lost during analysis.

c. Portion of sample could not be dissolved.

d. Regular sample valve at pump discharge leaking but used.

e. Valve at pressurizer pot used. Valve at pump discharge inoperable.

f. Entire sample dissolved after drying.

g. Slurry additions made at slurry circulation hours 0, 1, 4, 25 and 50.

i. Same as for run CS-25

j. The closely spaced samples between slurry circulation hours 287.2 and 294.3 are treated as a single sample in obtaining the average concentration.

TABLE 1.3.

LOOP CAKING AND CORROSION BASED ON SLURRY ANALYSIS AND INVENTORY

RUN CS-27

Slurry Circ. Hr.	Inventory		Circ. ThO ₂ kg ^a	Cake, ThO ₂ kg ^c	Cumulative Corrosion Products ^b		Differential Attack Rates	
	H ₂ O	ThO ₂			(Fe, Cr, Ni)	Ti	347 SS	Ti
	kg	kg			grams	grams	mpy	mg/hr
7.9	16.5	7.1	6.4	0.7	2.1	0.5	5.6	62
29.5	16.8	9.4	6.5	2.9	4.9	1.2	2.8	33
53.5	16.3	10.8	7.1	3.7	6.4	2.3	1.3	44
119.3	16.3	10.7	7.5	3.2	12.1	2.0	1.9	-4
167.3	16.2	10.7	8.0	2.7	12.1	4.1	0	44
215.8	16.0	10.4	7.1	3.3	16.9	6.9	1.7	49
287.2	15.8	10.3	4.6	5.9	20.0	3.7	1.0	-44
289.4	15.7	10.3	5.7	4.6	20.6	7.7	(d)	(d)
291.4	15.7	10.2	3.1	7.1	20.7	13.6	(d)	(d)
293.4	15.6	10.2	3.7	6.5	17.8	11.2	(d)	(d)
294.3	15.5	10.1	3.3	6.8	20.4	15.0	1.4	1580
	Cumulative Corrosion Rate						1.48	151
300.9	Final drain sample ^a				19.5	15.1		

a. Based on water inventory and circulating concentration.

b. Assumed to have been associated with thorium oxide.

c. All non-circulating thorium oxide and solids.

d. Value included in calculation of following period.

TABLE 1.4

CORROSION RATES OF PIN TYPE SPECIMENS, RUNS CS-25 AND CS-27

Test Conditions	Flow Rate ($\pm 10\%$)	Pin Material	No. Pins	Corrosion Rate, mpy		
				Minimum	Average	Maximum
RUN CS-25						
ThO ₂ Slurry Concentration (g Th/kg H ₂ O): 496-580 (543 avg) Temperature: 300°C Circulation Time: 49 hr Additions: 66-863 ppm O ₂ (Avg. 553 ppm)	11	309 SCb SS	1	---	4	---
		316 SS	1	---	4	---
		347 SS	2	2	3	3
		Mild Steel ^a	2	140	150	160
		Gold	1		0.4	
		Platinum	1		0.1	
		Ti (3% Al, 5% Cr)	2	0.1	0.5	1
		Ti RC-55	2	0.1	0.1	0.1
		Ti RC-70	1		0.1	
		Zircaloy-2	1		0.1	
			21	309 SCb SS	1	
316 SS	1				9	
347 SS	2			5	7	9
Mild Steel ^a	2			120	165	210
Gold	1				0.4	
Platinum	1				0.5	
Ti (3% Al, 5% Cr)	1				5	
Ti RC-55	2			3	4	4
Ti RC-70	1				4	
Ti 75A	1				4	
Zircaloy-2	1				1	
	41	309 SCb SS	1		22	
		316 SS	1		21	
		347 SS	2	18	21	23
		Mild Steel ^a	2	190	205	220
		Gold	1		4	
		Platinum	1		3	
		Ti (3% Al, 5% Cr)	1		8	
		Ti RC-55	2	9	10	11
		Ti RC-70	1		10	
		Ti RC-75A	1		10	
		Zircaloy-2	1		6	

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TABLE 1.4
(Continued)

Test Conditions	Flow Rate ($\pm 10\%$)	Pin Material	No. Pins	Corrosion Rate (mpy)		
				Minimum	Average	Maximum
RUN CS-27						
ThO ₂ Slurry Concentration: (g Th/kg H ₂ O): 166-403 (348 avg) Temperature: 300°C Circulation Time: 49 hr Additions: 984 ppm O ₂	10	309 SCb SS	1		2	
		316 SS	1		1	
		347 SS	2	1	1	1
		Mild Steel ^a	2	11	11	11
		Gold	1		0.1	
		Incoloy	2	1	1	1
		Platinum	1		0.1	
		Ti (3% Al, 5% Cr)	2	0.2	0.2	0.2
		Ti RC-55	1		0.2	
		Zircaloy-2	1		0.1	
	22	309 SCb SS	1		2	
		316 SS	1		4	
		347 SS	2	2	2	2
		Mild Steel ^a	2	13	13	13
		Gold	1		0.1	
		Incoloy	1		8	
		Monel	1		5	
		Platinum	1		0.2	
		Ti	1		2	
		Ti RC-55	2	2	2	2
		Zircaloy-2	1		0.1	
	41	309 SCb SS	1		6	
		316 SS	1		9	
		347 SS	2	6	7	8
		Mild Steel ^a	2	20	24	28
		Gold	1		0.6	
		Nickel	1		6	
		Platinum	1		1	
		Ti (3% Al, 5% Cr)	1		6	
		Ti RC-55	2	6	6	6
		Ti RC-70	1		6	
		Zircaloy-2	1		2	

a. ASME Type SA212 carbon steel.

a. ASME Type SA212 carbon steel.

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REFERENCES

- 1.1.a. S. A. Reed, E. L. Compere, S. R. Buxton, and H. C. Savage, HRP Dynamic Slurry Corrosion Studies: Summary of Runs CS-24W and CS-25, ORNL CF-56-8-88, August 10, 1956.
- 1.1.b. S. A. Reed, E. L. Compere, H. C. Savage, S. R. Buxton, and R.-M. Pierce, HRP Dynamic Corrosion Studies: Summary of Runs CS-26W and CS-27, ORNL CF-56-8-89 (to be issued).
- 1.1.c. E. L. Compere, H. C. Savage, et al., HRP Quar. Prog. Rep. Apr. 30, 1956, ORNL-2096.

1.2 In-Pile Slurry Loop Developments. - Some additional short-term water runs were made during the past quarter, as well as one run in which an attempt was made to add thorium oxide to the experimental in-pile slurry loop. The runs with water were to calibrate, measure and adjust various flow rates in the loop and pressurizer. One run of approximately 80 hr with water at 250°C was made to evaluate further the operational stability of the system and the reliability of the condensate purge system used to provide purge water feed to the pump rotor cavity. A steady condensate rate of approximately 1.9 liters per hour was obtained. This rate is sufficient for purge water feed to the pump rotor cavity, but it was considered necessary to increase this rate to provide additional clean water to operate a slurry addition device.^{1.2.a}

Since it had not been possible to produce sufficient condensate at temperatures below about 200°C to purge the pump bearings properly for slurry run HT-17, the loop was to be started up with water and thorium oxide was to be added by means of the 325 ml addition tank after operating temperature and pressure had been obtained.

