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0.0 SUMMARY

Pump Loops. Dynamic corrosion data and operating observations are reported for five slurry runs made in 100A pump loops. Two runs, of 22 and 11 hr duration, which marked the first slurry operation for loop BS, were made at 250°C, and at approximately 570 g of thorium per kilogram of water, with added oxygen. In each run, average particle size increased substantially, with spheroid formation, accompanied by deposition of cake in the pump and loop.

A test on loop CS employing previously circulated thorium oxide at 346 g of thorium per kilogram of water, at 300°C with added oxygen, for 266 hr, operated without incident. Substantially lower corrosion was observed on all materials than in a similar previous run which charged raw slurry. A test which circulated "standard" slurry at 400 g of thorium per kilogram of water, at 300°C with added oxygen, was terminated after 26 hr due to caking in the pump. An 83-hr run at 300°C under hydrogen atmosphere, at a concentration of 426 g of thorium per kilogram of water, was made using the same batch of slurry as was used in BS loop. Again spheroids were formed. A severe hard caking in the pump caused termination.

Successful addition of slurry while circulating at operating temperature and pressure was made in short runs on the experimental in-pile slurry loop. Concentration was not maintained as circulation continued.

Toroids. Studies are presented on the effects of $\text{Na}_4\text{P}_2\text{O}_7$ and Na_2SiO_3 as slurry additives, under oxygen or hydrogen atmospheres, on corrosion by thorium slurries circulating in toroids. A discussion of the effect of various electrolyte additives as anodic corrosion inhibitors and as dispersing agents is presented, leading to the conclusion that a number of substances appear to be able to function in both ways. Physical examination of a toroid after 4909 hr of slurry circulation service showed only slight attack with greatest attack in the vicinity of protuberances such as weld beads or pins.

Circulation of "standard" slurry in toroids at 200°C and 10 or 20 fps resulted in an increase in the particle size of the thorium spheroids from about 10 μ to over 20 μ , with possible fracturing at 20 fps. Circulation at 20 fps at 300°C also caused growth, and possible fracturing, but circulation at 26 fps at 200°C or 250°C caused degradation of the particles. Circulation of the raw slurry from which the "standard" slurry had been made under all these conditions resulted in no growth, but in normal degradation of the particle size. Corrosion attack rates for the "standard" slurry did not differ significantly in any of the above cases from either its raw slurry precursor or from other slurries produced under the same conditions.

1.0 PUMP LOOPS. (by S. A. Reed)

- 1.1 100A Pump Loops. During the quarter, five dynamic slurry corrosion tests were made in 100A pump loops BS and CS at circulating concentrations of approximately 350 to 500 g of thorium per kilogram of water.

Two tests, Runs BS-5 and BS-6 were the first slurry tests on loop BS. They were made at 250°C with the addition of oxygen using a new lot of 800°C-calcined thorium oxide prepared at ORNL. During circulation, the slurry appeared to develop into essentially two size fractions. One fraction, which circulated freely, was composed of spherical agglomerates, ranging in size from 7 to 20 μ in diameter while the second fraction, composed principally of particles 1 μ and smaller in diameter, formed hard, tenacious deposits in the centrifugal pump and on the corrosion specimens and specimen holders exposed at the higher velocities.

In loop CS one test, Run CS-28-29, was made at 300°C with the addition of oxygen to study the effect of particle degradation and corrosion as affected by previously pumped slurry.

A test with oxygen at 300°C, Run CS-30 using "standard" slurry, a previously circulated material composed of spherical agglomerates ranging from 8 to 30 μ in diameter, was terminated after 26.3 hr of slurry operation because of deposition of thoria in the centrifugal pump and pump cavity.

The third test in loop CS was made at 300°C with slurry prepared from the new lot of ORNL-produced thorium oxide. The system was operated under a reducing atmosphere provided by the addition of about two atmospheres of hydrogen, as well as hydrazine in excess of that required to remove all oxygen. This test was terminated after approximately 83 hr of circulation because of heavy deposits of thoria in the pump scroll and impeller.

In each test, slurry was added to the loops by incremental batch additions while operating at the selected temperature. The 100A pumps in both systems were equipped with aluminum oxide bearings and journals.

Corrosion data of individual pin and coupon specimens exposed during the five tests are presented in Table 1.4.

Run BS-5 was the initial slurry test in loop BS^{1.1.a}. Three sets of corrosion specimens were inserted in the loop. One set of pin specimens and a set of coupon specimens were placed in the main line at a flow rate of 13.5 gpm; one set of pin specimens was placed in the return line at a flow rate of 31.5 gpm. Flow through the mixing line was 18 gpm. All flow measurements were made with water at room temperature.

In accordance with usual practice, the system was operated with oxygenated water at 250°C for a period of 97 hr before adding slurry. The loop was then charged, while operating at 250°C, with two batch additions of slurry prepared from batch LO-14 thorium oxide to provide a calculated circulating concentration of 500 g of thorium per kilogram of water. The thorium oxide had been made at ORNL from especially pure thorium nitrate by oxalic acid precipitation at 70°C and calcination at 800°C. Before being used to charge the loop, the slurry was passed while wet through a 200-mesh screen.

The initial slurry sample was withdrawn from the system after 4.3 hr of operation. By chemical analysis, it contained 563 g of thorium per kilogram of water. A second sample taken after 21.5 hr of circulation contained 594 g of thorium per kilogram of water.

Immediately after withdrawing the second sample from the system, the flow of purge water to the rear of the pump ceased and the pump power demand became very erratic. Therefore, the test was

terminated after a total of 21.9 hr of operation on slurry. The system was cooled to room temperature, drained, flushed thoroughly with water, and then disassembled for inspection.

A thin, hard, tenacious deposit of thorium had formed in the channels of the three specimen holders and on the specimens themselves. Also, a wedge-shaped deposit of thorium had formed on the upstream surface of each pin specimen exposed in the return line sample barrel. Similar hard deposits of thorium were found adhering to the front hub of the titanium impeller, in the impeller vanes, and in the weep holes in the rear hub. A total of 28 g of thorium was removed from the impeller surface.

The suction nozzle of the centrifugal pump was also uniformly coated with a layer of thorium, the consistency of which was similar to that of dried plaster of Paris. No other deposits were found in the system.

Chemical and spectrographic analysis data for the slurry charge, of the samples withdrawn from the system and of the deposits showed no evidence of foreign constituents in the material other than the expected levels of the corrosion ions, iron, chromium, and nickel. However, sedimentation particle size data of the same materials indicated that a gradual increase in particle size had occurred during circulation. These data were confirmed by microscopic examination of the materials. While the slurry charge to the system contained only discrete crystalline particles of thorium, the samples withdrawn from the system during operation were composed of spherical opalescent agglomerates of slurry which appeared to have increased in size and number with circulation time. The spheroids ranged in size from about 7 to 20 μ in diameter.

No spheroids could be detected in the deposits. Sedimentation particle size data showed them to be composed primarily of particles ranging from 2 to $< 1 \mu$ in diameter. Chemical and particle

size data of the deposits and of samples withdrawn from the system during operation are given in Table 1.1. Photographs of the materials are shown in Fig. 1.1 to 1.3.

Run BS-6 was essentially a continuation of Run BS-5. After re-assembling the system and making a short performance run on oxygenated water, the slurry drained from Run BS-5, which contained 6694 g of thorium oxide, and an additional 2035 g of raw thorium oxide from the same batch, LO-14, was charged to the system to provide a calculated concentration of 530 g of thorium per kilogram of water. A sample taken from the loop 2 hr after the addition of thorium contained 565 g of thorium per kilogram of water.

After 10 hr operation with slurry, the pump power demand increased rapidly and a pulsating noise was noted in the pump. Therefore, the run was terminated after 11.1 hr of slurry circulation.

Inspection of the system after draining and rinsing with water revealed deposits almost identical in nature and in the same locations as those described previously for Run BS-5. Chemical analytical and particle size data for the run are shown in Table 1.1.

Pin specimens exposed for a total of 33 hr in the combined runs showed relatively high attack rates; e. g., at 19 fps, the austenitic stainless steels corroded from 5 to 28 mpy; platinum, 24 mpy; titanium and its alloys, 0 to 16 mpy; and Zircaloy-2, 8 mpy. Attack rates of coupon specimens exposed at a relative velocity of 11 fps were: austenitic stainless steels, 2 to 5 mpy; welded austenitic stainless steel, 12 mpy; Armco iron, 120 to 280 mpy.

Run CS-28-29 was made to observe the effect of particle size degradation on corrosion as affected by previously circulated slurry. The slurry charge, prepared from Batch LO-2 thorium oxide, had been circulated previously in loop CS for approximately 300 hr.

TABLE 1.1

SUMMARY OF SAMPLE DATA, RUNS BS-5 and BS-6

	BS-5				BS-6	
				Solids From Return Line and Impeller		
Slurry Circulation Time (hr)	0	4.3	21.5		4.9	
Slurry Concentration, g thorium per kilogram of water (calculated from density)	Charge Material	565	570		510	
g thorium per kilogram of water (chemical analysis)	1242	563	584		565	
mg of thorium per gram of slurry (chemical analysis)	515	343	350	818	344	
Fe, mg/g slurry	0.007	0.061	0.082	0.259	0.073	
Cr, mg/g slurry	< 0.005	0.021	0.010	0.050	0.011	
Ni, mg/g slurry	< 0.005	0.012	0.005	0.012	0.011	
Ti, mg/g slurry	< 0.02	< 0.02	0.03	0.08	< 0.02	
Al, mg/g slurry	0.02	0.02	0.04	0.15	0.06	
H ₂ O, mg/g slurry	---	---	---	54	---	
pH of slurry	10.6	7.80	8.30	---	8.90	
Sedimentation Particle Size (μ) ^a						
> 10 μ (% by wt)	6	37	64	0	> 26 μ (% by wt)	17
3-10 μ (% by wt)	45	23	21	25	7-26 μ (% by wt)	76
1-3 μ (% by wt)	28	14	5	36	3-7 μ (% by wt)	4
< 1 μ (% by wt)	21	26	10	39	1-3 μ (% by wt)	2
Average diameter (μ)	3.3	7.1	13.1	1.45	< 1 μ (% by wt)	1
					Average diameter (μ) (~ 14)	

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

Fig. 1.1. Original Slurry Charge for Run BS-5. 400X

Fig. 1.2. Agglomerates of Slurry Formed After 21.5 hr of Circulation in Run BS-5. 400X

Fig. 1.3. Thoria Deposit Removed from Pump Impeller After Run BS-5. Slurry circulated for 21.5 hr. 400X

Corrosion data obtained in loop CS using Batch LO-2 thorium oxide have been reported previously^{1,1.b}. However, in these tests, raw slurry with no previous pumping history was used to charge the loop. In each test, considerable degradation of the thorium particles had occurred during the first 10 to 30 hr of circulation, after which time thorium of an average particle size of about 0.6 μ was being circulated. Differential corrosion rates determined for various periods of a nominal 200 to 300-hr test have shown the highest rates of attack to occur during this period of particle attrition with a gradual leveling off thereafter. Therefore, it was of interest to obtain attack rates at the same conditions using slurry which had been previously circulated.

The three loop barrels contained pin-type corrosion specimens exposed to the slurry at relative velocities of 13, 22, and 43 fps. The system was charged with four batch additions of pumped slurry while operating at 300°C on oxygenated water.

