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RADIATION STABILITY OF AQUEOUS THORIA AND THORIA-URANIA SLURRIES

J. P. McBride

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

RADIATION STABILITY OF AQUEOUS THORIA AND THORIA-URANIA SLURRIES

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ABSTRACT

The results of 36 irradiation experiments in the LITR ($2.5-3.0 \times 10^{13}$ n/cm^2·sec) with various thoria and thoria-urania slurries at thoria blanket temperatures indicate that at relatively low irradiation exposures there is no gross deterioration of slurry handling characteristics. Particle damage occurred in most cases, but resistance to damage appeared to increase with increasing oxide firing temperatures. With the exception of cesium, strontium, and iodine, fission products were mainly associated with the slurry solids. Of the corrosion products (iron, chromium, nickel), only nickel appeared to a significant extent in the slurry supernatant.

During the course of the work a dash-pot-stirred autoclave was developed which permitted fluids and slurries to be stirred while under irradiation. Autoclave operation could be controlled in such a way that the relative viscosity of the autoclave contents could be measured as a function of temperature and while the material was being irradiated. Ability to stir was not impaired by irradiation even at fission power levels equivalent to the average power level of a thoria slurry in a breeder reactor blanket.

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1.0 INTRODUCTION

This report summarizes data obtained in irradiation experiments with aqueous thoria and thoria-urania slurries carried out in the LITR at temperatures of 250-300°C and a thermal neutron flux of 2.5-3.0 x 10^{13} n/cm^2·sec (1-16). The primary objective of the experiments was to determine whether or not there was a gross change in slurry behavior under reactor irradiation. The choice of slurry to be investigated was determined by the particular reactor concept envisaged and the then current opinion as to what was the best slurry oxide. All irradiations were carried out in an electromagnetically stirred stainless steel autoclave developed for the experiments and improved during the course of the irradiations. While information was obtained in postirradiation examinations on particle damage, fission product distribution, and corrosion product pickup, the principal information obtained was whether or not the slurry could be readily stirred while it was being irradiated.

Slurries of pure thorium oxide, thorium-uranium oxides containing 0.4, 4, and 8% natural uranium oxide, and thorium-uranium oxides containing 0.4% U-235 oxide were irradiated. Both light and heavy water were used. Concentrations varied from 250 to 1000 g Th/kg H_2O (D_2O).

2.0 EXPERIMENTAL

2.1 Slurry Preparation

The thorium oxides used in the experiments were prepared by thermal decomposition of thorium oxalate that had been precipitated from thorium nitrate solution (17-19). The uranium-bearing oxides were prepared in three ways: by wet-autoclaving mixtures of low-fired ThO_2 and UO_3 at 300°C and firing the recovered solids (20); by adsorbing uranium from a carbonate solution on a low-fired oxide and firing (21); and by coprecipitating thorium and uranous oxalates and firing to the oxide (20). The irradiation autoclaves were loaded with about 4 ml of slurry at room temperature, which expanded to approximately half fill the autoclave at the temperature of the irradiation. In early experiments H_2O was used and in the later experiments, D_2O. When mixed oxides containing U-235 were irradiated, either molybdenum oxide or palladium was added to catalyze the recombination of radiolytic hydrogen and oxygen (21-23). In some experiments an oxygen overpressure of 200 to 300 psi was added at room temperature and in two experiments a deuterium overpressure was used.

2.2 Autoclave Operation

The experiments were carried out in small cylindrical stainless steel autoclaves (Fig. 1). Thermocouples welded into the bottom closure and a 20-mil-i.d. steel

