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O. Summary:

Corrosion data are presented for three slurry runs at 300°C on the 100A pump loop using three different preparations of thorium oxide. Average circulating concentrations ranged from 581 to 1075 grams of thorium per kilogram of water. Operating problems including some caking and plugging are discussed. One water run was also made.

The attack rate by slurries in the pump loop on pin specimens of type 347 stainless steel appears to be proportional to the slurry concentration and to the square of the flow velocity. Platinum, gold, Zircaloy-2 and titanium appear to be attacked relatively less severely than stainless steel, which had a pin corrosion rate of 7 mpy at 20 fps and 1000 grams of thorium per kilogram of water.

Studies at 250°C in toroids found no effect of increased thorium oxide calcination temperature on the attack rate on type 347 stainless steel, titanium or Zircaloy-2 at various flow velocities.

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1. Operation and Maintenance -- (H. C. Savage, S. A. Reed, R. M. Warner)

(a) 100A Pump Loops

Most of the past quarter has been devoted to loop operational check out and loop modifications to improve the condensate flow to the pump bearings in 100A pump loop CS. In addition modifications to the loop, designed to provide more flexibility of operation were incorporated.

Following run CS-16^(1.1a), previously described, an oxygenated water run at 300°C was made. This run lasted for approximately 100 hours. During this run, it was determined that the operation of the condensate system, used to provide water to keep the pump bearing area free of slurry, was erratic and unreliable. However, it appeared that a condensate rate of 1 liter per hour could be maintained by operating the loop with steam pressurization. It was considered desirable to increase this rate by installing a more reliable condensate system.

While design changes were being made, a steam pressurized slurry run, CS-18, charged with thorium oxide at a concentration of 1200 grams of thorium per kilogram of water was made. This run lasted 97 hours. The loop temperature was 300°C, and the pressurizer was maintained at 325°C and 1700 psia. Oxygen was added to the pressurizer to a pressure of 140 psia prior to the start of the run. The run was terminated when operation of the pump became noisy. Upon disassembly the pump was found to have been damaged in the rotor chamber to the extent of deep grooves cutting through the rotor can exposing the iron and copper bar rotor core. The pump stator diaphragm was also deeply grooved, necessitating replacement. This damage resulted from excessive bearing wear which allowed the rotor to rub against the stator diaphragm.

Following run CS-18, the modifications as described below were made to the loop.

(1) The original condensate system, previously described^(1.1b), was removed and a new system consisting of a one liter hold-up tank close coupled to the pressurizer with a one-inch schedule 80 pipe with a 1/4 inch tube from the top of the pressurizer to the top of the condensate tank. This system is shown in Figure 1.1.1. A 2000 psi rotometer was installed in the condensate system to measure the condensate flow directly instead of the indirect heat balance method used previously.

(2) The by-pass line from the pump discharge to the top of the pressurizer was increased in size from 3/8-inch schedule 40 pipe to 1-inch schedule 80 pipe to provide more flow through the pressurizer, if required. The flow rate through this by-pass could be varied by use of appropriate restrictors.

(3) Heating of the top portion of the pressurizer was provided by means of resistance heating wire controlled by a variac to prevent steam condensation in the top of the pressurizer, which could otherwise result in gas binding of the condensate system.

(4) One of the three corrosion specimen sample barrels (1.1c) previously removed from the loop was reinstalled, making a total of three sample holders in the loop.

Following the modifications described above, a loop operational check run at 300°C using water and oxygen was made. This run, CS-19W, with both loop and pressurizer at 300°C, was made to check the operation of the new condensate system. The duration of the run was 72 hours, during which it appeared that the condensate system was capable of supplying 3 liters per hour of water to the pump bearing region.

Subsequently, the loop was charged for run CS-20 with thorium oxide slurry at a concentration of 1180 grams of thorium per kilogram of water. Approximately three hours after start-up of the loop, the flow of condensate to the rear of the pump stopped either due to lack of water in the condensate tank or loss of pressure drop between the pressurizer and the rear of the pump. Slurry was noted in the condensate rotometer. A pulsafeeder pump was connected into the condensate line in an attempt to restore the flow. However, this operation was not satisfactory due to lack of condensate under the loop operating conditions. Operation of run CS-20 was terminated at this point at 6.4 hours of operation. When the pump was removed, excessive wear of both front and rear graphitar bearings was observed. In addition the front impeller seal rings were worn and had to be replaced. Plugging and caking in the loop observed in this run will be discussed in a subsequent section of this report.

Prior to the start of run CS-21, a 1 gph pulsafeeder was connected in the line between the condensate tank and the rear of the pump. This was done so that a flow of pump purge water could be maintained in the event of the loss of pressure drop to the rear of the pump.

Run CS-21 of 30 hours duration was charged initially with thorium oxide slurry at a ratio of 1200 grams of thorium per kilogram of water. When the loop reached operating conditions of 300°C and 1300 psia, the pump purge water flow rate was set at 1.8 liters per hour. This depleted the one-liter condensate supply tank in 10 minutes indicating both a low level and that insufficient steam condensate was being produced to maintain this rate. The condensate tank was primed with the pulsafeeder and condensate flow restarted at 3 liters per hour. After three hours the supply of condensate again was depleted.