The system was temporarily shut down 73 hr after the initial slurry addition because of erratic pump performance.

After the pump was repaired, the test was resumed. Slurry was again charged to the system while operating on oxygenated water at 300°C and the test loop was operated routinely for an additional 192 hr. At run hour 264, one of the high-pressure sample valves on the system could not be secured satisfactorily. Consequently, it was necessary to terminate the run. Slurry had been circulated in the system a total of 266 hr (for both run CS-28 and 29) at shutdown. Corrosion rates are shown in Table 1.2.

Run CS-30 charge slurry had also been circulated in a loop system. The material was prepared by the Engineering Research Section as an experimental "standard" slurry by circulating an ORNL-produced, 800°C-calcined oxide at 200°C for a period of 100 hr in a 200A pump loop. The slurry was of an unusual character in that it was

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TABLE 1.2

COMPARATIVE CORROSION RATES AT 300°C

Thorium Oxide Batch	RUN CS-23			RUN CS-27			RUN CS-28-29			RUN CS-31		
	LO-2			LO-2			LO-2			LO-14		
	11 fps	21 fps	41 fps	10 fps	22 fps	41 fps	13 fps	22 fps	43 fps	13 fps	25 fps	41 fps
Corrosion Rate, mpy												
Austenitic SS	2-4	5-9	18-23	1	2-4	6-9	0.5	0.5	2-4	1-2	4-6	10-12
Gold	0.4	0.4	4	0.1	0.1	0.6	0.03	0.08	0.90	0.1	1	2
Titanium and Alloys	1	3-5	7-11	0.2	2	6	0.1	1.0	4-5	2	4	3-6
Zircaloy-2	0.1	1	6	0.1	0.1	2	< 0.1	< 0.1	1	< 0.3	4	13
Mild Steel	150	165	205	11	13	24	21	21	21	40	42	48
Average Loop Corrosion Rate, mpy		4.5			1.5			0.8			0.9	
Duration of Test, hr		49			301			266			83	
Average Circulating Concentration (grams of thorium per kilogram of water)		543			348			346			409	
Average pH of slurry		6.5			7			7			9.5	
Additive	O ₂ (~ 1000 ppm)			O ₂ (~ 1000 ppm)			O ₂ (~ 1000 ppm)			H ₂ (~ 15 ppm) N ₂ H ₄ (420 ppm)		
Degradation of Particles During Circulation (hr, approx.)	> 3 μ	1-3 μ	< 1 μ	> 3 μ	1-3 μ	< 1 μ	> 3 μ	1-3 μ	< 1 μ	> 3 μ	1-3 μ	< 1 μ
0	48	27	25	59	26	15	3	32	65	53	33	14
5	8	25	67	--	--	--	--	--	--	54	13	33
20	7	20	73	7	26	67	--	--	--	--	--	--
30	5	21	74	7	25	69	7	28	65	71	9	20
50	2	30	67	7	17	76	2	22	76	60	13	27
150				8	36	56	7	42	51	88	4	8
												(82 hr)
200				5	26	69	--	--	--			
300				3	32	65	2	21	77	(Spheroid formation)		

composed of spherical agglomerates ranging from approximately 8 to 30 μ in diameter. The detailed preparation of the material is outlined in ORNL-CF-56-10-8.

It was thought to be of interest to compare the corrosion characteristics of this material at 300°C with those of other slurries which had been previously pumped in loop CS. Three sets of pin-type corrosion specimens were exposed during the test at flows, measured on water at room temperature, of 6, 14, and 24 gpm. (10, 24, and 40 fps, respectively). Flow through the loop mixing line was 11 gpm.

The loop was charged initially, at room temperature, with 16.6 liters of supernatant liquid from the "standard" slurry and 120 psig of oxygen. Thoria was to be charged to the system as a concentrated slurry, containing approximately 1100 g of thorium per kilogram of water, in two batch additions while operating at 300°C. A total of 9850 g of thorium oxide was required to provide a calculated circulating concentration of 500 g of thorium per kilogram of water.

Both additions were made with difficulty. Ten hours were required to charge the first portion of slurry which contained about 7400 g of thoria. The normal charging schedule for such additions is 2 hr. The 1/4-in. tubing which connected the addition tank to the loop plugged repeatedly. Flow through the line could be maintained only by using a Lapp Pulsafeeder and by frequent back-washing of the line with liquid from the loop.

A Lapp Pulsafeeder was used continuously while making the second addition; however, the 1/4-in. line and high-pressure valve soon became plugged. An attempt was made to complete the addition through a sample valve on the system, but the valve and associated tubing also were plugged. Consequently, a total of only 7800 g of thorium oxide was charged to the system.

Twenty-six hours after the initial addition of slurry, the flow of purge water to the rear of the pump stopped. Coincident with this the pump power demand became extremely erratic and actuated the pump over-ride automatic control which shut the system down. Total operation with slurry in the system was 26.3 hr.

After the system was drained and thoroughly flushed with water, hard, tenacious deposits of thoria were found on both outer impeller surfaces and in the impeller suction and vanes. Similar material had been deposited around the weld pads on the pump head and on the thermal barrier. Photographs of these deposits are shown in Fig. 1.4 and 1.5. A softer deposit had filled the weep holes in the impeller.

The header to the No. 4 sample barrel contained a heavy deposit of pasty solids. The annulus between the header and the specimen holder was partially filled with a sticky deposit of slurry, and porous plugs of thoria had formed over both ends of the specimen holder. Flow through this section of the system was approximately 24 gpm.

Corrosion data calculated from weight losses of the pin specimens exposed during the test are of questionable value since the blockage in the No. 4 sample barrel would undoubtedly change the flow characteristics in the entire loop system. The rates were unusually high, however; e.g., at 10 fps, rates for the austenitic stainless steels ranged from 7 to 14 mpy.

Run CS-31 was made to study the attack by aqueous thoria slurry under reducing rather than oxidizing conditions. Heretofore, all dynamic slurry corrosion tests made in loops BS and CS were made under oxidizing conditions by injecting gaseous oxygen into the system to provide an oxygen concentration of ~ 500 to 1000 ppm.

Fig. 1.4. Thoria Deposits on Titanium Pump Impeller After Run CS-30. Standard slurry, 300°C, 26 hr.

Fig. 1.5. Thoria Deposits on Pump Thermal Barrier After Run CS-30. Standard slurry, 300°C, 26 hr.

The loop was charged at room temperature with 17.3 liters of water and then purged for approximately 30 min with argon gas to remove air from the system. After purging, 10 ml of 85% hydrazine hydrate, for removal of trace oxygen (estimated 20-fold in excess of requirement) and 30 psi hydrogen were injected into the system. The loop was heated to 300°C and operated for a period of 74 hr before adding slurry. A sample withdrawn from the system during this period contained, by chemical analysis, < 1 ppm oxygen and 24 ppm hydrogen.

Two batch additions of slurry were then charged to the system to obtain a calculated circulating concentration of 500 g of thorium per kilogram of water. Batch 10-14 thorium oxide was used. Five milliliters of 85% hydrazine hydrate were added to each slurry charge. After 26.7 hr of operation with slurry in the system, the sampled concentration was 509 g of thorium per kilogram of water.

At run hour 46, the pressure drop to the back of the pump had changed, and the flow of purge water to the pump bearings stopped. Flow was re-established by employing a Pulsafeeder which was used for the duration of the run. Pump operation became quite erratic.

After circulating slurry for a period of 70 hr, the sampled concentration of the loop had decreased to 344 g of thorium per kilogram of water. A third addition of slurry was made at that time in an attempt to increase the circulating concentration to the original level. System operation was very unstable after the addition and the pump power demand increased rapidly. Consequently, the run was terminated after 82.9 hr of slurry circulation.

Final disassembly and inspection of the system revealed heavy deposits of hard thorium on the pump scroll and thermal barrier. Similar material was found in the impeller vanes and on the impeller surface adjacent to the front hub. Portions of the hard deposits, which had apparently been dislodged from the pump cavity, were

located throughout the loop piping. A photograph of the pump thermal barrier and impeller is shown in Fig. 1.6. In general, the deposits were gray, appeared to be very dense, and were difficult to remove from the metal surfaces.

Analytical chemical and particle size data of the slurry samples withdrawn from the system during the run and of the various deposits are given in Table 1.3. Again, the formation of slurry spheroids occurred during circulation. Their relative size and rate of growth were of the same order of magnitude as those formed in Runs BS-5 and BS-6 which were made at 250°C with oxygen atmospheres.

Average corrosion rates collected during the 83-hr test are shown in Table 1.2. It is interesting to note that attack on the mild steel specimens exposed in Run CS-31, as well as those exposed in the previous tests using oxygenated slurry, appears to be relatively insensitive to slurry velocity. Further, if the data are normalized, by taking the product of the run time and corrosion rate, the attack on mild steel appears to diminish with increasing pH and in the presence of a reducing atmosphere. Additional tests will be made to study these factors.

The effect of particle degradation on the attack of materials using previously circulated slurry is shown in Table 1.2. Comparative data are presented showing the average attack rates and particle degradation in Run CS-28-29, along with those observed in two previous runs, CS-23 and CS-27, made at similar conditions.

Average attack rates in Run CS-28-29 using previously circulated slurry were, with the exception of the mild steel, about 50% lower than those observed in Run CS-27, using raw slurry. Note also in Run CS-27, the degradation of thorium particles which took place during the first 20 to 30 hr of circulation, whereas in Run CS-28-29, particle size distribution remained essentially unchanged.

Fig. 1.6. View of 100A Pump Impeller and Thermal Barrier After Run CS-31. LO-14 slurry, 300°C, H₂, 83 hr.

The effect of particle degradation is also strongly borne out in comparing corrosion rates in Run CS-25, a 49-hr test, and in Run CS-27, a 300-hr test. The rates are generally about half as great in Run CS-27, indicating that both highest corrosion rates and greatest particle degradation are associated with the early hours of the runs.

There is no clear explanation for the absence of a velocity effect on mild steel specimens exposed in Run CS-28-29. The data suggest, however, that the attack was mainly chemical in nature and at a sufficiently high rate to preclude any effect from the abrasive action of the slurry particles. The data do indicate, however, that corrosion rates for this material become substantially lower as the run durations are increased.

TABLE 1.3

SUMMARY OF SAMPLE DATA, RUN CS-31

Slurry Circulation hr	0.0	5.2	22.9	27.1	47.4	71.1	Solids Removed From Impeller Vanes After Shutdown	Solids Removed From Pump Scroll After Shutdown
Slurry Concentration g Th/kg H ₂ O	Charge							
From Chem. Anal.		3375		520	393	347	851	858
mg Th/g slurry (chem. anal.)	502	263		327	272	247	(Density - 8.53)	(Density - 8.84)
Fe, mg/g slurry	0.007	0.060		0.252	0.225	0.214	0.77	0.78
Cr, mg/g slurry	0.005	0.011		0.061	0.052	0.047	0.125	0.143
Ni, mg/g slurry	0.005	0.008		0.042	0.031	0.031	0.108	
Al, mg/g slurry	0.020	0.02		0.08	0.11	0.09	0.26	
Ti, mg/g slurry	0.020	0.10		0.02	0.05	0.11	0.25	
SO ₄ , mg/g slurry	0.010	0.10						
H ₂ O, mg/g slurry							(14.6 at 200°C, 3.5 at 800°C)	(15.6 at 200°C, 4.0 at 800°C)
pH of slurry	9.6	10.0		10.0	9.6	9.9		
Gas Analysis								
Oxygen (ppm)			1					
Hydrogen (ppm)			17					
Carbon Dioxide (ppm)			10					
Sedimentation Particle Size (a)								
10 (% by wt)	10	30		24	20	62	0	0
3-10 (% by wt)	43	24		47	40	26	5	30
1-3 (% by wt)	33	13		59	13	4	40	28
< 1 (% by wt)	14	33		20	27	8	55	42
Average Diameter, μ	3.3	4.5		7.0	4.8	12.5	0.8	1.5

(a) By gravitational sedimentation in 0.005 M Na₂P₂O₇ using neutron activation analysis.