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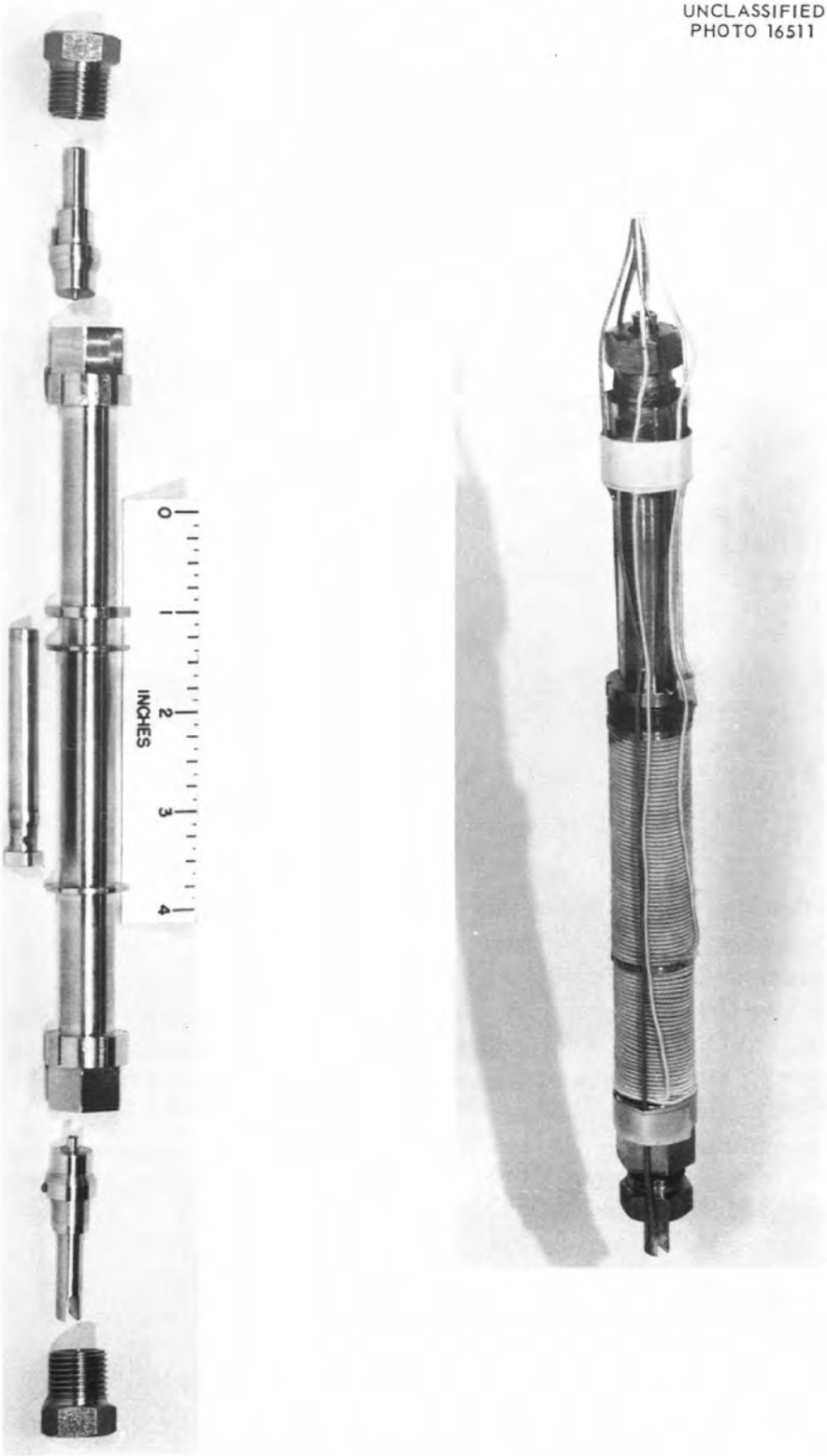

Fig. 1. Parts and assembly of in-pile autoclave.

capillary in the top permitted continuous measurement of temperature and pressure. Stirring was by a dash-pot stirrer of Armco iron clad in stainless steel, with a stainless steel stirring head. Continuous stirring of more than 2000 hr was demonstrated. The capacity of the autoclave with stirrer was approximately 14 ml.

The stirrer was made to reciprocate at 3 to 4 cycles/sec by alternately energizing two solenoid coils of double-glass-insulated aluminum wire wrapped around the autoclave body. The timing unit was a multivibrator circuit whose frequency of oscillation and cycle time division could be controlled by varying resistances in the circuit. The timer unit, in turn, controlled the grids of two pairs of thyratrons, which furnished power to the solenoids. Stirrer operation was monitored by a tickler coil connected to an oscilloscope. In addition, by means of a microphone connected to the irradiation facility, a metallic sound was heard when the stirrer struck the bottom of the autoclave. Dulling of the sound indicated failure of the stirrer to suspend the slurry.