Shortly after again restarting the condensate system by means of the pulsafeeder, the condensate pump purge flow was again lost apparently due to loss of pressure drop to the rear of the pump. From this time to the termination of the run (30 hrs.) the pump purge water flow was maintained at about 1 liter per hour by continuous use of the pulsafeeder. Heat balance calculations indicated that condensate was being produced at 360-1700 cc/hr.

Loop operation during the 30 hours of run CS-21 was erratic. Line temperature was varied between 225°C and 300°C and pressurizer between 245 and 300°C. One of the three sample barrels was plugged at start-up. The one-inch by-pass line with a flow rate of 19 gpm (7 ft/sec), based on measurements made with water, plugged during the run. These two plugs probably reduced the total loop flow and produced the loss of pressure drop to the pump. This pressure drop is dependent upon the pressure drop

across an orifice in the pump return line.

Calculations have indicated that the 1/4-inch tube from the top of the pressurizer to the top of the condensate tank is too small to prevent gas binding of the condensate system at the condensate flow rate desired (up to 10 liters per hour). This 1/4-inch line is being replaced with a 1-inch line and the pressure drop to the rear of the pump will be increased prior to the next run.

Based on analyses of slurry samples obtained during runs CS-18, CS-20, and CS-21 the concentration of thorium oxide in the circulating slurry varied over a wide range. During the 97 hours of operation of run CS-18, the concentration varied between 788 and 1621 grams of thorium per kilogram of water. Only one sample, an equal volume composite of supernate and settled slurry, was obtained after shutdown in run CS-20 at the end of the 6 hours of circulation. This sample had a concentration of 980 grams of thorium per kilogram of water. Four samples taken during the 30 hours of run CS-21 gave concentrations of 484 to 756 grams of thorium per kilogram of water.

Since the initial loop charge in all runs was at a concentration of 1200 grams of thorium per kilogram of water a loss of thorium oxide from the circulating slurry is noted in each run. Some of this loss can be accounted for in "dead" areas in the loop piping. The large loss of thorium oxide during run CS-21 is undoubtedly a result of the plugging of the one-inch by-pass line and one of the sample barrels. Chemical analyses of all samples taken and corrosion test results are given in Section 1.3 of this report.

(b) In-Pile Loop:

The experimental in-pile slurry loop has not been in operation during the past quarter. The pressurizer section and the condensate system required for purge water feed to the pump bearings have been modified to provide greater flexibility of operation. The in-pile type 5 gpm circulating pump has been equipped with aluminum oxide bearings and journals in an attempt to counteract the difficulties which have been experienced with the Graphitar bearings previously used. The loop is now being assembled for continued tests with thorium oxide slurries.

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Fig.1.1.1. Slurry Loop CS (As of Run CS-21)

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- 1.1b. *ibid*, Fig. 11.1, p. 107.
- 1.1c. H. C. Savage, F. J. Walter and R. M. Warner, HRP Quarterly Progress Report, October 31, 1954. ORNL-1813, Fig. 3.1, p. 65.

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1.2 Plugs and Cakes -- (E. L. Compere, S. A. Reed)

In Runs CS-20 and CS-21 some plugging and caking of certain loop parts was observed. It was felt that a description of the circumstances accompanying these occurrences would make it possible to avoid this in later runs.

Run CS-20 was charged with Batch D-47 thorium oxide, which had been produced by oxalic acid precipitation and 650°C calcination, followed by a calcination at 800°C. The material was used as received. Analyses of all thorium oxide preparations used during the quarter are given in Table 1.2.1. A charge to the loop of 23.8 kg ThO₂ and 17.70 liters of H₂O (total excluding 1 liter in condensate tank) was made to the loop, resulting in a makeup concentration of 1180 grams of thorium per kilogram of water. The pump was started and the loop brought to temperature.

Loss of condensate flow to the back of the pump occurred at about run hour 3. Slurry was noted in the condensate rotometer, indicating either a slurry carryover from the pressurizer or a backup from the pump. Carryover could have been caused by depletion of the condensate tank, and resultant increase in liquid level in the pressurizer. In any event condensate flow was not regained. The system was shutdown overnight. A sample of the slurry withdrawn after it had settled somewhat showed a very gray appearance. The condensate system was flushed after standing overnight, following which an attempt was made to resuspend the slurry. This attempt did not succeed, and the run was stopped. Two of the sample barrels, apparently open the previous day, appeared to be plugged.

Examination of the loop after thorough flushing found the pin holders plugged with relatively soft slurry paste (3860 grams of thorium per kilogram of water). On several of the opened halves of the pin holders a relatively hard cake was observed. One of these is shown in Figure 1.2.1. The holder was mounted vertically, the top being shown as the left edge of the photograph. The flow, as photographed, was left to right, or downward in the loop. The cake seemed made of several parts. There was a film of oxide of about 3/32" thickness covering the inside surface of the pin holder. Next to the metal it was white and chalky, whereas the half next to the flowing slurry was gray. Apparently the deposition of the gray layer may have coincided with loss of condensate flow to the pump bearings. This gray layer was quite hard. It seemed clearly indicated that this caking occurred during operation. Deposits may also be seen on the left, sufficient to plug the line. These were believed to be due either to settling of slurry on the first shutdown or a plugging at the start of the attempt to resuspend the slurry.