TABLE 1.4

CORROSION RATES OF PIN AND COUPON SPECIMENS
(Runs BS-5, BS-6, CS-28-29, CS-30 and CS-31)

Run No.	ThO ₂ Slurry Concentration (g Th/kg H ₂ O)	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps ± 10%)	Specimen Material	Number of Specimens	Corrosion Rate (mpy)		
								Min.	Avg.	Max.
BS-5	563-584	250	21.9	~ 1000 ppm O ₂	17	Pins				
						347 SS	1		5	
						Armco Iron	1		62	
						Titanium (3%Al, 5%Cr)	1		6	
BS-5	563-584	250	21.9	~ 1000 ppm O ₂	27	309 Scb SS	1		15	
						316 SS	1		16	
						347 SS	1		16	
						Armco Iron	1		68	
						Gold	1		10	
						Titanium RC-55	1		6	
						Titanium (3%Al, 5%Cr)	1		6	
BS-5	563-584	250	21.9	~ 1000 ppm O ₂	10	Coupons				
						309 Scb SS	1		7	
						347 SS	2	6.8	7	7.5
						Armco Iron	1		20	
BS-6	565	250	11.1	~ 1000 ppm O ₂	19	Pins				
						316 SS	1		28	
						347 SS	1		5	
						Armco Iron	1		1100	
BS-6	565	250	11.1	~ 1000 ppm O ₂	27	Titanium (3%Al, 5%Cr)	2	None Detected		
						316 SS	1		8	
						347 SS	1		8	
						Armco Iron	2	540	870	1200
						Gold	1	None Detected		
						Monel	1		110	
						Titanium (3%Al, 5%Cr)	1		6	
BS-6	565	250	11.1	~ 1000 ppm O ₂	11	Coupons				
						309 Scb SS	1		2	
						347 SS	2	2.1	2.2	2.3
						Armco Iron	1		280	

TABLE 1.4 (Continued)

Run No.	ThO ₂ Slurry Concentration (g Th/kg H ₂ O)	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps ± 10%)	Specimen Material	Number of Specimens	Corrosion Rate, (mpy)		
								Min.	Avg.	Max.
						Pins				
						309 SS SS	1		18	
						347 SS	1		13	
						Armco Iron	1		240	
						Gold	1		23	
BS-5 and BS-6	563-584	250	33	~ 1000 ppm O ₂	18	Platinum	1		24	
						Titanium(3%Al, 5%Cr)	1		10	
						Titanium RC-55	1		6	
						Zircaloy-2	1		8	
						309 SS SS	1		2	
BS-5 and BS-6	563-584	250	33	~ 1000 ppm O ₂	27	347 SS	1		13	
						Armco Iron	1		260	
						Titanium(3%Al, 5%Cr)	1		11	
						Titanium(4%Al, 4%Mn)	1		15	
						Titanium RC-55	1		6	
						Zircaloy-2	1		26	
						Coupons				
						304L SS	1		3	
BS-5 and BS-6	563-584	250	33	~ 1000 ppm O ₂	11	347 SS	1		5	
						347-347 SS weld	1		12	
						Armco Iron	1		120	
						Incoloy	1		15	
						Titanium 75A	1		35	
						Pins				
CS-28-29	346	300	267	357 ppm O ₂	13	309 SS SS	1		0.4	
						316 SS	1		0.5	
						347 SS	2	0.4	0.5	0.5
						gold	1		0.03	
						Incoloy	2	0.2	0.2	0.2
						Platinum	1		0.02	
						Mild Steel, SA-212 B	2	20	21	22
						Titanium(3%Al, 5%Cr)	2	0.0	0.1	0.1
						Titanium RC-55	1		0.2	
						Zircaloy-2	1		None Detected	

TABLE 1.4 (Continued)

Run No.	ThO ₂ Slurry Concentration (g Th/kg H ₂ O)	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps ± 10%)	Specimen Material	Number of Specimens	Corrosion Rate (mpy)		
								Min.	Avg.	Max.
CS-30	400	300	26.3	~ 600 ppm O ₂	24	309 SCb SS	1		16	
						316 SS	1		14	
						347 SS	2	14	15	16
						Mild Steel, SA-212 B	2	150	165	180
						Gold	1		2	
						Inconel X	1		15	
						Monel	1		14	
						Platinum	1		1	
						Titanium RC-55	2	1	1	1
						Titanium(3%Al,5%Cr)	1	None Detected		
CS-31	407	300	82.9	15 ppm H ₂ 400 ppm N ₂ H ₄	13	Zircaloy-2	1		1	
						Pins				
						309 SCb SS	1		0.8	
						347 SS	2	1.2	1.4	1.6
						Armco Iron	2	27	34	40
						Gold	1		0.2	
						Incoloy	1		0.2	
						Nickel	1		0.2	
						Monel	1		0.8	
						Platinum	1		< 0.1	
CS-31	407	300	82.9	15 ppm H ₂ 400 ppm N ₂ H ₄	25	Stellite 6	1		2	
						Stellite 98 M2	1		None Detected	
						Titanium(3%Al,5%Cr)	1		2	
						Zircaloy-2	1		None Detected	
						309 SCb SS	1		5	
						316 SS	1		6	
						347 SS	2	4	6	7
						Armco Iron	1		45	
						Mild Steel, SA 212 B	1		39	
						Gold	1		1	
CS-31	407	300	82.9	15 ppm H ₂ 400 ppm N ₂ H ₄	25	Inconel	1		2	
						Monel	1		1	
						Platinum	1		0.3	
						Stellite 6	1		2	
						Stellite 98M2	1		7	
						Titanium(3%Al,5%Cr)	1		4	

TABLE 1.4 (Continued)

Run No.	ThO ₂ Slurry Concentration (g Th/kg H ₂ O)	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps ± 10%)	Specimen Material	Number of Specimens	Corrosion Rate (mpy)		
								Min.	Avg.	Max.
CS-28-29	346	300	267	357 ppm O ₂	22	309 SCh SS	1		0.5	
						316 SS	1		0.5	
						347 SS	2	0.5	0.5	0.5
						Gold	1		0.1	
						Inconel X	1		6	
						Monel	1		2	
						Platinum	1		0.3	
						Mild Steel, SA 212	2	18	220	22
						Titanium RC-55	2	1	1	1
						Titanium(3%Al, 5%Cr)	1		1	
						Zircaloy-2	1	None Detected		
						309 SCh SS	1		3	
CS-28-29	346	300	267	357 ppm O ₂	43	316 SS	1		4	
						347 SS	2	1.8	2.1	3.4
						Mild Steel, SA 212	2	21	21	21
						Gold	1		0.9	
						Nickel	1		4	
						Platinum	1		2	
						Titanium RC-55	2	5	5	5
						Titanium RC-70	1		4	
						Titanium(3%Al, 5%Cr)	1		5	
						Zircaloy-2	1		1	
						Pins				
						309 SCh SS	1		7	
CS-30	400	300	26.3	~ 600 ppm O ₂	10	316 SS	1		7	
						347 SS	4	8	10	14
						Gold	1		1	
						Nickel	1		8	
						Platinum	1		2	
						Titanium RC-55	2	0	1	2
						Titanium RC-70	1	None Detected		
						Titanium(3%Al, 5%Cr)	1	None Detected		

TABLE 1.4 (Continued)

Run No.	Concentration (g Th/kg H ₂ O)	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps) 10%	Specimen Material	Number of Specimens	Corrosion Rate (mpy)		
								Min.	Avg.	Max.
CS ₂ 31	407	300	82.9	15 ppm H ₂ 400 ppm N ₂ E ₄	41	309 SCD SS	1		11	
						347 SS	2	10	11	12
						Armco Iron	2	47	59	71
						Mild Steel	1		48	
						Gold	1		5	
						Monel	1		6	
						Platinum	1		2	
						Stellite 6	1	None Detected		
						Stellite 98 M2	1		13	
						Titanium(3%Al,5%Cr)	1		6	
						Titanium(4%Al,4%Mn)	1		3	
						Zircaloy-2	1		13	

1.2 In-Pile Slurry Loop Development* Several short-term slurry runs were made with the experimental in-pile slurry loop during the past quarter. The first of these was made to evaluate the performance of the slurry addition tank which contained the revised reducer. The loop was operated at 250°C in the line and 259°C and 580 psia in the pressurizer for approximately 30 hr on distilled water to demonstrate stable operation. During this period, purge water flow rates of 20 cc/min and 10 cc/min were maintained to the pump rotor cavity and the slurry addition tank respectively. The slurry addition system was then isolated from the loop, drained and charged with 377 g of screened thorium oxide from batch L0-2 and 288 g of water. This charge would have resulted in a calculated loop concentration of 334 g of thorium per kilogram of water. The tank was opened to the loop, flushed with condensate at a rate of approximately 10 cc/min for 1-1/2 hr, and then opened for inspection. The tank contained only clear water indicating all of the slurry had been charged to the loop. The pump rotor cavity purge water flow rate was maintained at approximately 15 to 20 cc/min during the addition. However, several hours after the addition, the thermocouple attached to the pressurizer bottom by-pass line immediately downstream of the flow restrictor coupling indicated that flow had either partially or completely stopped in that section of line. Samples taken at that time contained approximately 90 g of thorium per kilogram of water. The loop was shut down, drained, and dismantled in an effort to locate the slurry which had been charged to the loop but did not appear in the circulating stream.

As indicated by the low thermocouple reading, a quantity of loosely settled slurry had accumulated immediately upstream of the flow restrictor coupling in the pressurizer bottom by-pass line. Whether or not the flow through the 1/4 in. dia orifice in this coupling had been stopped completely during the run could not be determined. An equal quantity of loosely settled solids were found in the bottom of the annulus around the sample holder in the core. The

* By R. M. Warner

velocity of the slurry at this location in the loop was calculated to be approximately 0.4 fps based on flow measurement data obtained with water in the HT-16 calibration run.

The next run was made with the 5-gpm pump operating on 80 cycle/sec power to determine if higher flow velocities and pump head would prevent the slurry from settling in the loop. After approximately 4 hr operation on water to ascertain stable loop operation, the slurry addition tank was charged with 332 g of screened thorium oxide from batch LO-14 and 292 g of distilled water. This charge represented a calculated loop slurry concentration of 290 g of thorium per kilogram of water.