The loop was charged with distilled water and 60 psi of oxygen added at room temperature. The slurry addition tank was charged with 350 g of thorium oxide from batch LO-2 and 290 g of water. This was sufficient to give a slurry concentration of 310 g of thorium per kilogram of water when charged to the loop and replaced with an equal volume of condensate.

The loop was operated at 250°C in the line and 257°C and about 600 psia in the pressurizer for 26 hr on water to demonstrate stable operation. During this period the condensate rate was approximately 3.4 liters per hour. At this point the slurry was added to the slurry addition tank and the tank was opened to the loop and flushed through with condensate at a rate of approximately 0.5 liters per hour. After 24 hr of operation under these conditions with the slurry tank open to the loop,

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a sample from the circulating loop contained less than 1 g of thorium per kilogram of water.

An examination of the contents of the slurry addition tank revealed that the majority of the thorium oxide had not been transferred to the loop, but had remained in the addition tank. The solids had settled on the wall of the tapered reducer at the bottom of the tank and the purge water feed appeared to have channeled through, leaving the settled material undiluted. This reducer has been changed to one with a more gradual taper from the 1.9-in.-OD tank to the 1/4-in.-OD line to the loop in an attempt to eliminate this channeling.

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REFERENCES

- 1.2.a H. C. Savage and R. M. Warner, HRP Dynamic Slurry Corrosion Studies (In-Pile Development). Summary of Runs HT-16-1W through HT-16-4W, ORNL CF-56-7-129.

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2.0 TOROIDS.

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It has been postulated^{2.a} that the behavior of thorium oxide slurries was critically dependent on the calcination temperature of the oxide and upon its particle size as well as on the solution in which the oxide particle was immersed. Studies in toroids on the attack rate of circulating thorium oxide slurries as a function of the calcination temperature of the oxide have been completed and reported^{2.b}. Some information is now available on the effect of the particle size of the oxide on the attack and behavior of circulating thorium oxide slurries and some preliminary data are now also available on the addition of phosphate ions to the aqueous slurry system.

Sizing of Thorium Oxide. As one approach to the problem of relating attack rates and particle size of thorium oxide, the available oxide produced by the ORNL Chemical Technology Division was separated into several fractions, each composed of a definite range of sizes of thorium oxide particles. These sized oxides were then circulated in toroids and the resulting attack rates compared on the basis of original size of the thorium oxide.

Fractionation of the thorium oxide was achieved by gravitational sedimentation of the solid dispersed in an aqueous solution. The first requirement of such a procedure was the production of a stable suspension of the dispersed solids. There was also required that the concentration of such a suspension be great enough to produce yields of each fraction sufficient for experimental purposes, and yet keep the size of the fractionating equipment within reason. A concentration of about 100 g of thorium oxide per liter of suspension was arbitrarily chosen as the minimum usable concentration. The third requirement was that it be possible to remove the dispersing agent from the thorium oxide when fractionation had been completed. These combined requirements rather limited the choice of dispersing reagent; among such agents investigated were pure water, solutions of ammonium hydroxide from 0.001 to 5 M, solutions of ammonium nitrate,

pure xylene and oxalic acid solutions. Only the solutions of oxalic acid, however, seemed to produce the required minimum concentration of independent particles not associated into flocs.

An empirical approach was used to select the optimum oxalic acid concentration for dispersion. For oxides calcined between 650°C and 1000°C, a concentration of about 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ was found capable of yielding a suspension of 100 to 300 g of thorium oxide per liter of suspension. Oxalic acid concentrations between 0.002 and 0.01 M gave satisfactory dispersions for oxides calcined between 1200 and 1600°C.

Recent studies of the subsidence of thorium oxide (i.e., settling of thick slurries) in solutions of oxalic acid have indicated that dispersions of 120 to 540 g of thorium oxide (D-17-650) per liter were obtained when the oxalic acid concentration was between 0.1 and 0.3 M (pH 1.2 to 3.2). For an oxide recalcined at 1200°C, a dispersed system was obtained in 0.001 to 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ at 120 g of thorium oxide per liter of suspension (pH 1.2 to 3.5) and in 0.01 to 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ at 600 g of thorium oxide per liter (pH 1.2 to 2.2); a suitable suspension was not obtained in 0.001 M $\text{H}_2\text{C}_2\text{O}_4$ (pH 6.8).

The general procedure for producing these dispersions was to use an original suspension containing 300 to 600 g of thorium oxide in a liter of oxalic acid of concentration approximately 2 to 3 times the optimum concentration as indicated above. This slurry was mixed in a Waring blender for about 15 min and then diluted with water to about 2 to 3 liters total volume to achieve the optimum oxalic acid concentration.

Gravitational sedimentation was then carried out in 1-liter-graduated cylinders using Stokes' Law as the basis for the size measurements. The suspension was permitted to stand for a time (2.5 hours) sufficient to settle out the largest particles ($> 3 \mu$); the supernatant suspension thus contained particles less than the largest size and was removed. The settled solids were resuspended with fresh oxalic acid solution and permitted to

settle again. The supernatant liquids containing particles smaller than the largest size ($< 3 \mu$) were permitted to stand for a time (20 hr) sufficient to settle out an intermediate size of particles (less than 3μ , larger than 1μ). The supernatant liquid over these solids thus contained particles too small for settling during this time interval (less than 1μ). Closer limits on the particle size distribution of the settled solids resulted from resuspending the settled solids and repeating the sedimentation. This operational scheme is described by Fischer^{2.c}.

Those solids which settled out during the time intervals of the sizing operation were easily collected and dried. However, the final supernatant fractions, which contained dispersions of the smallest particles (less than 1μ), presented a problem of separating the solids from the dispersing medium. Because of the very small particles present, gravitational sedimentation was not possible. Centrifugation at about 800 to 1800 G did not collect all the solids and those that did centrifuge down produced an almost intractable bed. Attempts to destroy the dispersing agent by decomposition or oxidation using potassium permanganate or hydrogen peroxide in both acid and alkaline medium, were unsuccessful. The solids could not be flocculated by boiling the suspension nor by neutralization of the oxalic acid with ammonium hydroxide.

However, studies of the subsidence of thorium oxide in solutions of oxalic acid showed that flocculation of the particles occurred when the oxalic acid concentration was increased much beyond that which caused dispersion (0.1 to $0.3 \text{ M H}_2\text{C}_2\text{O}_4$). This modification to the original method has been used with excellent results, the smallest-size particles becoming flocculated and settling out completely in 2 to 3 hr.

The collected thorium oxide from the several fractions was first dried and then the adsorbed and residual oxalic acid removed by thermal decomposition. The decomposition was somewhat patterned after the method described for thorium oxalate^{2.d}. The oxide was heated in quartz evaporating dishes in

a Lindberg furnace through which air was passed; the oxide bed depth was about 2 cm or less. The heating was carried out in three stages: 1 hr at 150°C, 2 hr at 375°C and 3 to 4 hr at 550°C. This treatment of the sized oxalic-acid-containing thorium oxide resulted in a carbon content little, if any, greater than that associated with the unsized starting material. For example, two fractions of D-17-650 thorium oxide after sizing and carbon removal gave ratios of mg carbon per g of thorium of 0.9 and 1.7, whereas unsized D-17-650 thorium oxide showed ratios of 1.4 to 1.6. The D-17 thorium oxide recalcined at 1400°C for 2 hr showed only 0.05 to 0.07 mg carbon per gram of thorium, a reduction in the carbon content apparently due to the higher temperature of calcination. The 1 to 3 μ fraction of this oxide before removal of oxalic acid showed 0.19 to 0.22 mg of carbon per gram of thorium present and only 0.08 to 0.10 after the thermal decomposition of the oxalic acid.