The radiation facility consisted of a double-walled aluminum tube ~7/8 in. i.d., which extended from the top of the LITR through approximately 20 ft of water into the reactor core. The autoclave was lowered into this tube on a bundle of wires containing the electrical leads, thermocouples, and pressure capillary. During reactor shutdown the autoclaves were maintained at ~280°C by the heat generated by the stirring coils. Heat was removed during reactor operation by air which flowed down the tube, over the autoclave, and back through the annulus provided by the double-walled tube. Radiation times were limited by reactor operating schedules, which required removal of the experiment during refueling operations.

2.3 Slurry Viscosity Measurements

The timing device used with the irradiation autoclave made possible the measurement of relative slurry "viscosity" both in-pile and out-of-pile. It was found that the time the stirrer required to reach its maximum height for a fixed solenoid current was dependent on the viscosity of the fluid being stirred. The "rise time" was determined by adjusting the frequency and load division so that the upper solenoid was de-energized the instant the oscilloscope indicated the stirrer had reached the top of its travel (Fig. 2). The rise time in seconds was then obtained by dividing the load division by the frequency. Calibration curves made with silicon oil were linear (Fig. 3). With these curves as a basis, it was demonstrated that slurries with viscosities of about 20 centistokes could not be stirred in the irradiation autoclave. Hence, ability to stir in-pile indicated the viscosity of the irradiated slurry to be less than this value.

Figure 4 shows the typical variation of slurry "viscosity" measured by this technique as a function of preparation method and slurry concentration. While the absolute values are not important and are not useful for engineering calculations, the measurement did permit a determination of relative ease of stirring in