The pins quite generally were covered even after scrubbing with a hard glassy translucent film of thorium oxide, resembling milk glass, and appearing to be a few tenths of a millimeter thick.

The pin holder and a filmed pin were furnished to the Engineering Research Section of the Reactor Experimental Engineering Division for further examination.

Table 1.2.1

Analyses of Thorium Oxide Batches, As Received

Batch No.	D-38	D-47	LO-2
Precipitant:	Oxalic Acid	Oxalic Acid	Oxalic Acid
Calcination Temp °C	800	800	800
Avg. Crystallite Size, Å	---	---	250
Area, m ² /g	---	---	16.5
Sedimentation Analysis:			
Avg. diameter, microns	7.2	5.5	2.3
Wt. percent: over 10 microns	16	34	20
3 to 10 microns	25	33	24
1 to 3 microns	37	20	36
under 1 micron	22	13	20
Loss on Ignition, 100°C, mg/g	0.64	---	1.7
Loss on Ignition, 900°C, mg/g	0.90	---	---
Analysis, mg/g			
Thorium	863	874	874
Carbon, total,	0.700	0.260	---
Carbonate	3.500	1.260	2.800
Nitrate,	---	---	below 0.001 (0)
Sulfate,	0.230	0.920	below 0.010
Phosphate,	---	---	0.015
Silicon,	below 0.010	---	0.031
Chloride	0.044	0.070	0.002
Fluoride	below 0.010	0.010	below 0.010 (3)
Iron	0.022	0.031	below 0.010 (9)
Nickel	below 0.005	0.014	below 0.010 (2)
Chromium	below 0.005	0.008	below 0.010 (1)
Lead	---	---	below 0.005
Silver	below 0.050	---	---
Aluminum	0.170	0.031 (1)	---
Sodium	below 0.200	---	below 0.010 (7)
Potassium	below 0.100	---	below 0.010 (0)
Lithium	below 0.100	---	below 0.010 (5)
Calcium	---	---	0.008
Magnesium	below 0.010	---	0.00007
Barium	below 0.200	---	below 0.100 (LL)
Cerium	---	---	0.0033 (LL)
Lanthanum	---	---	0.0003 (LL)
Neodymium	---	---	below 0.0013
Yttrium	---	---	below 0.0001
Ytterbium	---	---	below 0.0005

(1) substantially higher results have also been reported.

(LL) lower limit of analysis.

The forward side of the titanium pump impeller appeared to have a similar hard glassy coat of thorium oxide from the center half way out to the edge. A number of the holes in the rear hub were plugged also. A photograph of the forward side of this impeller is shown in Figure 1.2.2.

The various hard deposits appear to be associated with this particular thorium oxide product, which was relatively impure. No other LOOA loop runs with other oxides have produced deposits of this character.

Run CS-21 was charged with 20.4 kg of Batch LO-2 ThO_2 and 14.95 liters of water (total, excluding 1 liter in condensate tank) to give a charge concentration of 1200 grams of thorium per kilogram of water. Batch LO-2 ThO_2 was produced at ORNL by oxalate precipitation from unusually pure Th^{2+} thorium nitrate, and calcined in several stages, the final temperature being 800°C . This material has been produced in a large quantity, 5000-10000 lbs, for the use of the Engineering Research Section. Analysis of this material is given in Table 1.2.1.

It was noted from the beginning of the run that No. 4 sample barrel remained cold indicating no flow at all.

After about one hours satisfactory operation of the loop at 300°C (following 1-1/2 hours heating up period with circulation), it was noted that the temperature of the bypass mixing line from the pump discharge to the top of the pressurizer, began to fall slowly, approaching a final value of 40°C . The rate of fall in temperature was proportional to the difference from equilibrium temperature, indicating simple cooling of a non-flowing, well insulated line. Thus, apparently the plugging occurred fairly quickly. The bypass mixing line consisted of about 12 feet of 1-inch schedule 80 pipe with a 1/4 inch circular orifice on the upstream side. The flow rate (as determined on water) was 19 gpm corresponding to 7 fps. The run was continued for about one day and stopped. At about the time the flow through the bypass mixing line was lost, condensate flow to the pump bearings was also lost. This was possibly a result of a substantial loss in head occurring across the return line restrictor as the flow diminished, or more or less equivalently, between the pressurizer top and the pump bearings, as described in an earlier section.

Addition of CO_2 to a partial pressure of 50 psi, at hour 27 had no effect. When the loop was cooled after stopping the run the majority of the slurry was removed and the loop was flushed thoroughly with water. Various parts of the loop were then examined.

The bypass mixing line was found to be entirely clean and free of slurry. Except for moderate spatter above the mixing line inlet, little slurry was found in the pressurizer. The return line between the pressurizer and the pump suction was entirely clean except for the flared region of the pump suction nozzle. Here the line widened to accommodate the impeller inlet, and a deposit up to 3/8-inch thick was observed, which maintained a flow channel through it about equal to the bore of the impeller inlet or the return line leading up to it. Thus, only the widened part had a plug. This plug was quite firm, of about the hardness of cheese. A photograph of this deposit is shown in Figure 1.2.3.

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Y-12 Photo
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Fig. 1.2.1. Thorium Oxide Cake in Pin Holder from Pump Loop Slurry Run CS-20 (6Hours) Using Batch D-47 Thorium Oxide. Flow Downward (Left to Right)

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PLATE 1433-2
CS-20

Fig. 1.2.2. Thorium Oxide Deposit on Center of Titanium Pump Impeller, Run CS-20 (6 Hours) with Batch D-47 Thorium Oxide.