Results of some of these fractionations using the gravitational sedimentation technique as described above are shown in Table 2.1. The table shows, first, that recalcination of the D-17 thorium oxide up to temperatures of 1600°C for 4 hr, or 1400°C for 96 hr, did not alter the particle size distribution^{2.e} of the unsized oxide to any great extent. The ranges of per cent distribution for all these calcination temperatures showed: 38 to 47% (avg 42%) greater than 3 μ ; 37 to 52% (avg. 44%) between 1 and 3 μ ; 10 to 23% (avg. 15%) less than 1 μ ; and an average diameter between 2.2 and 2.7 μ (avg. 2.4 μ). The purity of each fraction of the sized D-17 oxides was at least 55% within the stated size and averaged closer to 70%. The purity of the 0 to 1 μ material was nearly 90% within that size interval.

That gravitational sedimentation was capable of yielding high-purity small-size thorium oxide was also demonstrated using CS-5-1000 thorium oxide. This oxide resulted from the circulation for 200 hr of D-17 thorium oxide in loop CS at a concentration of 500 g of thorium per kilogram of water with 1000 ppm oxygen at 250°C; the solids were separated from the slurry, dried and calcined at 1000°C for 7 hr. This oxide was then sized by gravitational sedimentation

in oxalic acid solution; the results are also shown in Table 2.1. The results showed that the fraction of large-sized particles ($> 1 \mu$) existing in the as-calcined product was decreased from 27 to 9%, while the amount of small-sized material ($< 1 \mu$) was increased from 73 to 91%. Although an over-all recovery of only 76% was obtained, these data refer to seven separate sedimentation runs containing a total of 2100 g of thorium oxide; the final fractions in each run were combined appropriately to yield product fractions whose analyses are shown in the table. Thus, almost 1000 g of thorium oxide were collected in Fraction C, of which 91% was less than 1μ in diameter.

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TABLE 2.1
SIZING OF THORIUM OXIDE BY GRAVITATIONAL SEDIMENTATION
IN
OXALIC ACID

CODE		Particle Size Distribution, %			
		>3 μ	1-3 μ	0-1 μ	Avg. Diam., μ
D-17-650	As Calcined	40	37	23	2.2
	Fraction A	59	31	10	3.7
	Fraction B	12	54	34	1.3
	Fraction C	6	6	88	0.4
	Recovery 83%				
D-17-1200	As Calcined	47	41	12	2.7
	Fraction A	65	25	10	4.9
	Fraction B	9	56	35	1.2
	Fraction C	6	4	90	0.5
	Recovery 90%				
D-17-1400-2	As Calcined	44	44	12	2.5
	Fraction A	74	25	1	4.5
	Fraction B	3	84	13	1.5
	Fraction C	5	4	91	0.6
	Recovery 99%				
D-17-1400-96	As Calcined	38	52	10	2.4
	Fraction A	81	19	0	5.1
	Fraction B	4	84	12	1.5
	Fraction C	5	9	86	0.6
	Recovery 96%				
D-17-1600-4	As Calcined	40	44	16	2.4
	Fraction A	70	26	4	4.9
	Fraction B	7	70	23	1.4
	Fraction C	5	9	86	0.7
	Recovery 88%				
D-17-1600-4	As Calcined	40	44	16	2.4
	Fraction A	78	20	2	5.8
	Fraction B	19	73	8	1.8
	Fraction C	4	6	90	0.7
	Recovery 91%				
CS-5-1000	As Calcined	12	15	73	~ 0.3
	Fraction A	17	42	41	1.2
	Fraction B	5	30	65	0.8
	Fraction C	5	4	91	~ 0.2

*Determined by gravitational sedimentation in 0.001 M $\text{Na}_4\text{P}_2\text{O}_7$ ^{21c}
with neutron activation analysis.

Effect of Thorium Oxide Particle Size. The evaluation of the effect of the particle size of the thorium oxide upon the attack of materials by circulating aqueous thorium oxide slurries has been difficult. Primarily this has been due to the fact that the thorium oxide particles which have so far been studied (oxalate precipitated, multi-stage calcined to the oxide) often become degraded upon circulation^{2.f} so that, at least during the early stages of circulation, a decreasing sized particle is being circulated. Ultimately, a steady state or equilibrium is reached in which the particle is of a size smaller than the original particle. The length of time for this process of degradation probably affects the degree of attack; it at least makes the evaluation of particle size and attack rate difficult since the particle size is not constant over the entire length of the study. Other factors which make the evaluation of the effect of particle size difficult are the usual errors inherent in small samples (especially, relying on small samples to be representative of large quantities of material), the limited range of sizes of thorium oxide particles so far available for study and, when the attack is severe, the contamination of the thorium oxide by corrosion products which may produce errors in the methods used for particle size determination.

A correlation between attack rate of type 347 stainless steel and ultimate (degraded) thorium oxide particle size was attempted under the consideration that the length of time required for degradation of the oxide to the ultimate (equilibrium) size was small compared to the duration of the entire run. The results of this attempted correlation are plotted in Fig. 1^{2.f.1}, which shows the results for all the type 347 stainless steel pins that have been exposed to slurries of 1000 g of thorium per kilogram of water at 250°C, 26 fps relative velocity and under oxygen pressure. Only results for thorium oxide produced by the ORNL Chemical Technology Division are included. These oxides were all produced by the thermal decomposition of thorium oxalate; some of these oxides were then recalcined at temperatures up to 1600°C, sized (see previous section) or circulated in loop CS prior to use. The average particle diameter of the unpumped, unsized thorium oxide was 2 to 3 μ . Determination of the particle size distribution of thorium oxide was by gravitational sedimentation in 0.001 M $\text{Na}_4\text{P}_2\text{O}_7$ ^{2.e}.

Fig. 2.1 shows that about 72% of the type 347 stainless steel pins gave rates between 0 and 12 mpy (average 4 mpy) while the average particle diameter of the circulated thorium oxide was between 0 and 1.4 μ (average 0.8 μ). There was no apparent correlation between attack rate and particle size within these boundaries.

An additional 18% of the type 347 stainless steel pins gave attack rates less than 8 mpy but in these cases the ultimate particle diameter of the thorium oxide after circulation was from 1.9 to 4.5 microns. These data were obtained from D-17 thorium oxide recalcined at 1400 or 1600°C. Although there may have been a reduction in attack rate from about 8 to 4 mpy as the particle size after circulation decreased from 4.5 to 0.8 microns, the data are far from conclusive; the degree of reduction of attack as the ultimate particle size after circulation decreased was very slight at best.

However, 8% of the type 347 stainless steel pins showed excessively high attack rates (24 to 40 mpy) and in these cases, relatively large particle sizes after circulation were also found (2.1 to 4.1 μ). These rates were so large that the thorium oxide had relatively large amounts of corrosion products associated with it (up to about 4% iron); there was also evidence that the system had become depleted in oxygen due to the severe attack. Closed symbols for these points are used in Fig. 2.1. It is probable that the high attack rates observed in these runs was a result of the depletion of oxygen in the system, a situation known to produce greater attack on type 347 stainless steel^{2,6}. It is not understood why sufficient attack should have occurred in these runs to consume most or all of the oxygen while, for similar periods of circulation and for similar sizes of thorium oxide particles, the same phenomenon did not occur in the runs discussed in the previous paragraph.