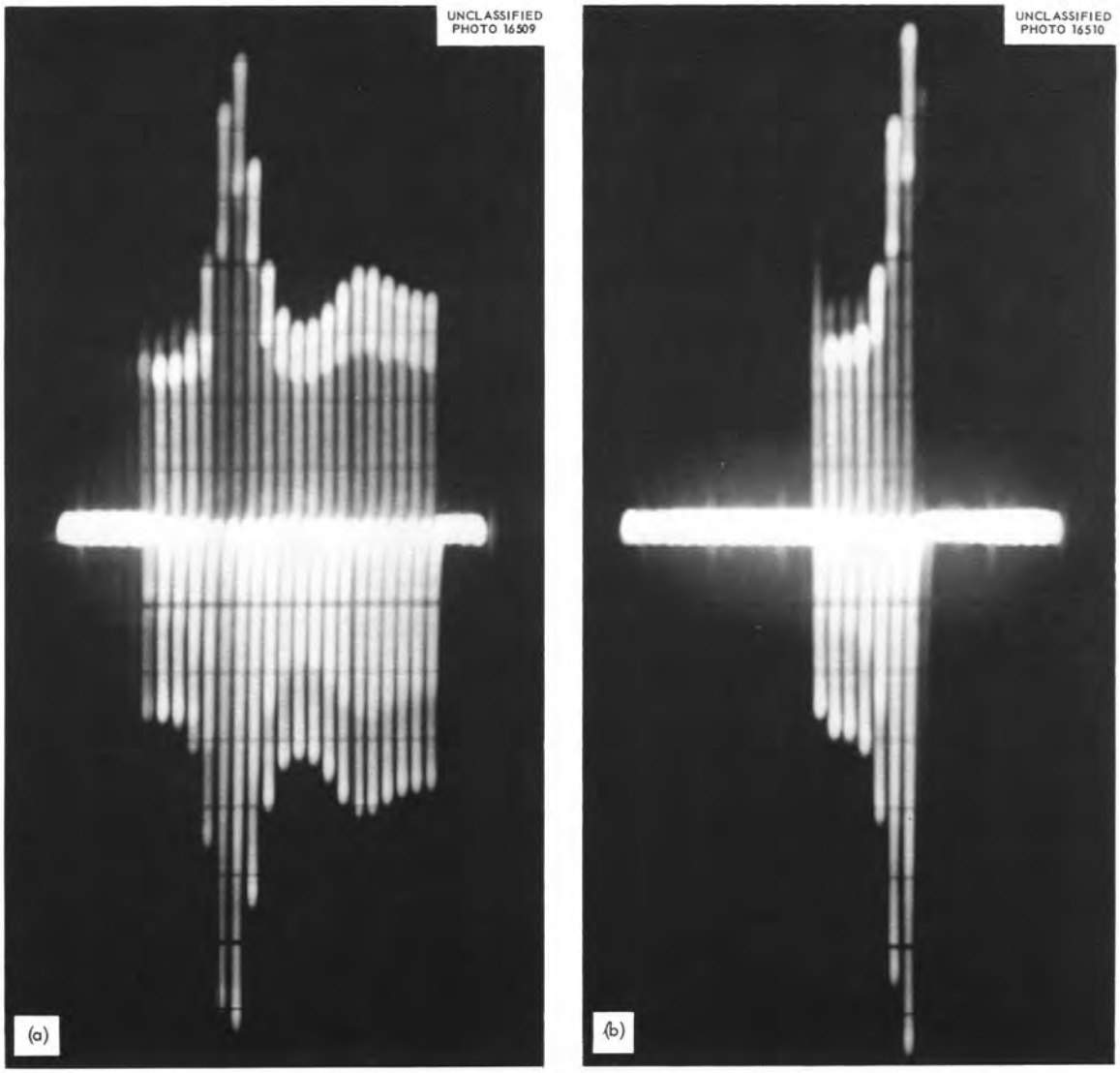

Fig. 2. (a) Oscilloscope trace of stirrer operation and (b) trace adjusted for viscosity measurements.

and out of pile. No significant change in ability to stir was observed as the result of a slurry being irradiated even at power levels (7 watts/g ThO_2) equivalent to the average power level of a blanket slurry (i.e., expts 28 and 29 where a viscosity of about 13 centistokes was observed both in and out-of-pile for 750 g Th/kg H_2O slurries).

3.0 RESULTS AND DISCUSSION

Table 1 summarizes the conditions of the various irradiations and the details of their recovery. References to the various HRP quarterly progress reports in which

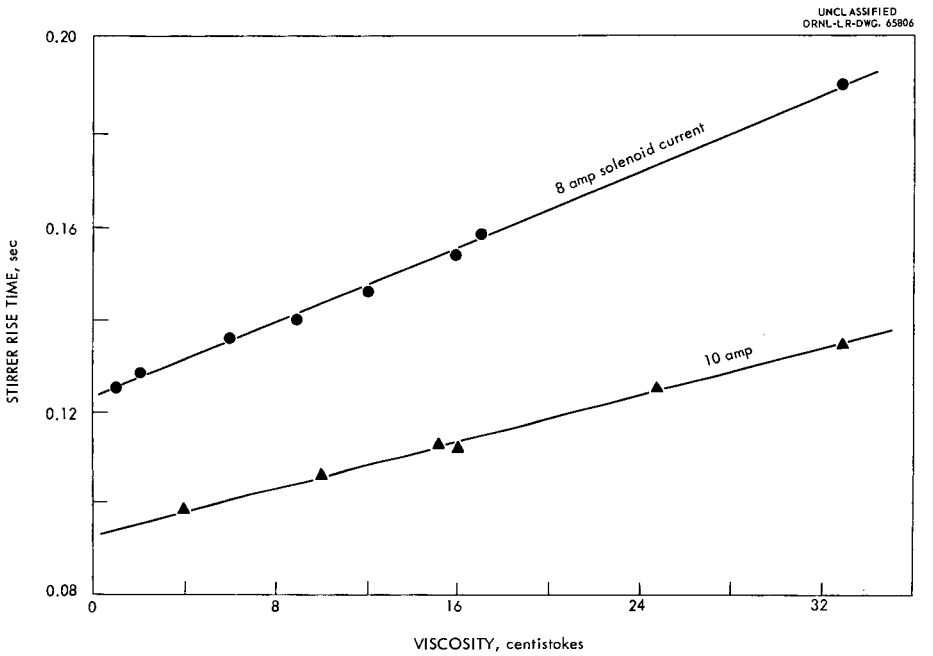

Fig. 3. Viscosity calibration curves for in-pile autoclave.