On opening the No. 4 sample barrel no slurry was observed in the pin holder. Some very thick but fluid slurry adhered to the bottom part of the holder when it was removed. The barrel was removed from the headers. A photograph of the downstream header is shown in Figure 1.2.5. The upstream part of the plug was gray, the downstream parts were white. It appears indicated that the gray part of this plug had been carried over from Run CS-20, while the white parts were from the charge to the present run. This would account for the existence of the plug from the beginning of the run.

A cap on the upstream header manifold near No. 2 sample barrel flange was also found filled with a slurry paste that had not rinsed out, while the corresponding cap on the downstream side was clean. The upstream cap received direct flow; the downstream cap projected perpendicular to entrant flow.

Samples of the above plugs were furnished the Engineering Research Section for further examination.

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Fig. 1.2.3. Deposit in Pump Suction Line, Inlet Flange, after Run CS-21 (30 Hours) with Batch LO-2 Thorium Oxide.

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Fig. 1.2.4. Slurry in Downstream Header for No.4 Sample Barrel, After Run CS-21 (30Hcurs) with Batch LO-2 Thorium Oxide.

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Fig. 1.2.5. Slurry Plug in Upstream Connection of No. 4 Sample Barrel After Run CS-21 (30 Hours) with Batch LO-2 Thorium Oxide. Plug Material Apparently Mostly Batch D-47 Oxide Held Over from Run CS-20.

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1.3 Data and Discussion -- (S. A. Reed, E. L. Compere)

Three additional short-term runs were made during the past quarter in 100A pump loop CS(1.3a) to obtain dynamic corrosion data with thorium slurries. Each test was made at 300°C with addition of gaseous oxygen to the system to provide loop overpressure and/or maintain approximately 1000 ppm of dissolved oxygen at temperature. The average corrosion rates of pin type corrosion specimens exposed in these runs are presented in Table 1.3.1. Results of chemical analyses of slurry samples withdrawn from the loop during each test are shown in Table 1.3.2.

Three different thorium oxide preparations were tested at a nominal slurry makeup concentration of 1200 grams of thorium per kilogram of water. Circulating concentrations as determined by analysis are given in Table 1.3.2. The three preparations were ORNL production batches D-38, D-47 and LO-2, all of which were calcined at 800°C. Analysis of these materials is given in Table 1.2.1.

Batch D-38 thorium oxide has been tested previously (1.3a) in Run CS-16 at an average slurry concentration of 1030 grams of thorium per kilogram of water. This preparation was circulated again this quarter in Run CS-18 at an average concentration of 1075 grams of thorium per kilogram of water. Both tests were made using steam pressurization, with loop temperature at 300°C and pressurizer temperatures at 310 to 325°C.

Corrosion data obtained in Run CS-18 were in good agreement with those data collected in the previous run, Run CS-16. At flow rates of approximately 75 fps, type 347 stainless steel showed an average attack rate of 103 mpy. Comparable rates of attack were also noted for the noble metals and titanium: gold, 54 mpy; platinum, 87 mpy; titanium 75A, 115 mpy. No evidence of pitting or localized attack was evident by microscopic examination.

Two pin type specimens of sintered Al_2O_3 were exposed in the run. These specimens, fabricated from a commercial Al_2O_3 pump bearing currently being used in the in-pile solution loops, was severely attacked by the slurry at the test conditions. An attack rate of 4000 mpy occurred at 76 fps.

The overall loop corrosion rate for Run CS-18 was 610 mpy; for the first 90.6 hours it was 31 mpy. The rapid increase after this time reflects the severe damage occurring to the pump rotor and stator in this run.

Due to operational difficulties encountered in Run CS-20, test specimens were exposed to slurry for a period of only 6 hours. Because of the short exposure time, only the lead pins of type 347 stainless steel in each specimen holder were removed and defilmed for examination. Rates calculated from weight losses of these specimens were 11 mpy at 16 fps, 14 mpy at 33 fps and 25 mpy at 49 fps. Hard deposits of thorium oxide resembling milk glass were noted on most pins. Batch D-47 thorium oxide was used in preparing the slurry for the test. The loop was operated with both loop and pressurizer at 300°C and a charge concentration of 1180 grams of

thorium per kilogram of water. The only sample withdrawn from the system was taken after the termination of the run and consisted of equal volumes from valves #1 and #3, probably supernatant and settled slurry respectively. It was found by chemical analysis to contain 980 grams of thorium per kilogram of water. A considerable quantity of slurry was found caked in the system while disassembling the loop.

Overall loop corrosion calculated from the rate of increase in nickel concentration was 0.2 mpy.

Slurry used in Run CS-21 was prepared from Batch LO-2 thorium oxide. The charge concentration was 1200 grams of thorium per kilogram of water. Average circulating concentration was 581 grams of thorium per kilogram of water. Both loop and pressurizer were operated at 300°C. With the exception of the three lead pins of type 347 stainless steel which were replaced after Run CS-20, the corrosion data for this run shown in Table 1.3.1 were calculated from the combined weight losses of specimens used in both runs CS-20 and CS-21 and represent a total exposure period of 36 hours.