As an alternate approach to the problem of relating attack rates and particle size, thorium oxide which had been fractionated to produce a sized oxide (see previous section) was circulated in toroids. The attack of type 347 stainless steel by these sized oxides at slurry concentrations of 1000 g of thorium per kilogram of water and 26 fps relative velocity, 250°C, and under an oxygen atmosphere are shown in Table 2.2.

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Fig. 1 Attack Rate on Type 347 Stainless Steel by Circulating Thorium Oxide Slurries in Toroids as a Function of the Average Thorium Oxide Particle Diameter After Circulation

TABLE 2.2

ATTACK ON TYPE 347 STAINLESS STEEL BY CIRCULATING
THORIUM OXIDE SLURRIES OF VARYING ORIGINAL PARTICLE SIZE

Sized D-17 Thorium Oxide
1000 g of thorium per kg of water
250°C
26 fps
100 psi oxygen

Calcination °C	Hr	Duration of Run, hr	Avg.* Attack Rate on Type 347 Stainless Steel			
			Fraction A > 3 μ	As-Calcined 85% > 1 μ	Fraction B 1-3 μ	Fraction C < 1 μ
650	**	316	2	(4)***	7	3
1200	7	232	12	3	4	1
1400	2	261	5	4	2	4
1400	96	214	6	7	9	1
1600	4	260	7	4	1	1

* Average of two pins each oxide; deviation between duplicate pins not more than ± 1 mpy.

** Original Batch D-17 thorium oxide, ORNL Chemical Technology Division product.

*** From average of many runs.

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Although the results are not perfectly definitive, qualitative microscopic examination of the pins confirms for all the runs the trends shown by the 1200, 1400 (96 hr) and 1600°C oxide experiments, that slurries of the smaller sized thorium oxide caused less attack on type 347 stainless steel than slurries prepared from larger sized thorium oxide. Attack by the circulating slurries of larger size thorium oxide was usually characterized by definite metal loss apparently through excessive polishing action and usually localized attack at the root of the pin. This was probably due either to the centrifuging action of the motion imparted to the toroid or to the turbulence of flow in that vicinity. The slurries of less than 1 μ size (Fraction C) did not produce this localized attack and visually produced no effect on the pins whatsoever.

The attack on titanium showed inconsistencies similar to those shown for the stainless steel in Table 2.2; these erratic results were most likely caused by differences in the time and degree of degradation of the oxide particles. In general, however, slurries composed of smaller-size thorium oxide particles showed less general attack than slurries composed initially of larger-size particles. The average rate decreased from about 4 to 8 mpy for the large-size particles (Fraction A, greater than 3 μ) to about 0 to 4 mpy for the small-size oxide (Fraction C, less than 1 μ) under the conditions shown in Table 2.2.

Little attack was found on Zircaloy-2 pin specimens exposed to sized slurries under similar conditions. The rates varied randomly between 0 and 5 mpy with an average of about 2 mpy.

Interesting qualitative observations were made on the slurries themselves after these runs with sized thorium oxide. For the oxides recalcined at 1200, 1400 or 1600°C, the slurry prepared from the smallest-sized fraction (Fraction C, less than 1 μ diameter) invariably produced the thickest slurry of all the fractions after circulation, was also the

whitest, settled the slowest although apparently flocculated (was in compaction settling) and adhered most strongly to glass. On the other hand, the slurry prepared from the 1200, 1400 or 1600°C oxide and fractionated to yield particles larger in diameter than 3 μ (Fraction A) yielded the thinnest slurry of all fractions after circulation, was the darkest (brown or black, indicating relatively large amounts of corrosion products), generally settled rapidly and adhered to glass only slightly. All the settled solids were readily redispersed.

The properties and behavior of the slurries of the as-calcined thorium oxide and Fraction B(1 to 3 μ) were between the two extremes described. The as-calcined material was somewhat more similar to the larger sized thorium oxide (Fraction A) while the 1 to 3 μ oxide (Fraction B) was somewhat more like the smaller sized oxide (Fraction C).

The gradual trend in properties of the circulated slurries of thorium oxide as the original particle size of the oxide changed suggested the comparison shown in Table 2.3. This table has been arranged in decreasing average size of the thorium oxide particle after circulation. It thus appears that those slurry properties shown in the second, third and fourth columns can be correlated with the ultimate (final) size of the thorium oxide particles. The amount of iron associated with the oxide, indicative of degree of attack on the stainless steel toroid, appeared to decrease with decreasing ultimate particle size (from about 1 mg Fe/g Th/day for sizes greater than 1.4 μ to about 0.3 mg Fe/g Th/day for sizes less than 0.8 μ). Certain erratic variations were seen in the Fe/Th ratios which were probably reflections of the variation in attack as the particles were degraded during circulation.

Observations of the slurries after circulation led to the qualitative descriptions concerned with the thickness and subsidence of the slurries.

TABLE 2.3

CORRELATION OF PROPERTIES OF CIRCULATED THORIUM OXIDE SLURRIES
WITH ULTIMATE PARTICLE SIZE:

CIRCULATION CONDITIONS: 1000 g of thorium per kilogram of water
26 fps relative velocity
250°C
100 psi oxygen
Type 347 Stainless Steel Toroids