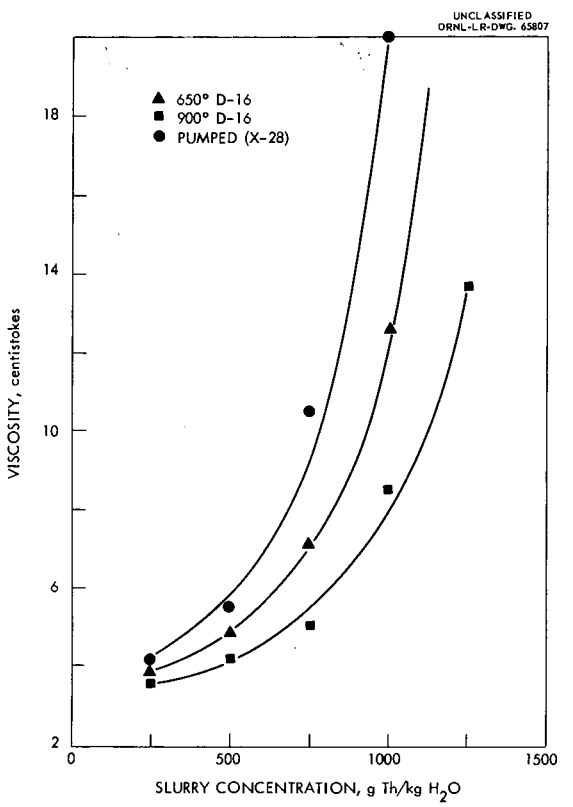

Fig. 4. Viscosities of ThO_2 slurries measured in in-pile autoclave.