As indicated in Section 1.2, plugging occurred again in Run CS-21 which necessitated termination of the test after 30 hours. Nevertheless, the data are typical in that they show the strong effect of slurry velocity. Attack, under the test conditions, appeared quite uniform and the various specimens of stainless steel and titanium were covered with a thin adherent corrosion film of metal oxide.

The over-all loop corrosion rate, calculated from the rate of increase in nickel concentration, was 0.04 mpy.

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Table 1.3.1
CORROSION RATES OF PIN TYPE SPECIMENS (RUNS CS-18, CS-20, and CS-21)

Run No	ThO ₂ Slurry Concentration (g Th/kg H ₂ O) ^a	Temp. (°C)	Time (hr)	Additions	Flow Rate (fps ± 10%)	Pin Material	No. Pins	Corr. Min.	Rate, Avg.	mpy Max.
CS-18	788 - 1621 (avg: 1075)	300	97	136 ppm O ₂	76	322W SS ^b	2	69	75	80
						347 SS	8	97	103	120
						Al ₂ O ₃	2	3900	4000	4100
						Gold	2	53	54	54
						Platinum	2	85	87	88
						Rhodium ^d	2	170	170	170
						Stellite 25	2	160	160	160
						Ti 75A	4	110	115	120
						Ti 150A	2	100	105	110
						Zr-2	2	66	67	68
CS-20	Est. 980	300	6	~1000 ppm O ₂	16	347 SS	1 ^e		11	
					33	347 SS	1 ^e		14	
					49	347 SS	1 ^e		25	
CS-21	484 - 756 (avg. 581)	300	36	300 ppm O ₂	16	304L SS	1		2	
						309 Scb SS	1		3	
						347 SS	3	1	2	3
						430 SS	1		3	
						17-7 PH ^f	1		3	
						Gold	1		1	
						Inconel X	1		2	
						Platinum	1		g	
						Ti 75A	2		g	
						Ti RC-70	1		g	
						Zr-2	1		g	
					33	347 SS	2	5	7	9
						430 SS ^f	1		14	
						17-7 PH	1		9	
						Carpenter 20	1		14	
						Gold	1		1	
						Inconel X	1		9	
						Platinum	1		2	
						Titanium (6% Al-4%V)	1		1	
						Ti 75A	2	1	2	2
						Ti RC-70	1		2	
						Zr-2	2	0	0.5	1

Table 1.3.1 (cont'd.)

Run No.	ThO ₂ Concentration ^a (g Th/kg H ₂ O)	Slurry	Temp. °C	Time (hr)	Additions	Flow Rate (fps ± 10%)	Pin Material	No. Pins	Corr. Rate, mpy		
									Min.	Avg.	Max.
CS-21						49	304L SS	1		20	
							309 SCb SS	1		16	
							316 SS	1		19	
							347 SS	3	10	15	18
							430 SS	1		31	
							Al ₂ O ₃ ^h	1		1300	
							Gold	1		9	
							Inconel X	1		19	
							Platinum	1		8	
							Ti 75A	2	9	9	9
							Zr-2	1		15	

^a See Table 1.3.2, column 5, this section.

^b Annealed.

^c Fabricated from a sintered Al₂O₃ pump bearing purchased from the Kearfoot Company.

^d 0.002" rhodium electroplated on type 347 stainless steel.

^e Lead pins - other specimens were exposed an additional 30 hr in Run CS-21.

^f Hardened.

^g No detectable weight change.

^h Sintered Al₂O₃ pin from commercial pump bearing - scrubbed weight.

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Table 1.3.2

CHEMICAL ANALYSES OF SLURRY SAMPLES FROM RUNS CS-18, CS-20 and CS-21

Run No.	Temp. (°C)	Loop Charge Concentration (g Th/kg H ₂ O)	Pumping Time (hr)	Thorium (g/kg of H ₂ O)	g per g of slurry			Aqueous Phase Conductivity, x 10 ⁻² (mho/cm) : pH		ThO ₂ used in Preparing Slurry (ORNL Batch No.) *
					Fe	Cr	Ni			
CS-18	300	1200	2	1030	63	17	9	2.3	8.55	D-38
			19	1258	370	93	66	0.1	9.20	
			24	918	346	89	55	0.3	8.25	
			91	788	2,100	488	384	5.3	5.60	
			92	1220	4,180	878	788	4.3	5.20	
			97	1621	50,600	10,350	9,400	0.4	6.15	
**CS-20	300	1220	6	980 **	64	18	6	4.7	9.60	D-47
CS-21	300	1200	3	756	120	27	23	---	9.10	LO-2
			9	500	27	7	9	4.0	9.55	
			22	484	43	8	7	---	6.00	
			30	584	56	16	9	2.9	9.25	

* Final Calcination Temperature:

D-38	-	800°C
D-47	-	800°C
LO-2	-	800°C

** Sample after end of run. A composite of equal volumes of material from pump discharge sample valve and pressurizer bottom sample valve.

REFERENCES

- 1.3a H. C. Savage, HRP Quarterly Progress Report; October 31, 1955,
ORNL-2004, pp. 106-114.