Avg. Diam., μ / dp, after Circula- tion	Relative Slurry Character After Circulation						Calcination			Avg. Diam., μ / dp, before Circula- tion
	mg Fe/g Th per day of Circu- lation	Slurry Thickness	Settling Rate ^o	pH		Oxide	Temp. °C	Time 2/ (hr)		
				Slurry	Supnt					
4.5	0.9	Thin	Fast	6.9	6.6	D-17	1600-A	4	4.9	
3.0	1.5	Thin	Fast	6.4	7.7	D-17	1400-A	96	5.1	
2.5	0.7	Thin	Fast	5.1	5.7	D-17	1400	24	2.8	
2.5	0.3	Thin	Fast	2.4	2.5	D-17	1600	4	2.4	
2.4	1.0	Thin	Fast	5.8	6.1	D-17	1400	96	2.6	
2.2	0.6	Thin	Fast	6.1	6.0	D-17	1600	4	2.4	
2.1	1.0	Thin	Fast	6.0	6.8	D-17	1400	4	2.2	
2.0	1.1	Thin	Slow	5.8	6.6	D-17	1400	96	2.4	
1.9	1.2	Thin	Mod. slow	6.4	6.8	D-17	1400-A	2	4.5	
1.4	0.2	Thin	Fast	5.4	5.3	D-17	1600-B	4	1.4	
1.4	0.2	Thin	Fast	4.8	4.8	D-17	1400-B	2	1.5	
1.4	0.6	Mod. thick	---	5.2	---	D-17	1200-B	7	1.2	
1.3	0.6	Mod. thin	Fast	6.8	7.1	D-17	650-B	d	1.3	
1.2	0.5	Mod. thick	Mod. fast	5.3	6.7	D-17	1400	2	2.7	
1.2	1.1	Mod. thick	---	5.9	6.1	D-17	1200	7	2.8	
1.1	0.5	Thick	---	e	---	D-17	1200	5-7	2.7	
1.1	0.8	---	---	5.5	---	D-17	800	8	2.4	
1.0	0.1	Thick	---	e	---	D-17	1000	5-7	2.5	
1.0	0.3	Thick	---	e	---	D-17	650	d	2.2	
1.0	0.3	Thick	Slow	7.1	---	D-17	650-A	d	3.7	
0.9	1.1	Thick	---	6.0	7.7	D-17	1400	2	2.5	
0.9	0.9	Thick	Slow	5.8	6.4	D-17	1400	4	2.4	
0.8	0.1	Mod. thick	Slow	6.3	6.1	D-17	1600-C	4	0.7	
0.8	0.6	Thick	Slow	5.5	6.4	D-17	1400-B	96	1.5	
0.8	0.5	Thick	---	e	---	D-17	1200	5-7	2.7	
0.8	0.3	Thick	---	e	---	LO-1	800	d	2.3	
0.8	0.1	Thick	---	e	---	D-17	650	d	2.2	
0.8	0.1	Thick	---	e	---	D-17	650	d	2.2	
0.7	0.4	Thick	Slow	4.8	---	D-17	1400-C	2	0.6	
0.7	0.0	Thick	---	e	---	D-17	1400-C	96	0.6	
0.7	0.2	Thick	Slow	6.0	6.4	D-17	800	4-8	2.4	
0.7	0.2	Thick	---	e	---	CS-5	650	d	1.0	
0.7	0.1	Thick	---	e	---	D-17	650	d	2.2	
0.7	0.2	Thick	Slow	6.0	---	D-17	650	d	2.2	
0.6	0.2	Thick	Slow	6.6	6.6	CS-21	1200	5	0.7	
0.6	0.2	Thick	Slow	6.9	6.8	CS-21	800	d	0.6	
0.6	0.2	Thick	Slow	7.7	---	CS-21	800	d	0.6	

TABLE 2.3 (Continued)

Avg. Diam., μ / dp, after Circula- tion	Relative Slurry Character After Circulation						Calcination			Avg. Diam., μ / dp, before Circula- tion
	mg Fe/g Th per day of Circu- lation	Slurry Thickness	Settling Rate ^b	pH		Oxide	Temp. °C	Time c/ (hr)		
				Slurry	Supnt					
0.6	0.3	Thick	Slow	6.8	6.5	LO-1	800	d	2.3	
0.6	0.4	Thick	Slow	8.3	7.1	D-17	800	4-8	2.4	
0.6	0.3	Thick	Slow	9.2	---	D-17	800	4-8	2.4	
0.6	0.3	Thick	---	7.2	7.5	CS-4	650	d	~ 0.4	
0.6	0.2	Thick	---	e	---	D-17	650	d	2.2	
0.6	0.3	Thick	---	e	---	D-17	650	d	2.2	
0.6	0.3	Thick	Slow	6.0	---	D-17	650	d	2.2	
0.5	0.4	Mod.thick	---	8.9	7.8	CS-4	1000	---	~ 0.3	
0.5	0.2	Thick	Slow	7.0	7.4	CS-4	650	d	~ 0.4	
0.4	0.8	Thick	---	6.5	---	D-17	1200-C	7	0.5	
< 0.1	0.3	Thick	---	e	---	D-17	650-C	d	~ 0.4	

a. Particle size distribution determined by gravitational sedimentation in 0.001 M $\text{Na}_4\text{P}_2\text{O}_7$

b. A "fast" settling rate would correspond to "hindered settling", whereas a "slow" rate would be indicative of "compaction settling", i. e., a flocculated, not a dispersed, system. All settled solids redispersed readily.

c. Letters refer to sized fractions of thorium oxide: A = greater than 3 μ fraction; B = 1 to 3 μ fraction; C = less than 1 μ fraction.

d. No recalcination of ORNL Chemical Technology product.

e. Slurry did not pour from toroid at room temperature.

These properties are seen to change markedly, dependent upon ultimate particle size but apparently independent of original particle size or final pH after circulation (over the approximate pH range 5 to 8). A transition region between approximately 1 and 2 μ separated the two extremes of thin-thick slurries and fast-slow settling rates observed at $>2 \mu$ and $<1 \mu$ respectively. Often slurries, whose ultimate particle size was smaller than about 1.3 μ , were so thick at room temperature after circulation that they could not be poured from the toroid. In these cases subsidence of the slurry could not be determined. The thickening of slurries upon circulation in loops has been reported^{2,h} but has not been correlated with particle size.

At first glance Table 2.3 also suggests that a correlation existed between these slurry properties and the maximum calcination temperature of the thorium oxide, since the data for many oxides of higher calcination temperature appear at the top of the table and the data for many oxides of lower calcination temperature appear at the bottom of the table. However, there are several inconsistencies that seem to refute this correlation and, in turn, suggest that the calcination temperature affected the degree of degradation of the oxide under these conditions of circulation. Thus, the slurry properties under discussion appear only indirectly related to the calcination temperature; the primary dependence appeared to be between these slurry properties and the ultimate particle size (after circulation).

That the slurry properties were dependent upon the particle size rather than the calcination temperature was suggested by those runs using sized oxide. Thus, circulation of D-17-1400-96, Fraction C; D-17-1400-2, Fraction C; D-17-1400-96, Fraction B; D-17-1600-4 Fraction C and unsized D-17-1400-4 thorium oxides produced thick slurries that showed compaction settling in spite of the high temperature used for recalcination; the ultimate sizes of these oxides were all less than 0.9 μ . On the other hand, oxides whose particle diameter remained greater than 1.4 μ during circulation yielded thin slurries that settled rapidly.

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Table 2.3 and Figure 2.2 suggest certain conclusions regarding degradation of thorium oxide during circulation in toroids. Figure 2.2 is a plot of the original average particle diameter vs the average particle diameter after circulation at 26 fps, 250°C, 1000 g of thorium per kilogram of water for between 174 and 475 hr (85% of the runs between 238 ± 44 hr). Points lying below the 45-degree line represent slurries whose particles became degraded during circulation; points on or very near the line represent slurries whose particle size was not detectably altered during circulation. The maximum temperature of calcination of the thorium oxide is represented by the appropriate symbol; the period of recalcination at 1400°C is also represented. Thorium oxide of original particle diameter about 1.3 μ or smaller appeared not to degrade appreciably during circulation in toroids under the described conditions. This statement held true for oxides calcined from 650 to 1600°C. Degradation of thorium oxide of original particle diameter greater than 1.3 μ appeared to be dependent upon the maximum temperature of calcination of the oxide and of the length of time at that temperature. Thus, the oxide calcined at 1600°C for 4 hr did not appear to degrade in any of the runs (within the limits of determination of the particle size); for example, the D-17-1600-4 oxide did not change in size after circulation for 475 hr (2.4 to 2.5 μ) whereas D-17-650 decreased in diameter from 2.2 to 1.0 μ during only 174 hr. The section dealing with the effect of phosphate additions shows that within only 41 hr of circulation thorium oxide (D-17) recalcined at 800°C for 8 hr was reduced in size from an original diameter of 2.4 μ to an ultimate size of 0.9 to 1.0 μ.