Approximately 1-1/2 hr after the addition was started, a sample of the loop circulating stream contained 109 g of thorium per kg of water. A visual inspection showed all of the slurry had been flushed from the addition tank. In an attempt to increase the concentration of the loop circulating stream, the addition tank was recharged with 318 g of screened thorium oxide from batch LO-14 and 293 g of distilled water. Approximately forty minutes after this addition to the loop was started, thermocouple readings indicated the core sample holder and the pressurizer bottom by-pass line had completely plugged. The run was discontinued.

Inspection of the loop following draining showed the slurry had accumulated in three different locations. The pressurizer bottom by-pass line upstream of the flow restrictor and the annulus of the core sample holder were both completely filled with a soft, pliable, loosely-packed slurry. Also, a soft, pliable bed of solids, approximately two in. in depth was found in the bottom of the pressurizer. However, the pressurizer could have been open to flow during loop operation, and the observed slurry could have settled before the loop was drained. Theoretical material balance calculations on the pressurizer are complicated by the lack of accurate concentration values for the circulating stream at the time the run was discontinued.

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2.0 TOROIDS. (by G. E. Moore)

2.1 Introduction. Experiments have been described previously which have investigated the behavior of thorium oxide slurries when circulated in toroids. Most of the work has dealt with slurry systems of concentration 1000 g of thorium per kilogram of water at 250°C under an oxygen atmosphere and at 26 fps relative velocity. The rate of attack on certain metals has been studied as a function of the calcination temperature of the oxide^{2.1.a} and the size of the thorium oxide particle^{2.1.b}. Previous work studied this effect of velocity^{2.1.a}, ^{2.1.c} while certain experiments also varied the slurry concentration^{2.1.d}, ^{2.1.e}, temperature^{2.1.f}, gaseous atmosphere^{2.1.b}, ^{2.1.d}, and electrolyte additions^{2.1.b}. More recently, studies were again initiated to determine the effect of certain electrolytes in the slurry^{2.1.b}.

Not only has information been gained on the effect these variables have on the attack rate of certain metals, but information on the behavior of the slurry and on the thorium oxide particles themselves have been obtained. Thus, the effect on thorium oxide particle size by the velocity of circulation^{2.1.c}, by the calcination temperature of the oxide^{2.1.b}, ^{2.1.c} and by the original size of the oxide particle^{2.1.b} has been determined.

Throughout these studies, three variables appeared to underlie the behavior of the thorium oxide slurries:

1. The maximum calcination temperature of the thorium oxide;
2. The size of the thorium oxide particle; and
3. The solution in which the oxide particle was immersed.

Superimposed on these three factors were other variables that also affected the behavior of the slurry, especially the rate of attack by the slurry on certain materials; these variables included the concentration of the slurry, the temperature, the relative velocity of circulation, and the gaseous atmosphere above the slurry system.

Because of the large number of variables, those last mentioned were generally maintained at constant values and the calcination temperature, particle size and electrolyte composition was studied by varying these factors appropriately. These variables, however, were not independent in their effects on slurry behavior but were so closely related that it was very difficult to study any one of them independently of the others.

The more intensive investigation in toroids of the effect of electrolytes added to the slurry system was a rather natural extension to the more general studies of thorium oxide slurries. The tetrasodium pyrophosphate system and the disodium hydrogen phosphate and sodium dihydrogen phosphate buffer system have now been studied more completely than previously reported^{2.1.b}. In addition, one experiment investigating the sodium metasilicate system has been completed. These experiments have used either an oxygen or a hydrogen atmosphere and the corrosion pin specimens have included SA-212 Grade B carbon steel.

Partly in view of the known degradation of thorium oxide particles being circulated as aqueous slurries^{2.1.g}, there had been proposed^{2.1.h} the production of a "standard thorium oxide slurry." Such a slurry was produced under certain specified conditions^{2.1.i} and has been studied in toroids under a variety of temperatures, slurry concentrations, and velocities.

A number of type 347 stainless steel toroids which have circulated thorium oxide slurries for about 4000 to 5000 hr have been replaced with new toroids. Examination of the interior surfaces of the used toroids has been started.

2.2 Dispersing Additives. The addition of electrolytes to aqueous thorium oxide slurries appears attractive for at least two reasons:

1. Often a more fluid (deflocculated) slurry results, and
2. By the proper choice of additives, a system may be realized that is more resistant to changes in the operating conditions of the system; stability may thereby result.

On the other hand, there are advantages to the use of a flocculated slurry; the relative merits of both systems have been discussed from engineering considerations^{2.2.a}. In any event, the attractiveness of dispersing additives warrants their more careful investigation.

Previous investigations^{2.1.b} in toroids with circulating thorium oxide slurries have shown that titanium can be severely attacked by both neutral and alkaline phosphate buffer solutions at 250°C under either oxygen or hydrogen atmospheres. Because the attack was dependent upon the concentration of phosphate, further investigations were carried out at phosphate concentrations believed to be low enough not to affect adversely the titanium and yet sufficient to influence the behavior of a thorium oxide slurry at a concentration of 1000 g of thorium per kilogram of water. This concentration appeared to be about 0.02 M phosphate.

In collecting data on phosphate systems at this concentration level, studies using 0.01 M Na_2SiO_3 were also included since this salt has also shown interesting dispersive effects on thorium oxide slurries^{2.2.b, 2.2.c}. Either hydrogen or oxygen atmospheres were used in an effort to determine the influence of this variable on the attack of type 347 stainless steel, SA-212 Grade B carbon steel, titanium 75A and Zircaloy-2. Each combination of electrolyte and atmosphere was studied at a slurry concentration of 1000 g of thorium per kilogram of water, 250°C and 26 fps relative velocity for 330 hr. A previously pumped thorium oxide (CS-21) was used in order that the oxide might possess a relatively small, stable particle size from the very beginning of the circulation. Properties

of this oxide are shown in Table 2.2.1, together with other thorium oxides pertinent in the discussion to be developed.

Table 2.2.2 summarizes the results of the study on thorium oxide slurries containing various additives circulated in toroids under oxygen or hydrogen atmospheres. Certain discrepancies are obvious from the table and require reinvestigation; nevertheless, certain conclusions do appear valid. Thus, type 347 stainless steel appeared relatively severely attacked in the presence of hydrogen (see Fig. 2.2.1) compared to that observed in the case of oxygen (Fig. 2.2.2). Attack rates for the stainless steel were about 3 to 7 mpy in the presence of oxygen and 9-20 in the presence of hydrogen; since the attack was so localized (near the root of the pin) in the case of hydrogen, the true rate was considerably greater (probably 50 to 200 mpy). A greater attack of the type 347 stainless steel toroid itself was also observed when hydrogen was used (2 to 4 mpy) as compared to that usually found in the presence of oxygen (1 mpy and less). The presence of the electrolytes shown in Table 2.2.2 did not appear to alter the general picture of the attack of the stainless steel in the two gaseous atmospheres.

The presence of a hydrogen rather than an oxygen atmosphere seemed to improve the appearance of SA-212 Grade B carbon steel exposed to circulating aqueous slurries. The chemical composition of the steel is tabulated in Table 2.2.3. Attack rates of about 5 to 10 mpy were observed on the carbon steel under hydrogen; attack appeared uniform (see Fig. 2.2.3) and did not change in character or magnitude in the presence of the additives used in these experiments. Although the generalized attack rates of SA-212 Grade B carbon steel in the presence of oxygen were little different from those in the presence of hydrogen, an intensified etch or very localized pitting attack was observed (see Fig. 2.2.4) both in the absence and presence of the added electrolytes (also see Section 2.3).

TABLE 2.2.1
PROPERTIES OF THORIUM OXIDE

Method of Preparation	CS-21 Product of Circulation of LO-2 in 100A Loop	LO-12 Oxalate-ppt'd. ORNL - Chem. Tech. Product	Standard Oxide Product of Circulation of LO-12 in 200A Loop
Calcination Temperature, °C	800	800	800
Specific Surface Area, m ² /g	22.2	15.8	29.5
Crystallite Size, Å	250	-	-
Particle Size Distribution, Weight Per Cent (a)			
Average diameter, $\bar{d}$ μ	0.6	3.4(2.1)(b)	9.5(15)(b)
> 10 μ	4	18 (17)	43 (86)
3-10 μ	6	36 (32)	42 (5)
1-3 μ	20	32 (-)	3 (-)
0-1 μ	70	14 (-)	12 (-)
Th, mg/g	868	866	870
Fe	0.087	0.030	0.431
Cr	0.021	< 0.005	0.156
Ni	0.017	< 0.005	0.061
Al	0.08	0.02	0.12
SO ₄	0.14	< 0.10	< 0.10
Cl	0.020	0.04	0.04
F	0.01	< 0.01	< 0.01
C	0.77	0.99	0.81

(a) By gravitational sedimentation in 0.001 M Na₄P₂O₇ (2.2.4).

(b) The recorded values are the average of three analyses in 0.001 M Na₄P₂O₇. The values in parentheses are the average of three analyses in a glycerin-water mixture of 0.005 M Na₄P₂O₇ having a viscosity of 19.53 centipoise at room temperature.

TABLE 2.2.2

EFFECT OF VARIOUS ADDITIVES UNDER OXYGEN OR HYDROGEN ATMOSPHERES ON AQUEOUS THORIUM OXIDE SLURRIES CIRCULATED IN TOROIDS

CONDITIONS: 1000 g Th/kg water
 CS-21 ThO₂ (average diameter (a), 0.6 μ)
 250°C
 26 fps relative velocity
 330 hours

Additive	Concentration M	Original Slurry		(1) Atm	Slurry Properties After Circulation								Attack Rate, mpy (d)				
		pH	Character		pH Slurry	pH Supnt.	Color	Re- suspension	Thick- ness	% Th Pour (b)	Settling (c)	Avg. Diam. μ (a)	347 SS Toroid	347 SS Fins	SA-212B	T1-75A	Zr-2
NaOH	- (j)	11	Thick	O ₂	7.6	7.6	Cream	Difficult	Thick	67	Slow	~ 0.1	1.1	6	5 (f)	6	-
NaOH	- (j)	10	Thick	O ₂	7.0	7.5	Dk. Cream	Easy	Thin	59	-	0.5	0.9	4	5 (f)	7	0
NaOH	- (j)	11	Thick	H ₂	9.5	-	Dk. Brown	Easy	Thick	55	Slow	0.9	3.4	17 (e)	4	4 (g)	-
NaOH	- (j)	10	Thick	H ₂	8.1	-	Brown	Easy	Thick	44	Slow	1.3	3.1	20 (e)	4	8 (g)	-
NaOH	- (j)	10	Thick	H ₂	8.8	8.5	Brown	Easy	Thick	40	Slow	1.0	1.9	18 (e)	11	8 (g)	-
Na ₄ P ₂ O ₇	0.01	11	Fluid	O ₂	7.3	7.5	Cream	Difficult	Thin	92	Dispersed	~ 0.1	1.1	4	4 (f)	5	0
Na ₄ P ₂ O ₇	0.01	11	Fluid	H ₂	9.8	9.7	Gray	-	Thin	79	Slow	0.5	1.6	9 (e)	6	3 (g)	0
(Na ₂ HPO ₄)	0.01	10	Fluid	O ₂	6.7	7.0	Cream	Difficult	Thin	84	Dispersed	0.2	1.1	3	4 (f)	2	0
(Na ₂ HPO ₄)	0.01	10	Fluid	H ₂	9.2	9.1	Brown	Easy	Thin	59	Dispersed	0.9	2.3	17 (e)	6	3 (g)	0
Na ₂ SiO ₃	0.01	10	Fluid	O ₂	6.7	7.1	Dk. Cream	Easy	Thin	74	Dispersed	0.5	0.9	7	8 (f)	20 (g)	0
Na ₂ SiO ₃	0.01	10	Fluid	H ₂	(h)	(h)	(h)	(h)	(h)	0	(h)	0.9	0.1	(6)(h)	(6)(h)	(4)(h)	(0)(h)

(a) From gravitational sedimentation in 0.001 M Na₄P₂O₇ (2.2.4); also see Table 2.2.1.