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1.4 Effect of Slurry Velocity and Concentration on Corrosion

It is desirable at this time to begin the examination of slurry corrosion data accumulated and reported during this and previous quarters (1.1a). It is felt that in order to permit satisfactory design of reactor slurry systems, it will be necessary to consider the effects of a number of variables on corrosion, as well as on engineering properties which are studied by other sections. The corrosion data considered below thus represent only one aspect of a complex problem, and corrosion will probably exercise a strong influence on design only under certain conditions.

Many variables can be expected to influence the rate of attack of a circulating slurry on the materials of construction. Some of these factors are given in Table 1.4.1 along with an indication of the ranges over which they have been studied in either toroids or 100A pump loops. Some correlation of toroid data is presented elsewhere in this report; only pump loop data is to be discussed below, and only runs through CS-18 are included.

Data on the attack rate on type 347 stainless steel by slurry are presented in Figures 1.4.1, 1.4.2, and 1.4.3. In Figure 1.4.1 the attack rates on pins, coupons in straight channel holders and coupons in tapered channel holders are plotted on logarithmic coordinates against velocity, for runs CS-7, CS-8, and CS-9. The data are consistent with a slope of 2, indicating a possible dependence of attack rate on the square of the velocity. The pin and coupon data appear to agree, although the pin attack rates are somewhat higher than the coupon rates. This was probably due to increased turbulence, and indicates the importance geometric factors are likely to play.

In Figure 1.4.2, velocity effects are studied in terms of the attack rate on type 347 stainless steel pins, corrected to a concentration of 1000 grams of thorium per kilogram of water by a first power concentration dependence. The data agree with a dependence on the square of the velocity. A temperature effect was also apparent here. Rates at 300°C were higher by a factor of 1.7 than the rates at 250°C.

In Figure 1.4.3, the effect of slurry concentration is shown, after correction of rates to a common velocity of 20 fps by a velocity-squared factor. The data are consistent with a dependence of attack rate on the first power of concentration.

Data for other materials appear to be reasonably consistent with this dependence on concentration and the square of velocity. In Table 1.4.2 below, the attack rates have been adjusted to 1000 grams of thorium per kilogram of water and 20 fps, arbitrarily using such a dependence. The effect of certain other factors is indicated in the last column. It may be seen that the greatest resistance to attack was offered by gold and platinum, and next by Zircaloy-2, and titanium and its alloys. The stainless steels followed, with little difference apparent among all tested members of 300 and 400 series, except that type 347 stainless steel generally appeared among the best of the group.

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Table 1.4.1
Status of Evaluation of Factors Likely
to Influence Slurry Corrosion

Factors	Ranges Studied	
	Torroid	100A Loop
SYSTEM:		
Concentration, g Th/Kg H ₂ O	100-1500 (2200)	240-1075
Velocity	5 - 26	8 - 76
Temperature	(200) <u>250</u> (300)	250 - <u>300</u>
Time, hr	100-200	76-258
Geometry	pins	pins, coupons
OXIDE:		
Precipitation method	3	1 - hot oxalate
Avg. particle size, microns	< 1 - 3	2 - 3
Calcination Temperature, °C	650-1600	650-800-950
Uranium oxide inclusion	----	----
MEDIUM AND MATERIAL:		
pH	3 - 9	5 - 9
Electrolytes	CO ₂ , SO ₄ , F ⁻ , Al	----
Gas	O ₂ -He-N ₂	O ₂
Materials	347, Ti, Zr-2, Al	21 steels 23 nonferrous mat'ls.
EFFECTS:		
Caking	Yes	Yes
Thickening	Yes	Yes
Bearing wear	---	Yes
Radiation	---	---
Degradation or aging	---	---

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Fig.1.4.1. Comparison of Attack By Flowing Slurry on Different Shapes and Arrangements of Type 304 Stainless Steel Specimens.

Fig. 1.4.2. Effect of Slurry Flow Velocity on Corrosion Rate of Type 347 Stainless Steel.

Fig. 1.4.3. Effect of Slurry Concentration on Corrosion Rate of Type 347 Stainless Steel.

Table 1.4.2
Estimated Relative Attack Rates of Slurry on Various Materials of Construction

No of Obs'ns.	Metal	Velocity Range, fps	Attack rate, mpy		Other Factors
			Observed Range	Est. Rate at 20 fps and 1000 g Th/Kg H ₂ O	
21	Pt	8-76	0.02-86	2	Temp. 2X, Vel., oxide 3X. Vel; oxide 3X.
11	Au	8-76	0.1-64	2	
8	Zr-2 also Zr	35-76	2 - 67	3	
14	Ti-75A also all Ti based alloys.	8-76	0.3-115	4	Temp. 1.7X
29	347 SS Also other 300-400 series steels within factor 2.	8-76	0.4-106	7	
12	Nickel	18-47	2-26	12	
9	Inconel, Inc-X	15-43	3-49	24	Oxide character and water effects. Oxide character and water effects.
10	Stellite 25	8-76	1-210	14	
11	Stellite 98M2	8-76	3-600	40	
1 + 1	Al ₂ O ₃ ; Sapphire	42; 76	500; 4000	280	
5	ThO ₂ + 0.5% CaO	8-30	Disintegrated		
1	Graphitar (H ₂ O only)	----	Consumed		

The above data have been accumulated while striving to attain suitable long term loop operation. Consequently, many important variables have as yet been explored inadequately, and the above interpretation of the data at present on hand should be regarded as tentative.