In general, the oxide recalcined at 1400°C for at least 4 hr did not show appreciable degradation during circulation, whereas oxide calcined for only 2 hr at 1400°C did show considerably greater degradation. Some variation from these generalities do exist for this calcination temperature. For example, D-17-1400-2 changed from 1.5 to 1.4 μ during 261 hr circulation while D-17-1400-96 changed from 1.5 to 0.8 μ during 214-hr circulation. Although degradation of a D-17-1400-96 oxide occurred in another experiment (from 5.1 to 3.0 μ) in 214 hr, the final size was still much larger than usually found (less than 1.2 μ) which may also indicate a certain

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resistance to degradation for this particular treatment of the oxide.

Oxides calcined up to 1200°C for 7 hr degraded upon circulation if their original diameter was larger than approximately $1.3\ \mu$. The ultimate size was approximately 0.6 to $1.2\ \mu$.

It is realized, of course, that the maximum temperature to which thorium oxide is exposed and the period of such exposure alter the physical character of the oxide. Properties of thorium oxide, such as adsorption of ions, and ultimately, viscosity, subsidence and probably other quantities, depend upon this maximum calcination temperature. Although there now appears to be, under certain specific conditions of circulation, correlation between calcination temperature and degradation and between certain slurry properties and ultimate particle size, other factors, as mentioned above, also govern the properties of the slurry system. It becomes even more apparent now, however, that the particle size of the thorium oxide (and its change during certain operations) and thus, directly or indirectly, the maximum calcination temperature, are of prime importance in the study of aqueous slurries.

Effect of Length of Calcination Time. As a corollary to the determination of the effect of calcination temperature of the thorium oxide on the attack rate of materials of interest by circulating thorium oxide slurries, the effect of the length of calcination time at a given temperature on the attack rates was studied. Portions of D-17 thorium oxide were recalcined in platinum dishes for periods of 2, 4, 24 or 96 hr at 1400°C . Marked changes in the crystallite size as determined by x-ray line broadening and in the specific surface area as determined by low temperature nitrogen absorption were observed^{2,1}. However, there was no detectable change in the particle size distribution of the samples as determined by gravitational sedimentation in $0.001\ \text{M}\ \text{Na}_4\text{P}_2\text{O}_7$. A summary of these changes is included in Table 2.4.

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Fig. 2.2 Extent of Degradation of Thorium Oxide Upon Circulation of Aqueous Slurries in Toroids.

TABLE 2.4

EFFECT OF LENGTH OF CALCINATION TIME AT 1400°C ON PROPERTIES OF THORIUM OXIDE

D-17 Thorium Oxide
1000 g of thorium per kilogram of water
250°C - 263 hr circulation
26 fps relative velocity
100 psi oxygen

	Hours of Recalcination at 1400°C				
	0	2	4	24	96
Crystallite Size, Å	107	2500	3700	4600	> 5000
Specific Surface Area, m ² /g	30.3	1.40	1.31	1.16	0.89
Avg. Particle Diameter, μ					
As Calcined	2.2	2.7	2.2	2.8	2.6
After Circulation	(0.7)*	1.2	2.1	2.5	2.4
Attack Rate, mpy					
Type 347 SS	(4)*	4, 4	4, 4	4, 5	6, 6
Titanium 75A	(4)*	3	2	2	7
Zircaloy-2	(1)*	3	---	2	2
Type 347 SS toroid	(1)*	2	3	2	3

* Previous data

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This table also presents the results of circulating these oxides as aqueous slurries of 1000 g of thorium per kilogram of water at 26 fps relative velocity and 250°C under an oxygen atmosphere for 263 hr. The attack rates in Table 2.4, determined from weight loss data of the corrosion pin specimens, appear independent of the length of time of calcination at 1400°C up to 96 hr. However, microscopic examination of the type 347 stainless steel corrosion pin specimens showed a localized attack near the root of some of the pins; the 96-hr oxide showed the greatest localized attack while the oxides calcined for shorter times did not produce this attack on the type 347 stainless steel (except for one of two pins exposed to the 4-hr calcined thorium oxide). The 4 and 96 hr oxides produced thin slurries after circulation, the 24-hr slurry was somewhat less fluid while the 2-hr oxide slurry was moderately thick.

It thus appears that at least under the conditions of this recalcination (1400°C, 1000 g of thorium oxide each charge) 2 hr at temperature was sufficient to produce marked changes in the physical properties of the thorium oxide while calcinations for 4-hr and longer produced only relatively minor further changes. However, the 2-hr calcined thorium oxide degraded upon circulation as a slurry to a greater extent than oxides calcined for longer periods of time. There seemed to be a correlation in the degree of degradation of the oxide during circulation and the production of a thick slurry. The 96-hr calcination produced an oxide whose aqueous slurry appeared to yield higher attack rates, especially of a localized nature, than those oxides calcined for shorter periods of time.

Effect of Phosphate Additions. The behavior and properties of aqueous thorium oxide slurries are dependent upon the electrolytic character of the medium in which the thorium oxide is immersed. Some properties of thorium oxide in a number of such electrolytes have been studied^{2,3}. One of the aqueous media in which thorium oxide can be readily dispersed and which yields fairly concentrated suspensions of thorium oxide is a solution of tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$. Such solutions are used in the

gravitational sedimentation sedimentation of thorium oxide for particle size distribution determinations^{2.e} and have often been mentioned in regard to engineering studies to provide aqueous dispersions of thorium oxide. The effect of additions of aqueous tetrasodium pyrophosphate solutions and other phosphate buffer solutions to thorium oxide slurries on the attack rates of materials of interest has now been determined in some preliminary tests. The effect of phosphoric acid additions has been previously reported^{2.k}.

A number of experiments in toroids have been completed which have studied the effect of various concentrations of tetrasodium pyrophosphate solutions with and without thorium oxide present at 250°C, 26 fps relative velocity and with either oxygen or hydrogen atmospheres. Fewer experiments using the phosphate buffer system of disodium hydrogen phosphate - sodium dihydrogen phosphate have been completed while some static autoclave experiments are also under way. These tests are summarized in Table 2.5. Since some of the runs containing phosphate were of rather short exposure, data for control runs are included in the table in the event the attack should show a time dependence. The concentrations of phosphate that are used in this section refer to the original concentration and not the concentration when the solution was at equilibrium with the thorium oxide.

The data in Table 2.5 show that titanium can be severely attacked by both neutral (sodium dihydrogen phosphate - disodium hydrogen phosphate buffer solution, pH approximately 7) and alkaline (tetrasodium pyrophosphate solution, pH approximately 11) circulating thorium oxide slurries at 250°C under either oxygen or hydrogen atmospheres. The attack appeared dependent upon the concentration of phosphate and appeared more severe under an hydrogen atmosphere than under oxygen.