Table 1. Summary of LITR Slurry Irradiations

2.5-3.0 x 10^{13} n/cm^2·sec flux; 250-300°C temperature

Expt	Slurry	Catalyst, μg/g Th	Medium	Slurry Conc, g Th/kg H_2O	Initial Autoclave Gas Phase, psi at R.T.	Irradiation Time, hr	Stirring Time Under Irradiation, hr	Reason for Termination	Cooling Time, months	Method of Removal	Solids Recovered, %[b]	Ref.
3	D-16 ThO_2, 650°C fired oxalate	None	H_2O	500	Air	258	120	Eq. failure	0.4	Poured	(67)	1,2
5	ThO_2, 900°C-fired oxalate	None	H_2O	500	Air	175	12	Not stirring	1	Poured	(79)	1,2
8	D-16 ThO_2, 650°C-fired oxalate	None	H_2O	500	Air	165	165	Scheduled	3	Rinsed	-	2,3
9	Pumped D-30 ThO_2, 950°C-fired oxide mixture	None	H_2O	500	Air	200	200	Scheduled	3	Poured	(73)	2,3
11	Th-0.5% Nat U oxide, 900°C-fired autoclaved mixture	1150 PdO	H_2O	1000	Air	151	67	Eq. failure	1.7	Poured	(64)	3,4
12	Same	1150 PdO	H_2O	1000	Air	68	68	Eq. failure	1.3	Poured	(63)	3,4
13	Same	1150 PdO	H_2O	1000	Air	172	172	Scheduled	0.6	Poured	(59)	3,4
17	Same	1150 PdO	H_2O	1000	300 O_2	92	9	Not stirring[a]	12	Rinsed	53	4,7,16
18	Same	1150 PdO	H_2O	1000	Air	20	6	Not stirring[a]	11	Poured	21	4,7,16
19	Th-0.4% U-235 oxide, 900°C fired coprecipitated oxalates	1150 PdO	H_2O	1000	300 O_2	210	65	Not stirring[a]	10	Poured	6	4,7,16
20	Same	1150 PdO	H_2O	500	250 O_2	85	62	Eq. failure	-	-	-	5
21	Same	1150 PdO	H_2O	750	Air	168	168	Scheduled	10	Poured	52	5,7,16
24	Same	30,000 MoO_3	H_2O	750	Air	116	92	Not stirring	-	-	-	5
25	Same	30,000 MoO_3	H_2O	750	250 O_2	192	172	Scheduled	7	Rinsed	20	5,7,16
26	TO-10-900-24 ThO_2, 900°C-fired oxalate	None	H_2O	750	Air	198	198	Scheduled	6	Rinsed	33[c]	6,7,16
27	200 A-6 ThO_2, pumped, 800°C-fired ThO_2 (15-μ spheres)	None	H_2O	750	Air	344	344	Scheduled	5.5	Rinsed	>21	6,7,16
28	Th-0.4% U-235 oxide, 800°C-fired coprecipitated oxalates	30,000 MoO_3	H_2O	750	250 O_2	136	44	Eq. failure	4.5	Poured	4	6,7,16
29	Same	30,000 MoO_3	H_2O	750	250 O_2	310	290	Scheduled	4	Poured	12[c]	6,7,16
30	Same	30,000 MoO_3	0.02 m H_2SO_4	750	300 O_2	247	118	Scheduled	1	Poured	11	8,9
31	Same	30,000 MoO_3	0.02 m H_2SO_4	750	300 O_2	343	168	Not stirring	1	Poured	10	9
33	Pumped ThO_2, 1600°C-fired oxalate	None	H_2O	500	Air	336	320	Scheduled	0.5	Rinsed	>29	9
34	ThO_2, 1000°C fired oxalate	30,000 MoO_3	H_2O	750	Air	57	0	Eq. failure	0.7	Poured	13	10
37	Pumped and dried ThO_2, 1600°C-fired oxalate	None	D_2O	750	300 O_2	212	212	Eq. failure	1	Poured	29	10
38	Th-0.4% Nat U oxide, 1000°C-fired coprecipitated oxalates	None	D_2O	750	300 O_2	332	62	Eq. failure	3	Poured	9	10,11
40	Th-0.4% U-235 oxide, 1300°C-fired coprecipitated oxalates	10,000 MoO_3	D_2O	500	Air	322	322	Scheduled	2	Poured	55	11
44	Th-4% Nat U oxide, 1000°C-fired coprecipitated oxalates	None	D_2O	750	Air	49	49	Leaked	3	Dry	76	11,12
46	Same	None	D_2O	500	Air	361	361	Scheduled	2	Rinsed	97	11,12
47	Same	None	D_2O	250	Air	354	354	Scheduled	1	Rinsed	65	11,12
48	Same	None	D_2O	250	Air	310	310	Scheduled	1	Poured	8	12,13
49	Same	None	D_2O	250	200 D_2	350	350	Scheduled	1.5	Rinsed	d	12,13
50	Th-3% Nat U + 0.5% U-235 oxide, Westinghouse loop drain 2-IPF-IV (23)	120 Pd	D_2O	500	250 O_2	127	0	Not stirring	1	Poured	38	13,14
51	Same	120 Pd	D_2O	500	250 D_2	153	120	Leaked	0.4	Poured	56	13,14
52	ThO_2+0.5% U-235 oxide, 650°C-fired oxalate	145 Pd	D_2O	500	250 O_2	286	23	Not stirring	2	Poured	9	13,14
53	Same	145 Pd	D_2O	250	250 O_2	242	242	Eq. failure	2	Rinsed	74	14,15
54	Th-8% Nat U oxide, 1050°C-fired ThO_2+adsorbed U carbonate	None	D_2O	250	Air	335	335	Scheduled	2	Poured	74	14,15
55	Same	None	D_2O	500	Air	370	370	Scheduled	2	Dry	28	15

[a] Out-of-pile control experiments also stopped stirring after a few hours stirring. [b] Values in parentheses estimated from volume of recovered solids; other values based on Th determinations. [c] Autoclave leached with hot HNO_3-HF; only 1 mg Th leached from each autoclave. [d] Sample spilled.

the experiments were first reported are given in the final column of the table. Data on particle damage, fission product distribution, and corrosion product pick-up appear in Tables 2 to 5.