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2.1 Toroid Operation -- (G. E. Moore, E. L. Compere, R. M. Warner)

During the past quarter runs have been completed at low slurry circulation velocities. Results of these and earlier runs are included in the tabulation in the following section.

The majority of the available toroid operating time has been devoted to solution runs involving additions of lithium and cesium sulfate to uranyl sulfate solutions. Results of these runs are given in the solution section report, (ORNL-CF-56-1-167).

Replacement variable-speed DC motors for the remaining three toroid rotators have arrived and installation has begun. Two such motors have been in use during the past quarter, and have proven to be reliable and capable of operating satisfactorily at rotational speeds permitting tests in the range from 5 fps up to 40 fps, where other apparatus strength factors appear to limit the maximum working speed.

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2.2 The Effect of Slurry Velocity and Calcination Temperature on Corrosion Rate in Toroids -- (G. E. Moore and E. L. Compere)

Interest in aqueous thorium oxide slurries prepared from oxide calcined at high temperature (1000°C or greater) has stemmed from observations that such slurries at room temperature handle more easily (that is, are more fluid) after circulation than slurries prepared from lower calcined oxide. The attack of some metals of interest by circulating slurries prepared from thorium oxide calcined at temperatures from 650 to 1600°C has now been observed over a range of slurry velocities. These studies have been carried out in type 347 stainless steel toroids.

The thorium oxide used in the experiments was ORNL-produced material identified as Batch D-17. Properties of this oxide are shown in Tables 2.2.1 and 2.2.2. Portions of the oxide were recalcined at temperatures up to 1200°C in a Lindberg furnace for approximately 7 hours while other samples were recalcined at 1400 and 1600°C (2.2b).

At first it appeared that recalcination of the thorium oxide at the higher temperatures caused sintering and particle growth (2.2c). More recent experiments have suggested that the observed increase in the weight per cent of large sized particles and corresponding decrease in weight per cent of small sized particles was due to agglomeration during particle size measurements. This was a result of improper concentration of dispersing electrolyte for material calcined at certain temperatures. After determining the optimum electrolyte concentration for the dispersion of thorium oxide of minimum and maximum calcination temperature, the results shown in Table II were obtained.

These results show that the particle size distributions of the two oxides are very similar and that no gross change in distribution occurred after calcination of this oxide at 1600°C . The changes in distribution in the 0 to 1 and 1 to 3 micron ranges in the oxide calcined at 1600°C may be the result of a small amount of particle growth although the differences in values are almost within the reproducibility of the determination (estimated to be about ± 5 weight per cent).

Aqueous slurries of these unsized oxides were circulated at concentrations of 1000 grams of thorium per kilogram of water in type 347 stainless steel toroids at 250°C and with excess oxygen pressure. Corrosion pin specimens of type 347 stainless steel, titanium 75A and Zircaloy-2 were used to determine the attack rates. The runs were of approximately 200 hours duration at relative velocities of 26 fps and approximately 400 hours at the lower velocities.

The results summarized in Table 2.2.3 show that for any particular velocity up to 26 fps the attack rates of any one of the materials by the slurries was independent of the calcination temperature of the oxide. The table also shows that on a few occasions significantly greater attack rates were obtained than were generally found. These higher values may be due to inhomogeneities in these particular samples of oxide (for example, inclusion of more abrasive material). In any event it seems possible to obtain comparably low attack rates over the range of calcination temperatures and velocities investigated.

Table 2.2.1

Properties of ORNL Batch D-17 Thorium Oxide

Maximum calcination temperature (°C)	650
Thorium (%) [*]	86.1
Iron (ppm)	31
Chromium (ppm)	11
Nickel (ppm)	9
Sulfate (ppm)	120
Carbon (ppm)	1400
Aluminum (ppm)	10

* After drying at 110 to 150°C. Theoretical, 87.9%.

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Table 2.2.2

Particle Size Distribution of ORNL Batch D-17
Thorium Oxide as Estimated by Gravitational
Sedimentation (2.2a)

Maximum Calcination Temperature °C	650	1600
$\text{Na}_4\text{P}_2\text{O}_7$ for Optimum Dispersion, (M)	0.005	0.001
Average Particle Diameter, microns	2.2	2.3
Particle Size Distribution (Wt.%)		
over 10 microns	15	9
3 - 10 microns	26	27
1 - 3 microns	36	49
below 1 micron	23	15

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Table 2.2.3

Attack Rates of Type 347 Stainless Steel, Titanium 75A and Zircaloy-2
by Circulating Thorium Oxide Slurries

Thorium oxide: ORNL Batch D-17

Slurry concentration: 1000 g of Th per kg of H₂O

Temperature, °C: approximately 250

Oxygen pressure, psi: approximately 100 (250°C)