Some experiments were carried out in the absence of thorium oxide slurries, both at 26 fps relative velocity and in static autoclaves. Little, if any, effect of velocity was observed at 250°C with oxygen when the solution was 0.01 M $\text{Na}_4\text{P}_2\text{O}_7$. However, with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ the attack on type 347 increased from about 0.8 mpy to 3 to 12 mpy and the attack on

SUMMARY OF EXPERIMENTS STUDYING THE EFFECT OF PHOSPHATE SOLUTIONS AT 250°C

g Th per kg H ₂ O	ThO ₂	Calcination		Additive	M	Rel Vel fps	Atm	pH		Avg. Part. Diam., μ^a		Length of Run hr	Average Attack Rate, mpy			
		Temp °C	Time hr					Supernatant	Liq	Before Circ.	After Circ.		SAE			
													Initial	Final	347 SS	Ti
0	----	----	----	Na ₄ P ₂ O ₇	0.01	0	O ₂	10	8.0	----	----	192	0.4 ^b	0.8 ^b	----	0.2 ^b
0	----	----	----	"	"	26	"	10	7.2	----	----	41	2,2	0	+	----
0	----	----	----	"	"	"	"	10	7.6	----	----	89	2,3	2	0	----
0	----	----	----	"	0.1	0	O ₂	10	8.3	----	----	864	0.8	2.4	----	1.3
0	----	----	----	"	"	26	"	10	8.9	----	----	41	12	23	+	----
0	----	----	----	"	"	"	"	10	8.0	----	----	65	8	21	2	----
0	----	----	----	"	"	"	"	10	8.8	----	----	90	3	16	0	----
1000	CS-4	650	(c)	None	----	26	O ₂	---	7.4	~0.4	0.5	244	3,4	2	1	----
1000	CS-4	650	(c)	Na ₄ P ₂ O ₇	0.005	26	"	---	8.5	~0.4	0.6	244	7,7	4	0	----
1000	D-17	650	(c)	None	----	26	O ₂	---	2.2	2.2	-1.0	174	8	6	2	----
1000	D-17	1200	5-7	None	----	"	"	---	6.3	2.7	----	174	3	5	1	----
1000	D-17	650	(c)	Na ₄ P ₂ O ₇	0.08	"	"	---	9.8	2.2	0.6	174	10,11	16	+	----
1000	D-17	1200	5-7	"	"	"	"	---	12	2.7	0.8	174	11,11	119	1	----
1000	D-17	800	8	None	----	26	O ₂	---	7.0	2.4	1.0	41	12	11	1	----
1000	D-17	800	8	"	----	"	"	---	7.5	2.4	0.9	41	10,10	7	1	----
1000	D-17	800	8	Na ₄ P ₂ O ₇	0.01	"	"	---	9.4	2.4	1.0	90	13	8	2	----
1000	D-17	800	8	"	0.1	"	"	---	6.5	2.4	1.8	65	18,20	42	1	----
1000	D-17	800	8	"	"	"	"	---	9.7	2.4	----	90	15,15	28	1	----
1000	D-17	800	8	NaOH	----	26	O ₂	11	6.4	2.4	1.2	294	3	3	1	----
1000	D-17	800	8	Na ₄ P ₂ O ₇	0.1	"	"	11	10	2.4	0.6	294	14,24	91	+	----
1000	D-17	800	8	NaOH	----	26	H ₂	11	---	2.4	2.9	294	35,35	8	2	----
1000	D-17	800	8	Na ₄ P ₂ O ₇	0.1	"	"	11	10	2.4	0.9	294	5,5	>1860	0	----

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TABLE 2.5 (Continued)

g Th per kg H ₂ O	ThO ₂	Calcination		Additive	M	Rel Vel fps	Atm	pH		Avg. Part. Diam., μ^a		Length of Run hr	Average Attack Rate, mpy			
		Temp °C	Time hr					Supernatant Initial	Liq Final	Before Circ.	After Circ.		347 SS	TH	Zr-2	SAE 1030
0	----	----	----	(Na ₂ HPO ₄) (NaH ₂ PO ₄)	0.01 each	0	O ₂	6.6	6.8	----	----	192	0.2 ^b	0.0 ^b	----	+ ^b
0	----	----	----	"	0.1 each	"	"	6.5	6.6	----	----	864	0.1	0.2	----	0.6
1000	D-17	800	8	None	----	26	O ₂	7.3	5.5	2.4	1.1	402	2	4	1	----
1000	D-17	800	8	(Na ₂ HPO ₄) (NaH ₂ PO ₄)	0.1 each	"	"	6.9	---	2.4	1.0	402	11,20	> 320	1	----
1000	D-17	800	8	None	----	26	H ₂	7.4	---	2.4	1.4	(402) ^d	(5,6) ^d	(1) ^d	(0) ^d	----
1000	D-17	800	8	(Na ₂ HPO ₄) (NaH ₂ PO ₄)	0.1 each	"	"	7.0	---	2.4	0.8	402	6,6	> 1360	1	----

a. Particle size distribution determined by gravitational sedimentation in 0.001 M Na₄P₂O₇.

b. Not defilmed, test continuing.

c. No recalcination of ORNL Chemical Technology product.

d. Dry after run.

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titanium increased from 2.4 mpy to 16 to 23 mpy as the velocity changed from 0 to 26 fps. These data also suggested that at 26 fps the rate of attack decreased with time of circulation for both stainless steel (12, 8 and 3 mpy for 41, 65 and 90 hr) and titanium (23, 21, and 16 mpy for similar times).

The presence of 1000 g of thorium per kilogram of water in the circulating phosphate solution increased the rate of attack on type 347 stainless steel and titanium. For 0.01 M $\text{Na}_4\text{P}_2\text{O}_7$ the attack on the steel increased from 2 mpy (no slurry) to 13 mpy and for titanium from 1 mpy to 8 mpy. The effect of slurry was more pronounced in the 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ solution where the attack on steel increased from 3 to 16 mpy (no slurry) to 14 to 24 mpy while the attack on titanium increased from 16 to 23 mpy (no slurry) to 28 to 91 mpy in the presence of slurry.

At least under certain conditions, the maximum calcination temperature of the thorium oxide became significant. Thus, in 0.08 M $\text{Na}_4\text{P}_2\text{O}_7$, a slurry of 1000 g of thorium per kilogram of water prepared from oxide recalcined at 1200°C gave an attack rate of 119 mpy on titanium at 26 fps relative velocity, 250°C , and under oxygen atmosphere. Under similar conditions with a 650°C calcined oxide a rate of only 16 mpy was observed. The attack on stainless steel for both oxides was 10 to 11 mpy. The greater attack by the slurry of 1200°C oxide may be related to the greater concentration of phosphate that may be present in solutions at equilibrium in this case compared to the slurry containing the 650°C oxide. The larger concentration of phosphate in solution at equilibrium with the 1200°C oxide compared to the 650°C oxide arises from the decreased surface area of the oxide as the maximum calcination temperature is increased. An analogous situation was shown to exist for thorium sulfate additions^{2,a}.

The effect of increasing phosphate concentration on the attack rates in the presence of slurry was not as large for the type 347 stainless steel as for the titanium. Thus, for the steel in the absence of phosphate,

rates from 3 to 12 mpy were observed and varied erratically to rates of 14 to 24 mpy for 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. On the other hand, attack on titanium 75A showed 3 to 11 mpy in the absence of phosphate and increased to 28 to 91 mpy in 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. There was little indication of enhanced attack on either the steel or the titanium for solutions less than approximately 0.01 M $\text{Na}_4\text{P}_2\text{O}_7$.

Much less information is available for the Na_2HPO_4 - NaH_2PO_4 system than for the tetrasodium pyrophosphate system. Somewhat less attack on type 347 stainless steel, titanium 75A and SAE 1030 carbon steel (A212) was found in the static autoclave experiments when the solution was 0.01 or 0.1 M each Na_2HPO_4 - NaH_2PO_4 rather than 0.01 or 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. On the other hand, very severe attack (more than 320 mpy) of a titanium pin was found after exposure to a slurry of 1000 g of thorium per kilogram of water containing 0.1 M Na_2HPO_4 - 0.1 M NaH_2PO_4 at 250°C, 26 fps relative velocity and under oxygen.