Reference to Table 1 will show that little difficulty was experienced in stirring the slurries under irradiation for periods longer than 300 hr and at power levels up to 7 watts/g oxide. Where stoppages occurred, they could in general be attributed to equipment failure or to the limitations of the dash-pot-stirred autoclave. As indicated above, ability to stir at all set an upper limit to possible irradiation-induced viscosity change.

Table 2. Particle Size Effects in Irradiated Thoria Slurries

Flux: 2.5-3.0 x 10^{13} n/cm^2·sec
Temperature: 250-300°C

Expt No.	Oxide	Exposure, fissions/g x 10^{-14}	Average Particle Size, μ		% <0.7 μ		Fractional Increase in % <0.7 μ, Irradiated/Unirradiated
			Unirradiated Solids[a]	Irradiated Solids	Unirradiated Solids[a]	Irradiated Solids	
8	650°C-fired ThO_2	0.5	2.0	1.7	11	31	2.9
3		2.0	2.0	<0.7	11	64	6.1
27	800°C-fired ThO_2	4.0	(2.0)	3.4	(15)	24	1.6
5	900°C-fired ThO_2	0.5	(1.1)	0.9	(32)	37	1.2
26		0.8	0.8	0.8	40	47	1.2
9	950°C-fired ThO_2	0.8	0.8	0.6	43	53	1.3
33	1600°C-fired ThO_2	4.0	(1.3)	1.3	(16)	16	1.0

[a]Values in parentheses obtained on solids from a control experiment, others from original solids.

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Expt No.	Oxide	Exposure, fissions/g x 10^{-14}	Average Particle Size, μ		% <0.7 μ		Fractional Increase in % <0.7 μ, Irradiated/Unirradiated
			Unirradiated Solids[a]	Irradiated Solids	Unirradiated Solids[a]	Irradiated Solids	
8	650°C-fired ThO_2	0.5	2.0	1.7	11	31	2.9
3		2.0	2.0	<0.7	11	64	6.1
27	800°C-fired ThO_2	4.0	(2.0)	3.4	(15)	24	1.6
5	900°C-fired ThO_2	0.5	(1.1)	0.9	(32)	37	1.2
26		0.8	0.8	0.8	40	47	1.2
9	950°C-fired ThO_2	0.8	0.8	0.6	43	53	1.3
33	1600°C-fired ThO_2	4.0	(1.3)	1.3	(16)	16	1.0

[a]Values in parentheses obtained on solids from a control experiment, others from original solids.

While most irradiated slurries were readily poured from the autoclave, material recoveries based on thorium determinations were poor. The fact that only small quantities of solid were involved (1 to 4 g) and that remote handling of the irradiated experiments was particularly difficult may have contributed to this result. There was evidence too that the thorium analyses of the hot materials were not completely reliable, since in expts 26 and 29 where thorium recovery was poor (33 and 12%, respectively), washing out the autoclaves with hot HNO_3-HF resulted

Table 3. Particle Size Effects in Irradiated Thoria-Urania Slurries

Flux: 2.5-3.0 x 10^{13} n/cm^2·sec
Temperature: 250-300°C

Expt No.	Mixed Oxide	Exposure, fissions/g x 10^{-16}	Average Particle Size, μ: Unirradiated Solids	Average Particle Size, μ: Irradiated Solids	% <0.7 μ: Unirradiated Solids	% <0.7 μ: Irradiated Solids	Fractional Increase in % <0.7 μ, Irradiated / Unirradiated
38	1000°C-fired Th-0.4% nat U oxide	0.14	(0.8)	0.6	(44)	60	1.4
44		0.15	1.1	0.8	10	40	4.0
48		0.9	1.1	0.4	9	73	8.1
49		1.1	1.1	3.0	9	34	3.8
47		1.1	1.1	1.1	10	32	3.2
46		1.1	1.1	1.0	10	34	3.4
54	1050°C-fired Th-8% nat U oxide	2.0	1.3	2.0	4	18	4.5
55		2.2	1.3	0.6	4	56	14
17	900°C-fired Th-0.5% U-235 oxide	4.9	2.0	1.0	11	34	3.1
21	900°C-fired Th-0.4% U-235 oxide	7.2	(0.9)	1.9	(17)	31	1.8
40	1300°C-fired Th-0.4% U-235 oxide	13.8	(1.7)	1.5	(32)	23	<1.0

[a] Values in parentheses obtained on solids from a control experiment, others from original solids.

in only negligible additional thorium recovery. In addition, in seven out of nine experiments in which low material recoveries were obtained (≤ 13%) stirring stopped for various reasons and the slurries were irradiated in a settled condition, with the possibility that resuspension was rendered more difficult. The long cooling times before the irradiated slurries were recovered may also be a factor in the poor material recoveries.