(b) The percent of the total thorium charged to the toroid that could be poured from the toroid at room temperature after circulation.

(c) A "slow" rate indicates a flocculated system in compaction settling. The notation "dispersed" indicates that after at least 16 hr of undisturbed settling at room temperature, much solid remained dispersed throughout the aqueous phase; some solids did settle during this length of time.

(d) Calculated on basis of uniform, general corrosion.

(e) Severe localized attack was present. See Figures 2.2.1 and 2.2.2.

(f) Localized pitting was observed. See Figures 2.2.3 and 2.2.4.

(g) Relatively severe attack. Compare Figures 2.2.5, 2.2.6, and 2.2.7.

(h) Could not pour from toroid at room temperature after circulation. However, a leak could have occurred and reported results may not apply.

(i) Approximately 100 psi oxygen (250°C) or 1 atm hydrogen (room temperature).

(j) Although the amount of sodium hydroxide required to adjust the pH to the stated value was not determined, other experiments suggest a concentration of 0.005 - 0.01 M NaOH to be reasonable.

Figure 2.2.1 (Plate 1756)

Type 347 Stainless Steel Exposed to Thorium Oxide Slurry of
1000 g of Thorium per Kilogram of Water for 330 Hr at pH 11,
26 fps relative velocity, 250°C Under Hydrogen Atmosphere.

(12.5X)

Figure 2.2.2 (Plate 1755)

Type 347 Stainless Steel Exposed to Thorium Oxide Slurry of
1000 g of Thorium per Kilogram of Water for 330 Hr at pH 11,
26 fps Relative Velocity, 250°C Under Oxygen Atmosphere.

(12.5X)

TABLE 2.2.3CHEMICAL ANALYSIS OF A-212 GRADE B CARBON STEEL

<u>Element</u>	<u>Weight Per Cent</u>
C	0.163
Mn	.58
P	.017
S	.042
Si	.24

Figure 2.2.3 (Plate 1760)

SA-212 Grade B Carbon Steel Exposed to Thorium Oxide Slurry of
1000 g of Thorium per Kilogram of Water for 330 Hr at pH 11,
26 fps Relative Velocity, 250°C Under Hydrogen Atmosphere
(12.5X)

Figure 2.2.4 (Plate 1759)

SA-212 Grade B Carbon Steel Exposed to Thorium Oxide Slurry of
1000 g of Thorium per Kilogram of Water for 330 Hr at pH 11,
26 fps Relative Velocity, 250°C Under Oxygen Atmosphere

(12.5X)

In the absence of additives, the attack of titanium 75A was slightly greater, based on microscopic examination of the pins, when hydrogen was used as the blanket gas (Fig. 2.2.5) as compared to oxygen (Fig. 2.2.6); weight loss data gave approximately the same rate of attack for both gases. As predicted, the concentration levels of $0.01\text{ M Na}_4\text{P}_2\text{O}_7$ or $0.01\text{ M NaH}_2\text{PO}_4$ - $0.01\text{ M Na}_2\text{HPO}_4$ were low enough so that no enhanced attack on titanium was found when these electrolytes were used, although severe attack was observed at greater phosphate concentrations^{2.1.b}. Compared to the 0.02 M phosphate system, the titanium 75A pin, exposed to the slurry containing $0.01\text{ M Na}_2\text{SiO}_3$ and oxygen, was much more severely attacked (Fig. 2.2.7). The results in the corresponding experiment using hydrogen in place of oxygen may be invalid since there was some evidence of a leak in system during circulation.

In all the experiments described, Zircaloy-2 showed negligible attack, both from weight loss data and from microscopic examination of the corrosion pins.

The original slurries of 1000 g of thorium per kilogram of water adjusted to pH 10 to 11 with sodium hydroxide were quite thick in contrast to those slurries of the same concentration containing 0.02 M phosphate or 0.01 M silicate which were quite thin and fluid. Qualitatively, circulation did not appear to alter this property of the slurry. The thickness of the slurry at room temperature after circulation was reflected in the degree to which the slurry could be poured from the toroid at room temperature after the run. In the cases of those slurries containing phosphate or silicate, from about 60 to 90% of the thorium oxide originally charged to the toroid was removed after circulation, whereas only from about 40 to 70% was removed when no electrolyte was present (other than sodium hydroxide).

The data pertaining to the ease of resuspension of settled solids seems inconsistent and should be redetermined, preferably in some

Figure 2.2.5 (Plate 1758)

Titanium 75A Exposed to Thorium Oxide Slurry of 1000 g of
Thorium per Kilogram of Water for 330 Hr at pH 10, 26 fps
Relative Velocity, 250°C Under Hydrogen Atmosphere
(12.5X)

Figure 2.2.6 (Plate 1757)

Titanium 75A Exposed to Thorium Oxide Slurry of 1000 g of
Thorium per Kilogram of Water for 330 Hr at pH 11, 26 fps
Relative Velocity, 250°C Under Oxygen Atmosphere

(12.5X)

Figure 2.2.7 (Plate 1782)

Titanium 75A Exposed to Thorium Oxide Slurry of 1000 g of Thorium
Per Kilogram of Water Containing 0.01 M Na_2SiO_3 for 330 Hr at
pH 10.5, 26 fps Relative Velocity, 250°C Under Oxygen Atmosphere
(12.5X)

quantitative manner; however, the nature of the subsidence of the settled slurries appears consistent; those slurries containing no dispersing electrolyte (except sodium hydroxide) settled slowly, i.e., they exhibited a flocculated system in compaction settling. On the other hand, those slurries containing phosphate or silicate generally produced a dispersed system, i.e., even after 16 hr of undisturbed subsidence at room temperature, much thorium oxide remained suspended throughout the aqueous phase; some solid generally did settle out during this length of time, of course.

Because the experiments were not particularly designed to study the uptake of electrolyte by the thorium oxide, no quantitative data on the adsorption of phosphate or silicate by the thorium were obtained. Some information (qualitative, however, because of probable analytical difficulties) indicated that the silicate and phosphate were probably quite strongly adsorbed.

- 2.3 Corrosion Inhibition. "Inhibition" may be defined as the reduction in the velocity of chemical reaction. With this definition applied to corrosion and under suitable circumstances, oxygen, salts of anions which form sparingly soluble compounds with the ions of the metal under consideration, adsorbed substances, etc. can all be regarded as "corrosion inhibitors." In this section, only inhibition in aqueous media will be considered. However, it is intended to present only a very brief review of the inhibition of metallic corrosion in aqueous media. Gatos^{2.3.a} has presented a discussion on metallic inhibition and data from his paper and from Evans^{2.3.b} have formed the basis of the following considerations.

At the start, it should be stated that corrosion inhibition is rarely an all-or-none proposition and, accordingly, can become quite complex. Thus, Evans^{2.3.b} was forced to distinguish between "stimulators", "intensifiers", "deterrents", and "safe" and "dangerous inhibitors". Some substances which may increase the

rate of corrosion at low concentrations, may function as inhibitors at high concentrations. And, conceivably, at even higher concentrations the rate may again increase. (e.g., inhibition at moderate concentrations may be due to the deposition of a protective film which may dissolve as a complex ion in greater concentrations of inhibitor).

Oxygen at ordinary pressures may increase the velocity of attack on iron in neutral solutions; however, at high pressures under suitable conditions, oxygen can function as an inhibitor. The behavior of carbon steel in high-temperature, oxygenated water is discussed in a separate memorandum^{2.3.c}. Many resistant materials owe their stability to protective films, which depend, either directly or indirectly, upon the availability of oxygen.

A number of inorganic electrolytes have either been used or have been proposed to be used as electrolytes to disperse thorium oxide in aqueous suspension. It so happens that these same electrolytes can function as "anodic inhibitors"; the possible dual role of these salts, by which both inhibition of corrosive attack, as well as production of highly dispersed thorium slurries may be realized simultaneously, provides interesting speculations. In view of this possibility, a review of the theory of inhibition, published experimental evidence and the application of these results to data observed with aqueous thorium slurries containing these inhibitor-dispersants seems indicated.

Using the electrochemical theory of corrosion^{2.3.b} "anodic inhibitors" are those substances which induce "anodic polarization"; that is, those substances which retard the anodic reaction. Such anodic inhibitors must be employed in sufficient amounts to insure complete inhibition; if added in insufficient quantities to stop the attack completely, the corrosion is severely localized. They are thus known as "dangerous" inhibitors. Substances known to be anodic inhibitors are chromates, phosphates, carbonates, silicates, etc.

The action of many anodic inhibitors has been shown by means of potential measurements. By such methods Na_2SiO_3 , Na_2CO_3 , NaOH , Na_2HPO_4 , NaH_2PO_4 and Na_3PO_4 have been shown to inhibit the corrosion of steel in aerated neutral or alkaline water. Oxygen plays an important role, for in deaerated solutions containing the same substances, no inhibition took place^{2.3.a, 2.3.b, 2.3.c} through^{2.3.f}. However, Na_2CrO_4 and NaNO_2 (and to a lesser extent, Na_2MoO_4 and Na_2WO_4) are effective in both aerated and deaerated solutions.

There have been proposed at least two theories to explain the mechanism of the action of inorganic anodic inhibitors:

1. The Protective Film Mechanism postulates the formation of protective insoluble films on the metal in the presence of the inhibitor. In the case of inhibitors with non-oxidizing anions (hydroxide, phosphate, silicate, etc.), the films are thought to be $\alpha\text{-Fe}_2\text{O}_3$ and are believed formed entirely by dissolved oxygen. Thus, these inhibitors do not participate directly in the formation of the protective film, but are believed merely to contribute to repairing discontinuities in the oxide films. In the case of inhibitors with oxidizing anions (nitrates, chromates, and to a much lesser extent, molybdates and tungstates), the protective film in aerated solutions again is formed primarily by dissolved oxygen; in deaerated solutions, however, these inhibitors can react directly with iron to form protective oxide films.
2. The Adsorption Mechanism does not rely on the formation of protective films consisting of stoichiometric chemical compounds to bestow passivity on a metal but rather, postulates that inhibition is due to physical and activated adsorption (chemisorption). The theory does not deny that oxide films are formed but often concludes that anions adsorbed at the oxide-solution interface are responsible for passivation, rather than the metal oxide film^{2.3.g, 2.3.h}.