The good resistance of carbon steel to these phosphate solutions at 250°C under oxygen pressurization in static autoclave tests suggests further investigation in toroids. It is reasonable that the better resistance to phosphate solutions shown in static tests was due to the presence of insoluble phosphate films which provided protection of the base metal; the existence of such protection in circulating systems is unknown^{2.1.1}.

Rather preliminary tests comparing oxygen or hydrogen atmospheres are also summarized in Table 2.5. The attack by circulating slurries of 1000 g of thorium per kilogram of water at 26 fps relative velocity and 250°C can be summarized as follows (no phosphate present): the attack by aqueous slurries of pH 11 on type 347 stainless steel increased from 3 mpy with oxygen over-pressure to 35 mpy with hydrogen; the attack on titanium under similar conditions increased from 3 mpy (oxygen) to only 8 mpy (hydrogen). At pH 7 the effect of replacing oxygen with hydrogen was possibly less pronounced.

In 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$, the attack on type 347 stainless steel decreased from 14 to 24 mpy (oxygen) to about 5 mpy (hydrogen), while the attack on titanium increased from 91 mpy (oxygen) to more than 1860 mpy (hydrogen). In 0.1 M Na_2HPO_4 - 0.1 M NaH_2PO_4 the attack on the stainless steel decreased slightly from 11 to 20 mpy (oxygen) to about 6 mpy (hydrogen) while the attack on titanium was severe in either oxygen (320 mpy) or hydrogen (more than 1360).

Under all the experimental conditions described above, Zircaloy-2 showed negligible attack, yielding rates of 2 mpy or less.

The corrosion of titanium has been discussed from interpretation of equilibrium potential - pH diagrams for the Ti- H_2O system^{2.m}: although titanium is an active metal, its passivity is most likely due to a protective film of TiO_2 . The resistance of stainless steel also depends on the maintenance of a protective oxide film^{2.1.2}. Thus, the integrity of an oxide film on these metals must depend not only upon the oxidizing ability of the environment but as well on the presence of complexing anions or anions which form insoluble salts. Protection may be conferred if precipitation of an insoluble salt on the metal provides a protective film. Thus, titanium may be corroded^{2.m} in strongly oxidizing solutions (e.g., in presence of hydrogen peroxide) in both acidic and alkaline media due to the formation of soluble per- compounds; titanium may be corroded by solutions containing good complexing ions (e. g., fluoride) by dissolution of the protective film; and titanium may be corroded in a strongly reducing medium, especially if acid probably due to the greater solubility of hydrous oxides of divalent titanium, which would exist in a strongly reducing medium.

Thus, for titanium (as well as for stainless steel and Zircaloy-2) the exact combination of oxidizing environment, acidity, relative solution velocity, complexing anions and/or anions forming insoluble salts and possibly other variables determine the degree of attack by the medium. An interpretation of the data in Table 2.5 in the light of the known factors affecting the passivity of these metals will not now be undertaken.

Pertinent to such discussion, however, is the remarkable insolubility of the Group IVA phosphates (tetravalent Ti, Zr, Hf, Th) in dilute acid or alkaline media^{2.2} and the complexing of Fe(III) by phosphate or its precipitation in weakly basic media^{2.1.1, 2.2}.

Figure 2.3 illustrates the severity of the attack on titanium 75A when exposed to circulating thorium oxide slurries of 1000 g of thorium per kilogram of water containing 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ at 250°C and 26 fps relative velocity for 294 hr. Under the oxygen atmosphere an attack rate of 91 mpy was calculated from weight loss data while with hydrogen a rate in excess of 1900 mpy was obtained.

FOOTNOTES AND REFERENCES

- 2.a. G. E. Moore and E. L. Compere, HRP Quar. Prog. Rep., July 31, 1955, ORNL-1943, p 140.
- 2.b. G. E. Moore and E. L. Compere, Dynamic Slurry Corrosion Studies, Quarter Ending Jan. 31, 1956, ORNL CF-56-1-168 (March 27, 1956), p 33.
- 2.c. E. K. Fischer, Colloidal Dispersions, John Wiley and Sons, Inc., New York (1950), p 37.
2. 2.d. D. E. Ferguson, et al., HRP Quar. Prog. Rep. Oct. 31, 1953, ORNL-1658, p 113.
- 2.e. G. W. Leddicotte and H. H. Miller, Anal. Chem. Semiann. Prog. Rep. Oct. 20, 1954, ORNL-1788, p 21.
- 2.f.1. G. E. Moore and E. L. Compere, Dynamic Slurry Corrosion Tests, Quarter Ending Apr. 30, 1956, ORNL CF-56-4-139, p 16.
- 2.f.2. C. E. Schilling, HRP Quar. Prog. Rep., Oct. 31, 1955, ORNL 2004, p 179.
- 2.g. G. E. Moore and E. L. Compere, HRP Quar. Prog. Rep., Oct. 31, 1954, ORNL-1813, p 100.
2. 2.h. D. G. Thomas, J. D. Perret and S. R. Buxton, HRP Quar. Prog. Rep., Oct. 31, 1954, ORNL-1813, p 123.
- 2.i. V. D. Allred, J. P. McBride and S. R. Buxton, HRP Quar. Prog. Rep., July 31, 1955, ORNL-1943, p 181.
- 2.j.1. D. G. Thomas, et al., HRP Quar. Prog. Rep. Oct. 31, 1954, ORNL 1813, p 125.
- 2.j.2. D. E. Ferguson, J. P. McBride, et al., ibid., p 145.
- 2.j.3. V. D. Allred, J. P. McBride and E. V. Jones, HRP Quar. Prog. Rep., Oct. 31, 1955, ORNL-2004, p 172.
- 2.k. R. N. Lyon, et al., HRP Quar. Prog. Rep., July 31, 1954, ORNL-1772, p 114.
- 2.1.1. U. R. Evans, Metallic Corrosion, Passivity and Protection, Longmans, Green and Co., New York (1946), p 282, 326, and 597.
- 2.1.2. ibid., p 238
- 2.m. J. Schmets and M. Pourbaix, International Committee of Electrochemical Thermodynamics and Kinetics, Butterworths Scientific Publications, London (1955), p 167.

FOOTNOTES AND REFERENCES (Continued)

- 2.n. E. deB. Barnett and C. L. Wilson, Inorganic Chemistry, Longmans, Green and Co., New York (1953), p 142.
- 2.o. I. M. Kolthoff and E. B. Sandell, Testbook of Quantitative Inorganic Analysis, Third Edition, The Macmillan Company, New York (1952), p 313.

Fig. 2.3. Titanium 75A Corrosion Pin Specimens

(a) Unexposed Control Specimen.

After exposure for 29¹/₂ hr in toroids at 26 fps relative velocity and 250°C to 0.1 M Na₄P₂O₇ solutions of 1000 g of thorium per kilogram of water (D-17-800-8 thorium oxide), pH 10.9 with an atmosphere of:

(b) Approximately 100 psi oxygen (250°C)

(c) Hydrogen (1 atmosphere at room temperature)

The approximate attack rates were: (b) 90 mpy; (c) 1900 mpy.

Only the lower approximate half of the pins were exposed to the circulating slurry.

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