Fraction of toroid filled by slurry at temp.: 0.5

Max. Calcn. Temp. °C	Relative Velocity fps	Type 347 SS			Titanium 75A			Zircaloy-2		
		No.	mpy range	mpy avg.	No.	mpy range	mpy avg.	No.	mpy range	mpy avg.
650	5	2	0.2-0.3	0.2	1	---	0.2	0	---	---
800		2	0.4-0.5	0.4	1	---	0.7	1	---	+
1200		2	0.2-0.3	0.2	1	---	0.3	1	---	+
650	15	2	2.4-2.8	2.6	1	---	0.9	0	---	---
800		2	2.2-2.3	2.2	1	---	2.8	1	---	1.9
1200		2	1.5-1.8	1.6	1	---	2.2	1	---	0.1
1600		2	1.9-2.2	2.0	1	---	0.8	1	---	0.5
650	26	33	0.5-12.	3.4	14	+ -5.5	2.0	14	+ -2.4	1.3
800		4*	6.0-8.0	5.6	4	7.4-9.9	8.3	4	0.2-1.9	1.4
		1*	-----	20.						
1000		4*	29.-37.	33.	2	10.-12.	11.	2	1.6-2.0	1.8
		5*	2.7-3.8	3.4	1	---	1.1	1	---	0.6
1200		5	3.1-5.4	4.3	3	2.0-5.1	3.1	3	0.4-1.1	0.8
1400		2	4.1-5.4	4.8	1	---	3.2	1	---	1.2
1600		2	1.8-2.1	2.0	1	---	2.5	1	---	1.4
All	5	6	0.2-0.5	0.3	3	0.2-0.7	0.4	2	---	+
	15	8	1.5-2.8	2.1	4	0.8-2.9	1.7	3	0.1-1.9	0.8
	26	51*	0.5-12.	3.8	26	0.3-13.	3.8	26	0.1-2.4	1.3
		5*	20.-37.	31.						

* Two groups of values obtained, as shown.

The effect of slurry velocity on the attack rates of the materials is shown at the bottom of Table 2.2.3 where the values for all calcination temperatures of thorium oxide are grouped together. Attack rates for both type 347 stainless steel and titanium 75A appear best to show an approximately 1.5 power dependence on the velocity while the data for Zircaloy-2 are too few for any such conclusion.

It should be pointed out again that the attack rates determined in toroids are relative within themselves and the relation of their magnitude to the rates determined under other conditions (for example, in loops) is unknown. As a first approximation the rates obtained in toroids may be lower than rates in loops under similar conditions by a factor of two since circulation in toroids consists of approximately equal volumes of vapor and solution each revolution (slug flow); therefore, the corrosion pins and toroid walls are immersed in the solution only one-half of the total time of the run. On the other hand, other factors (for example, impingement of the liquid on the specimens, turbulence, etc.) are not so easily evaluated so that no such simple relationship between data obtained in toroids and loops or other equipment necessarily exists.

Extreme variation in character of the circulated slurries was observed in the experiments described above. Slurries of 1000 grams of thorium per kilogram of water concentration prepared from oxalate precipitated 650°C calcined oxide were very thick at room temperature after circulation at 15 and 26 fps whereas slurries of thorium oxide calcined at approximately 1000 to 1200°C and higher were much more fluid at room temperature after circulation.

REFERENCES

- 2.2a G. W. Leddicotte and H. H. Miller, Analytical Chemistry Semiannual Progress Report, October 20, 1954, ORNL-1788, p. 21.
- 2.2b These high temperature calcinations were carried out by Dr. C. E. Curtis of the Ceramics Section of the ORNL Metallurgy Division.
- 2.2c ORNL Status and Progress Report, September, 1955, ORNL-1980, p. 12.

3.1 Distinguishing Inconel from Stainless Steel -- (S. H. Wheeler and G. E. Moore).

During operations connected with the In-Pile Loop program it was discovered that at least one of a large group of corrosion coupons had been fabricated from Inconel rather than type 347 stainless steel as ordered. Consequently, the identification and elimination of Inconel from this group of type 347 stainless steel in-pile corrosion specimens was undertaken.

The hydrostatic weighing method (suspended sinker) for the determination of the density of a solid (3.1a) was used and proved to be a satisfactory non-destructive test for differentiating Inconel (density 8.51) from stainless steel (density 7.95). Certain experimental difficulties were at first experienced due to the small size of the coupons but with reasonable care the results summarized in Table 3.1-1 were obtained.

Spectrographic analyses showed that all the coupons whose densities were about 8.5 were indeed Inconel while several coupons of density about 8.0 were shown similarly to be type 347 stainless steel.

Thus, of 359 coupons examined, 15, or slightly over 4%, were found to be Inconel. All the Inconel specimens were characterized by air weights of greater than 1.0 or 2.0 grams (depending upon the size of the coupon) in contrast to the stainless steel weights of less than 1.0 or 2.0 grams respectively. There was no correlation between the material and the code number stamped on the coupon. The estimated time per density determination was about seven minutes.

Table 3.1.1

Results of Density Determinations by Hydrostatic Weighing
Method

<u>Coupon Size, in.</u>	<u>Number</u>	<u>Weight Range (Air), grams</u>	<u>Density Range</u>
1/2x1/2x1/16	310	1.87 to 1.94	7.90 to 7.99
1/2x1/2x1/16	13	2.01 to 2.06	8.42 to 8.48
1/4x1/2x1/16	34	0.94 to 0.97	7.91 to 8.08
1/4x1/2x1/16	2	1.01 to 1.02	8.45 to 8.50

Literature values: Inconel 8.51

18-8 Stainless Steel 7.95

REFERENCES

- 3.1a Physical Methods of Organic Chemistry, A. Weissberger, Editor, Vol. I, Part I, Interscience, N. Y. (1949), p. 293.

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