Certain other experimental evidence may be cited from which the necessity of maintaining oxygen present for inhibition may be inferred. Recently, Wanklyn^{2,3,1} summarized the corrosion of mild steel in high-temperature water; among the substances regarded as ineffective in the inhibition of mild steel at 316°C by water of less than 0.05 ppm oxygen in stirred (max., 2 fps) autoclaves were: disodium phosphate, silicic acid, lithium tungstate, lithium dihydrogen phosphate, dilithium phosphate, lithium arsenate, lithium arsenate plus oxygen, ammonium phosphate, sodium molybdate and potassium pertechnetate. However, many of these same substances have been shown to be good inhibitors in the presence of aerated or oxygenated water.

Gatos^{2,3,a} has listed some inorganic and organic anodic inhibitors and the concentrations required for the inhibition of certain metals in specific environments. These data apparently refer to lower temperature systems (< 100°C). Since theory and experiment have indicated that oxygen can affect the corrosion mechanism in a most important manner, experiments at high temperature as a function of the oxygen and inhibitor concentration appear desirable.

Almost all of these substances discussed as anodic corrosion inhibitors have been considered as possible agents for dispersing aqueous thorium oxide slurries. It seems likely that under conditions which produce inhibition in high-temperature water, these materials might also function effectively in aqueous slurry systems. At least one complication arises from the possibility of erosion by the slurry particles. The adsorption of the inhibitor by the thorium oxide particles must also be considered so that sufficient electrolyte is present in the aqueous phase of the slurry to provide an inhibitor concentration great enough to prevent localized attack. Too great a concentration may be undesirable, since extensive attack by such solutions may be encountered, (e.g., titanium by 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$). There is the possibility that the concentration of additive sufficient for optimum dispersion of thorium oxide may not give maximum inhibition or vice versa.

The results so far obtained in toroids using these dispersing-inhibitors are consistent with the above considerations, although a great deal more work is necessary in order to understand more fully these systems.

The effect of phosphate solutions at 250°C with and without thorium oxide present on the attack of type 347 stainless steel, titanium 75A and SAE 1030 carbon steel were previously reported^{2.1.b}. More recent results of those tests in the absence of thorium and which were conducted in static autoclaves are summarized in Table 2.3.1. Similar tests in the absence of phosphate were not carried out. The average attack rates in oxygenated solutions of 0.01 M $\text{Na}_4\text{P}_2\text{O}_7$ or 0.01 M NaH_2PO_4 -0.01 M Na_2HPO_4 (approximately 0.2% PO_4 solutions) at 250°C of type 347 stainless steel and SAE 1030 carbon steel were essentially identical; no apparent attack was observed on any of the specimens. Before defilming, both the type 347 stainless and the SAE 1030 carbon steels were covered with thin black films.

The data in Table 2.3.1 show that, in general, an increase in corrosive attack accompanied an increase in phosphate concentration. Such a correspondence was also seen in toroid runs at 26 fps with type 347 stainless steel and titanium in the tetrasodium pyrophosphate system (absence of thorium slurry)^{2.1.b}.

Circulation of aqueous thorium oxide slurries at a concentration of 1000 g of thorium per kilogram of water in toroids at 26 fps relative velocity and at 250°C gave the following results:

1. Titanium 75A was relatively severely attacked in the presence of 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ or 0.1 M NaH_2PO_4 -0.1 M Na_2HPO_4 under either a hydrogen or an oxygen atmosphere. As a matter of fact, 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ in the absence of thorium slurry, but with oxygen, gave increased attack on titanium over that obtained for 0.01 M $\text{Na}_4\text{P}_2\text{O}_7$ ^{2.1.b}.

TABLE 2.3.1

EFFECTION OF PHOSPHATE SOLUTIONS AT 250°C UNDER OXYGEN ON CERTAIN METALS

Conditions: Static Autoclaves
Approximately 150 psi oxygen (250°C)

Additive	Concentration	pH		Length of Run, Hr	Average Attack Rate, mpy (b)		
		Initial	Final(a)		347 SS	Ti	SAE 1030
$\text{Na}_4\text{P}_2\text{O}_7$	0.01	9.8	6.8-8.0	1728	0.3	0.1	0.3
$\text{Na}_4\text{P}_2\text{O}_7$	0.1	8.5	8.3-8.5	864	0.8	2.4	1.3
$\left\{ \begin{array}{l} \text{NaH}_2\text{PO}_4 \\ \text{Na}_2\text{HPO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} 0.01M \\ 0.01M \end{array} \right.$	6.8	6.3-6.8	1032	0.1	0.0	0.2
$\left\{ \begin{array}{l} \text{NaH}_2\text{PO}_4 \\ \text{Na}_2\text{HPO}_4 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1M \\ 0.1M \end{array} \right.$	6.5	6.6	864	0.1	0.2	0.6

(a) Range of all runs.

(b) Electrolytically defilmed in inhibited H_2SO_4 at about 80°C. The thin film on titanium was not removed by this treatment.

2. Titanium was relatively severely attacked in the presence of 0.01 M Na_2SiO_3 under oxygen (Table 2.2.2).
3. Mild steel gave relatively low attack rates under these conditions as shown in Table 2.2.2. A hydrogen atmosphere apparently was better than an oxygen atmosphere; in the latter case, localized pitting was observed which might indicate that the oxygen concentration (approximately 100 psi) was too low. No effect of phosphate or silicate on the attack was apparent.
4. From Table 2.2.2, it appears that the attack on type 347 stainless steel was governed by the gaseous atmosphere; a hydrogen atmosphere gave relatively severe localized attack, whereas an oxygen atmosphere yielded lower attack rates and little localization. The effect of either phosphate or silicate on the attack rates was not apparent in these tests.
5. Zircaloy-2 remained essentially unaffected throughout these experiments (Table 2.2.2).

In the absence of other information, the results for carbon and stainless steels and titanium summarized in Table 2.2.2 can be explained solely on the basis of the gaseous atmosphere present. The previous results (2.1-2) also showed a strong dependence on the gaseous atmosphere and a dependence on the concentration of additive as well.

- 2.4 Toroid Examination: During the past two years, twelve type 347 stainless steel toroids have been used to circulate thorium oxide slurries. These toroids have now been removed from service and replaced with entirely new units for use in future studies, even though the old toroids were continuing to give satisfactory service. However, considerable mechanical wear on the Parker fittings, through which corrosion pin specimens are inserted, was observed. It was considered desirable to replace these toroids when convenient rather than to experience unscheduled shutdowns or loss of experimental data as a result of leaks at the mechanical closures.

The replacement of these toroids with new units has now permitted the sectioning and examination of several of these older toroids, each of which has circulated thorium oxide slurries under a wide range of conditions for about 4000 hr. Although metallurgical examination of these toroids has not been completed, preliminary examination has revealed only slight attack of the toroid walls with certain areas of much greater metal loss.

Figure 2.4.1. illustrates the manner in which the toroids were sectioned for metallographic examination. By cutting the toroids in this fashion, the outer wall was preserved intact; this was believed desirable, since the bulk of the attack was expected to occur in this region due to the centrifugal forces imposed on the fluid to cause circulation.

Figures 2.4.2 and 2.4.3 are photographs of the inside surface of the outer wall of type 347 stainless steel toroid after 4909 hr of circulation of aqueous thorium oxide slurries; approximately 4100 hr were at 250 or 300°C, 26 fps relative velocity, 1000 g of thorium per kilogram of water and with an oxygen atmosphere. These photographs overlap the area of the circumferential weld of the toroid and include the areas adjacent to two ports through which corrosion pin specimens were introduced into the toroid; the combined photographs thus show a little over one-quarter of the area of the outer half of the pipe exposed to the circulating media.

In the photographs of Figures 2.4.2 and 2.4.3, the direction of circulation in the toroid was from right to left; the areas immediately downstream from protuberances (corrosion pins and welds) showed bright, shiny, polished bare metal, whereas areas immediately upstream from these points were covered with a thin, dark, (presumably) metal oxide film. In contrast to these observations, the inner half of the pipe exposed to the circulating media was generally covered with a dark, apparently thin, metal-oxide film; the only areas of bare metal here were immediately opposite the

Figure 2.4.1 (T 11155)

Type 347 Stainless Steel Toroid
Sectioned for Metallographic Examination

Figure 2.4.2 (T 11154)

Interior Surface of Outer Half of Type 347 Stainless Steel Toroid
After Exposure to Circulating Aqueous Thorium Oxide Slurries For
Approximately 4900 Hr. (Downstream From Circumferential Weld).

Figure 2.4.3 (T 11153)

Interior Surface of Outer Half of Type 347 Stainless Steel Toroid
After Exposure to Circulating Aqueous Thorium Oxide Slurries For
Approximately 4900 Hr. (Upstream From Circumferential Weld).

Figure 2.4.4 (T 11164)

Cross-Section Through Parker Cap After Exposure to Circulating
Aqueous Thorium Oxide Slurries for Approximately 4900 Hr.

holes through which the corrosion pin specimens had been introduced. When the opening was used as a thermocouple well and no pin was ever present, the area opposite the port was covered with the dark, thin film.

On the basis of the photographs and the descriptions just given, it is apparent that areas near protuberances, which are likely sources of turbulence, are relatively free of film and are apparently subjected to a very mild polishing action by the slurry.

However, areas immediately adjacent to such protuberances (as near the corrosion pin entrances) or the protuberances themselves (welds, and, incidentally, often pin specimens) showed relatively greater metal loss than other areas. This is particularly apparent in Fig. 2.4.3 at the pin port; Fig. 2.4.4 is a slightly enlarged photograph of the cross-section through the Parker cap and shows more clearly the eroded area at the pin opening. The source or cause of the small striae and the small comet-shaped depressions seen in Fig. 2.4.2, 2.4.3, and 2.4.4 has not yet been determined. The circumferential weld was also much more attacked relative to other areas, although this is not particularly clearly shown in the photograph.

Qualitatively, the surface attack at these areas of turbulence or protuberance was not alarming but did demonstrate the enhanced attack at points of impingement or increased turbulence. A more quantitative assay of damage to the toroid itself by circulating aqueous thorium oxide slurries may be obtained when the metallographic examination of parts has been completed.

- 2.5 Circulation of a "Standard" Slurry. There had been proposed (2.1.8) the production of a "standard" thorium oxide slurry aimed at acquiring a quantity of slurry so prepared and treated that it would undergo no further change in physical properties with time or with handling or circulation. Essentially, the manufacture of such an

"interim standard slurry" consisted of circulating an aqueous slurry of pure oxalate-precipitated, multistage-calcined, (800°C maximum), thorium oxide in a loop in order that substantially all of the anticipated degradation of the oxide particles should take place (2.1.1). A description of the production of such an oxide and its characterization are given in detail in references 2.1.1 and 2.5.a. It was believed that the slurry so produced could be regarded as "standard" in the sense that its properties should show a minimum of change with further handling and thus would be suitable as a comparative standard.

Because of the quantity of oxide desired, circulation was carried out in a 200-gpm pump loop (200A, type 347 stainless steel); the approximate conditions of exposure were 100 hr at a temperature of 200°C and a slurry concentration of 500 g of thorium per kilogram of water using the purest available thorium oxide (Batch LO-12). Such circulation increased the stainless steel corrosion product content (iron, chromium, and nickel) and perhaps also the aluminum content over that of the charge material. Both materials contained moderate amounts of chlorine; the properties of both oxides are summarized in Table 2.2.1. A distinguishing feature of the so-called "200A Standard Slurry" was its unusually large average particle diameter (approximately 50 wt. per cent greater than $10\text{ }\mu$ diameter) (2.1.1 and Table 2.2.1).

Because of the unique size and method of formation of the oxide particles composing the "Standard" slurry, a number of experiments in toroids have been carried out in an attempt to learn the behavior and fate of the oxide particles during circulation under a variety of conditions of temperature, velocity, and slurry concentration. In general, three techniques have been employed to evaluate the slurry character after such circulations: (1) determination of particle size distribution by gravitational sedimentation using the neutron activation technique (2.2.j) in $0.001\text{ M Na}_4\text{P}_2\text{O}_7$, or in a high viscosity medium of glycerol-water and $0.005\text{ M Na}_4\text{P}_2\text{O}_7$;

Although slides of adequate quality have often been prepared by the above technique, the non-homogeneity of the sample caused by separation of particles of different size, has been a problem. The preparation of consistently good mounts is desirable in view of the benefits made possible through optical photography.

The slide containing the thorium oxide was photographed at 400 diameters by Mr. R. S. Crouse (2.5.b) using a Bausch and Lomb Balphot Metallograph. The chief disadvantage of the method was the difficulty in locating a microscopic field characteristic of the entire sample; considerable care was taken to photograph a representative field in order to avoid introducing error caused by the separation of large sized oxide from the main mass of material as described above. All photographs were made at the same magnification (400 X) to assist in comparing the sizes of the oxides; at this magnification 1 mm on the print represented 2.5μ (prior to any reduction associated with reproduction).

Quantities of Batch LO-12 thorium oxide and the "Standard" slurry, obtained by circulating an aqueous slurry of LO-12 thorium in a 200A loop, were received for study in toroids. Chemical analysis and determinations of the particle size distribution were obtained for these oxides and are recorded in Table 2.2.1. Photographs of these materials are shown in Fig. 2.5.1 and 2.5.2.

Table 2.5.1 summarizes the toroid runs which have been completed in the study of the "Standard" slurry and its precursor, Batch LO-12, while the photographs in Fig. 2.5.3 to 2.5.12 record the character of the thorium oxide particles at appropriate points during the investigation. Quantitative comparisons of particle sizes of the thorium oxides determined by gravitational sedimentation and estimated from the photographs were not made, inasmuch as it was extremely difficult to estimate the weight per cent distribution of the particles from the photographs. However, qualitatively, the agreement appeared good.

(2) optical photography of the slurry; (3) measurement of the rate of subsidence of the thorium oxide particles either in their supernatant liquid or in pure water.

Of these methods, the optical photographs were perhaps the most revealing for this was the only one of the three techniques which disclosed the shape or character of the individual oxide particle. Because photographs taken during this study have been so helpful in describing the results of the experiments, the technique of preparing the oxide for photography will be summarized. Approximately 0.1-0.5 g thorium oxide, either dry or as a slurry, was added to about 4 ml 0.001 - 0.005 M $\text{Na}_4\text{P}_2\text{O}_7$ and shaken by hand to disperse the thorium. A drop or two of this suspension was added to a 1 x 3 in. glass slide and spread over an area of approximately 0.5 in.² by tilting the slide and permitting the suspension to flow under gravity. There was a tendency for the larger-sized particles to collect at the periphery of the drop, leaving the smaller-sized particles near the center. It was found that spreading the suspension by mechanical means (e.g., by spreading it using another glass slide) often comminuted the large particles, although shaking the aqueous suspension in glass vials did not appear to alter the size. The drop was covered with a thin cover glass which was then held in place by small strips of Scotch cellophane tape. This did not prevent the water from evaporating but did produce slides of dried thorium oxide that often remained dispersed and did not agglomerate. It was found that without the use of a dispersing agent, the oxide was not adequately dispersed and large agglomerates of solids were obtained; when this occurred, it was almost impossible to distinguish the nature of the ultimate particles. It was also found impossible to take photographs unless the suspension was permitted to dry due to rapid Brownian movement of the smaller particles (exposure time required was approximately 10-30 sec). Qualitatively, Brownian movement appeared to become pronounced when the thorium oxide particle diameter was very approximately 0.5 μ ; the motion could be reduced, and sometimes even stopped, by adding glycerin to the suspension.

Figure 2.5.1 (T 10862)

LO-12 Thorium Oxide Used to Charge 200A Loop for Production
of Standard Slurry and to Charge Certain Toroid Runs (400X)

Figure 2.5.2 (T 11123)

Thorium Oxide Produced in 200A Loop as "Standard Slurry"
(400 X)

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TABLE 2.5.1

RESULTS OF CIRCULATION OF 200A STANDARD SLURRY AND ITS PRECURSOR BATCH LO-12 THORIUM OXIDE IN TOROIDS

Oxygen Concentration ~ 100 psi at temperature

Rel. Vel., fps	Temp. °C	Br Circulation	Slurry	Concentration g Th/kg H ₂ O	Attack Rates, mpy			Final ThO ₂ Size, μ		Settling Rate (c)		Final pH		Cl mg/l Supot.	Photo Figure No.
					347 SS	TH-75A	Zr-2	(a) Grav.Sed.	(b) Photo	Prerun	Postrun	Slurry	Supot.		
10	200	97	LO-12 (d)	500	2,5	0	0	1.4	1	0.0040/500	0.00026/880	9.0	7.9	6	2.5.11
			Standard(e)	500	2,6	+	1	19-26	25-38	0.0065/500	0.25/260	7.9	7.3	11	2.5.12
			Standard(e)	1000	2	+	0	24-27	30-48(r)	0.0035/1000	0.37/3560	7.8	7.4	10	2.5.3
			Standard(e)	1500	1,1	0	2	24-26	38(f)	0.0060/1500	0.17/1170	8.4	-	-	-
20	200	97	LO-12	500	5,5	2	1	0.8	1	0.0040/500	0.000023/950	8.2	-	-	-
			Standard	500	1,2	1	+	19	23-33	0.0065/500	0.18/285	6.7	6.7	68	2.5.4
			Standard	1000	5	+	+	19-21	0.5-30(g)	0.0035/1000	0.22/666	7.3	-	-	2.5.5
			Standard	1500	2,2	0	2	6-14	4	0.0066/1500	0.014/1390	7.8	6.5	21	-
20	300	100	LO-12	500	3,3	7,8	-	1.2	0.5-1.5	-	0.00071/610	6.3	7.7	7	-
			Standard	500	1,1	+,+	-	14	20-35(g)	-	0.18/238	-	7.5	6	2.5.6
			Standard	1500	1,1	+,+	-	18	23-35(g)	-	0.022/1960	-	8.3	10	2.5.7
26	200	100	LO-12	500	2,5	1	-	0.5	Very Small	-	0.00044/94	7.3	7.6	8	-
			Standard	500	0,1	+,+	-	~ 0.2	8-13(h)	-	Very Slow	6.8	7.1	21	2.5.8
			Standard	1000	1,1	+,+	-	1.0	8-15(h)	-	(1)	-	-	-	-
			Standard	1500	1,1	1	-	3.0	2-8	-	0.0022/824	7.1	7.5	-	2.5.9
26	250	225	LO-12	1000	3,3	4	-	0.5	0.8	-	-	6.9	-	-	-
			Standard	1000	4,4	7	3	0.6	1	-	(1)	-	-	-	2.5.10

- (a) The average particle diameter on a weight basis determined by gravitational sedimentation (2.2.4). The first value was obtained in 0.001 M Na₄P₂O₇, the second value in glycerin-water containing 0.005 M Na₄P₂O₇.
- (b) Estimated from photographs at 400X magnification.
- (c) The rate of subsidence in cm/sec at the stated concentration in "g of thorium per kilogram of water"; the two values are separated by the diagonal bar.
- (d) Initial average diameter, 3-4 μ (grav. sed.); 3 μ (photographic). See Table 2.2.1 and Figure 2.5.1.
- (e) Initial average diameter 9-17 (grav. sed.); 10-20 plug fines (photographic). See Table 2.2.1 and Figure 2.5.2.
- (f) No fines observed.
- (g) Also chips of oxide.
- (h) Irregular-shaped.
- (i) Little or no slurry poured from toroid at room temperature after run.

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Figure 2.5.3 (T 10861)

200A Standard Slurry After Circulation in Toroid at
10 fps Relative Velocity, 200°C, 1000 g of Thorium
per Kilogram of Water With Oxygen for 97 Hr (400X)

Figure 2.5.4 (T 11118)

200A Standard Slurry After Circulation in Toroid at
20 fps Relative Velocity, 200°C, 500 g of Thorium
per Kilogram of Water With Oxygen for 97 Hr (400X)

Figure 2.5.5 (T 10928)

200A Standard Slurry After Circulation in Toroid at
20 fps Relative Velocity, 200°C, 1000 g of Thorium
per Kilogram of Water With Oxygen for 97 Hr. (400X)

Figure 2.5.6 (T 11094)

200A Standard Slurry After Circulation in Toroid at
20 fps Relative Velocity, 300°C, 500 g of Thorium
per Kilogram of Water With Oxygen for 100 Hr. (400X)

Figure 2.5.7 (T 11096)

200A Standard Slurry After Circulation in Toroid at
20 fps Relative Velocity, 300°C, 1500 g of Thorium
Per Kilogram of Water With Oxygen for 100 Hr. (400X)

Figure 2.5.8 (T 11119)

200A Standard Slurry After Circulation in Toroid at
26 fps Relative Velocity, 200°C, 500 g of Thorium
Per Kilogram of Water With Oxygen for 100 Hr. (400X)

Figure 2.5.9 (T 11092)

200A Standard Slurry After Circulation in Toroid at
26 fps Relative Velocity, 200°C, 1500 g of Thorium
Per Kilogram of Water With Oxygen for 100 Hr (400X)

Figure 2.5.10 (T 10889)

200A Standard Slurry After Circulation in Toroid at
26 fps Relative Velocity, 250°C, 1000 g of Thorium
Per Kilogram of Water With Oxygen for 225 Hr (400X)

Figure 2.5.11 (T 10897)

Batch LO-12 Thorium Oxide Slurry After Circulation in
Toroid at 10 fps Relative Velocity, 200°C, 500 g of
Thorium Per Kilogram of Water With Oxygen for 57 Hr.

(400 X)

Figure 2.5.12 (T 10927)

200A Standard Slurry After Circulation in Toroid at
10 fps Relative Velocity, 200°C, 500 g of Thorium
Per Kilogram of Water With Oxygen for 97 Hr (400X)

Thus, the distribution of particle sizes obtained by gravitational sedimentation for the Batch LO-12 and "Standard" thorium oxides (Table 2.2.1) may be compared with photographs of these oxides (Fig. 2.5.1 and 2.5.2). For the Batch LO-12 oxide, gravitational sedimentation gave an average diameter between 3 and 4 μ with about 80 wt % of the material smaller than 10 μ diameter; Fig. 2.5.1 shows that almost all the particles were less than 10 μ diameter with a count-average of very approximately 3 μ . On the other hand, the "Standard" oxide by gravitational sedimentation in 0.001 M $\text{Na}_4\text{P}_2\text{O}_7$ gave an average diameter from 9-10 μ with about 60 wt % less than 10 μ , whereas gravitational sedimentation in a glycerol-water mixture containing 0.005 M $\text{Na}_4\text{P}_2\text{O}_7$ (19.53 centipoise viscosity) gave an average diameter of about 13-17 μ and only 10-20 wt % less than 10 μ diameter. Fig. 2.5.2 shows some material of the "Standard" slurry to be about 20 μ in diameter, some of an intermediate size (10-13 μ), many particles (by count) 2-5 μ in diameter and some particles < 2 μ . Thus, it is apparent that it becomes quite tedious to determine the particle size distribution on a weight basis from photographs. Nevertheless, the photographs seem to present an accurate accounting of the behavior and fate of the particles during the experiments.

Comparison of Fig. 2.5.1 and 2.5.2 shows that a considerable distribution of large-sized particles was produced as a result of circulating LO-12 thorium oxide in the 200A loop. As a matter of fact, a "growth" of oxide particles occurred since particles were observed in the "Standard" slurry that were much larger than were seen to be present in its precursor, Batch LO-12. The production of such large, single particles of thorium oxide from LO-12 thorium could not be duplicated in toroids under a variety of conditions as shown in Table 2.5.1. As a matter of fact, circulation of many slurries in toroids has never before resulted in a definite increase in size of the particles; on the contrary, particle degradation has generally occurred. Exceptions to this general rule

occurred for thorium oxides of very high calcination temperatures of very small initial size; in both cases, no significant change in size was observed (2.1.2).

However, circulation of the "Standard" Slurry in toroids was another matter, for in this case under suitable conditions, many more larger-sized particles resulted than were present initially.

The uniqueness in character of the "Standard" slurry compared to the more usual properties exhibited by Batch 10-12 thorium oxide, is illustrated convincingly by comparison of Fig. 2.5.11 and 2.5.12. Fig. 2.5.11 is a photograph of Batch 10-12 thorium oxide after circulation in a toroid at 10 fps relative velocity, 200°C and a slurry concentration of 500 g of thorium per kilogram of water for 97 hr under oxygen. The particles are generally of a very small size, probably of diameter 1 μ or smaller. Identical conditions of circulation using the "Standard" slurry produced the particles shown in Fig. 2.5.12.

When the "Standard" slurry was circulated at low speeds (10 fps), very large particles were produced as shown in Fig. 2.5.12 and 2.5.3. When the velocity of circulation of the "Standard" slurry was increased to 20 fps, it appeared again that particles were produced of a size larger than present in the "Standard" slurry, but not quite as large as those produced at only 10 fps relative velocity (Fig. 2.5.4). Under the same conditions, 20 fps, 200°C, 100 hr) except for a greater slurry concentration (1000 vs. 500 g of thorium per kilogram of water), not only was a growth in the size of the particles observed, but it also appeared as though some particles had been shattered into irregular chips and fragments (Fig. 2.5.5). Still at 20 fps relative velocity but at 300°C, there seemed to have occurred both a growth of particles and a fracturing of particles at slurry concentrations of 500 and 1500 g of thorium per kilogram of water (Fig. 2.5.6 and 2.5.7). Of interest in Fig. 2.5.7 is the hemispheroid near the bottom of the

photograph; the existence of such a particle strongly suggests that particles of the "Standard" slurry "grew" to a size of about 30 μ diameters and then fractured. A similar mechanism may be true for other particles seen in Fig. 2.5.5, 2.5.6, and 2.5.7. with smoothing of jagged, rough edges upon further circulation after fracture.

It appears that this postulated mechanism of growth and fracture of thorium particles is consistent with the results observed at 26 fps. When the "Standard" slurry at a concentration of 500 g of thorium per kilogram of water was circulated at 26 fps for 100 hr at 200°C, the resultant particles appeared as in Fig. 2.5.8; there appear to be many particles in the size range 10-20 μ diameter, but these are very irregularly shaped while many particles in a slightly smaller size range (8-10 μ) are also present. Fig. 2.5.9 is a photograph of the particles from a similar run at a concentration of 1500 g of thorium per kilogram of water; the particles appear as fairly uniformly shaped spheroids of diameter 2-8 μ . Circulation of the "Standard" slurry at 26 fps for 225 hr at 250°C and a slurry concentration of 1000 g of thorium per kilogram of water resulted in almost entirely small-sized particles as shown in Fig. 2.5.10. There do appear to be several particles in the center of the photograph of diameter approximately 6-9 μ , but most of the oxide seems to show a diameter of about 1 μ and smaller.

Thus, the mechanism suggested in the above paragraphs to describe the results obtained by the circulation of "Standard" slurry in toroids may be summarized briefly as follows: The behavior of the "Standard" slurry appeared dependent primarily upon the relative velocity of circulation and secondarily upon the temperature and slurry concentration. Two competing mechanisms dependent upon the relative velocity are postulated: the first was a "growth" or increase in size of thorium particles. This factor appear to predominate at low slurry velocities. However, at higher velocities, a competing reaction became increasingly important, namely, the

degradation or fracturing of the particles after growth. Thus, at low velocities, only a growth was observed while as the speed of circulation was increased, the fracturing of the large particles became increasingly important. It seems possible that the presence of corrosion pin specimens in the moving fluid provided surfaces for direct impact by the circulating oxide particles and thereby influenced the degradation and growth of the oxide.

The effects caused by changes in the concentration of the slurry and in the temperature were of secondary importance compared to the effect of velocity changes. As a first approximation, the results could be interpreted as being independent of slurry concentration and circulation temperature, since no definite trend could be associated with these variables (Table 2.5.1). The period of circulation may be a very important factor, however, as seen by comparing the data at 26 fps (Table 2.5.1, and Fig. 2.5.8, 2.5.9, and 2.5.10).

Examination of the pin specimens exposed during the runs summarized in Table 2.5.1 showed only slight attack. In this respect, the results are again surprising. A larger attack by thorium oxide particles which maintained such large size during circulation, would have been expected on the basis of previous results (2.1.2), even at lower velocities but certainly at the 26 fps level. It is believed, however, that the present results do not refute the previous postulate of increasing attack with increasing particle size but rather are another reflection of the unparalleled properties shown by the "Standard" slurry.

Perhaps even more significant than the relatively low values of the attack rates were the observations that those pins exposed to the circulating "Standard" slurry invariably accumulated a deposit of thorium oxide (except in the run at 26 fps for 225 hr). These deposits ranged from hard, adherent, thin, transparent layers to bulky wax-like deposits that could not be removed by mere scrubbing

with a bristle brush. The deposition did not appear to show preferential orientation with respect to the direction of circulation. Photographs of these deposits are shown in Fig. 2.5.13 and 2.5.14. The deposits appeared very similar to those found on the pins exposed to circulating slurries of Ames thorium oxide (2.5.3). No noticeable deposits of thorium oxide were found on pins exposed to the LO-12 oxide under the same conditions which produced deposits when the "Standard" slurry was being circulated.

Salient differences in the thorium particle size have been seen to exist in the product "Standard" slurry compared to the Batch LO-12 oxide from which it was produced. Significant differences in behavior during circulation in toroids were also seen to exist between these oxides. In contrast to the behavior in toroids shown by Batch LO-12 thorium oxide, the "Standard" slurry produced very large spheroids and very hard thorium deposits upon surfaces placed directly into the circulating medium. Under similar conditions (for example, 26 fps relative velocity, 250°C, 1000 g of thorium per kilogram of water, 225 hr, oxygen), it was not possible to pour the "Standard" slurry from the toroid at room temperature after circulation, whereas the slurry of Batch LO-12 oxide poured fairly well (approximately 60% removed based on the quantity originally charged to the toroid).

It is believed that these differences in physical properties and behavior may likely be due to differences in the chemical composition of the two oxides. Relatively large increases in the iron, nickel, and chromium contents of the "Standard" slurry over that of the Batch LO-12 oxide were found (Table 2.2.1 and Reference 2.1.9). Of these, it appears possible that chromium might exert considerable influence, especially if present as hexavalent chromium (i.e., chromate or dichromate); aluminum may possibly be another ion of great influence (aluminum or aluminate ions).

Figure 2.5.13 (Plate 1753)

Type 347 Stainless Steel Pin Exposed to Standard Slurry at 1000 g of Thorium
Per Kilogram of Water, 200°C, 26 fps Relative Velocity With Oxygen for 100 Hr

(12.5X)

Figure 2.5.14 (Plate 1754)

Titanium 75A Pin Exposed to Standard Slurry at 1000 g of Thorium Per
Kilogram of Water, 200°C, 26 fps Relative Velocity With Oxygen for 100 Hr
(12.5X)

On the other hand, it is not impossible that much more subtle differences in chemical composition might account for large differences in physical properties and behavior. To estimate the amounts of impurities or contaminants that could influence the properties, character and behavior of the slurry, the following considerations seem pertinent. If a specific surface area of $17 \text{ m}^2/\text{g}$ be assumed (a typical value for an 800°C calcined thorium oxide from nitrogen adsorption determinations) and the cross-sectional area for a hydrated molecule or ion adsorbed on the surface of the solid taken to be approximately $100 \text{ \AA}^2$ (radius of sphere, 5-6 $\text{\AA}$), only approximately 0.03 millimoles of adsorbate are required to saturate completely in a monomolecular layer 1 gram of oxide. It would seem that something less than complete saturation of the surface of a particle might easily cause discernible differences in the properties of the oxide. In addition, it seems likely that some of the surface available to the small nitrogen molecule (cross-sectional area assumed to be about $16 \text{ \AA}^2$) may not be available to a large hydrated ion. With these considerations, perhaps only 3 micromoles per gram would be sufficient to alter these properties of the oxide noticeably.

These values may be transposed into weight units depending upon the molecular weight of the adsorbate; for example, assuming a molecular weight of 100 (approximately that of sulfate or phosphate), 3000 ppm would saturate the available (nitrogen) surface, while only 300 ppm might be sufficient to alter the behavior of the oxide; for a molecular weight of approximately 30 (Al, Si, etc.) 900 ppm would be required to saturate the surface and possibly only 90 ppm to cause an appreciable effect.

Thus, it is readily apparent that even very small amounts of impurities, appropriately adsorbed on the thorium oxide particles, could conceivably produce large effects in the properties of the particle. It is often very difficult to detect reliably small concentrations of particular ions in the presence of large amounts of

thorium; and, unfortunately, with our present knowledge, the specific impurity capable of producing a change in the character of the oxide has not been determined. It may well be that a number of chemical species may each impart a similar behavior, and, therefore, the concentration level of each may be well below the levels indicated above.

The iron, chromium, nickel, and aluminum contents of the "Standard" slurry were determined analytically to be greater than shown to exist in the Batch 10-12 oxide. Other impurities not looked for may also be present, of course. However, aluminum (and other ions, such as titanium, zirconium, etc.) in the presence of large amounts of thorium and/or other ions may be especially difficult to determine accurately. Unfortunately, so far there is no firm experimental evidence that any of these impurities can account for the observed effects.

At least one reason for investigating additions to the aqueous slurry (see Section 2.2) was the possibility of securing a system that was relatively insensitive to small changes in operating variables; that is, a system that would be stable with respect to changes in ionic content of the solid, in pH of the medium, etc. Such insensitivity gained by the use of additives or by other means seems especially necessary if the character of the thorium oxide slurry is as responsive to small changes in chemical composition as appears likely; a case in point is that of the "Standard" slurry.

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