The supernatants of most slurries contained only a fraction of a percent of the uranium and thorium in the system. In two cases, LITR-53 and 54, the supernatants

Table 4. Fission Product Distribution in Irradiated Slurries

Expt No.	Slurry Oxide	Oxide Firing Temp, °C	% of Fission Product Activity in Supernatant, c/m·ml supernatant / (c/m·ml supernatant + c/m·g oxide)						
			Cs	Sr	I	Zr	Nb	Total R.E.	Pa
37	Pumped and dried ThO_2	1600	2	8	-	0.2	2	0.1	0.02
38	Th-0.4% nat U oxide	1000	11	4	0.5	0.03	0.3	0.5	0.01
19	Th-0.4% U-235 oxide	900	5	0.6	-	0.1[a]	0.004	0.3	0.2
21	Th-0.4% U-235 oxide	900	4.8	0.1	-	0.4[a]	0.02	0.1	0.4
29	Th-0.4% U-235 oxide	800	11	16	-	<0.01[a]	-	0.3	0.004
34	Th-0.5% U-235 oxide	1000	66	3	0.2	2	5	0.3	<0.001
40	Th-0.4% U-235 oxide	1300	86	0.04	-	0.01	0.02	0.02	0.02
50	Th-3% nat U + 0.5% U-235 oxide[a]	650	4	11	<0.01	0.2	0.3	0.8	0.03
51	Th-3% nat U + 0.5% U-235 oxide[a]	650	21	7	0.4	4	11	5	5
	0.02 m $Th(SO_4)_2$ Added Before Irradiation								
30	Th-0.4% U-235 oxide	800	21	9	0.3	0.07	0.09	1	-
31	Th-0.4% U-235 oxide	800	11	3	<0.01	<0.01	<0.01	0.3	-

[a] Zr-Nb activity.

Table 5. Corrosion Products in Irradiated and Control Slurries

Expt No.	Slurry Material	Slurry Conc, g Th/kg H_2O	Control Experiment: Total Stirring Time, hr	Control Experiment: Fe, g/kg H_2O	Control Experiment: Ni, g/kg H_2O	Control Experiment: Cr, g/kg H_2O	Irradiation Experiment: Total Stirring Time, hr	Irradiation Experiment: Fe, g/kg H_2O	Irradiation Experiment: Ni: Super-natant g/kg H_2O	Irradiation Experiment: Ni: Solids, g/kg H_2O	Irradiation Experiment: Cr, g/kg H_2O
33	Pumped 1600°C-fired ThO_2	500	320	6.8	1.3	1.3	330	37	0.56	7.8	0[b]
37	Pumped 1600°C-fired ThO_2	750	321	37	6.0	2.3	244	18	0.02	2.4	2.0
38	1000°C-fired Th-0.4% nat U oxide	750	84	1.4	0.25	0.17	62	16	0.52	7.4	0.13
47	1000°C-fired Th-4% nat U oxide	250	350	22	19	2.7	450	67	0.01	7.8	2.4
40	1300°C-fired Th-0.4% U-235 oxide	500	240	16	2.6	1.5	355	9.3	0	3.6	0[b]
					0.02 m $Th(SO_4)_2$ Added						
30	900°C Th-0.4% U-235 oxide	750	226	7.1	0.96[a]	0	265	90	0.35	12	4.5
31	900°C Th-0.4% U-235 oxide	750	-	-	-	-	168	33	0.76	5.9	3.5

[a] 0.15 g Ni/kg H_2O found in supernatant.

[b] Analyzed for but none found.

failed to clear even on centrifugation and contained 19 and 23% of the thorium, respectively, and 76 and 2.5% of the uranium.

The stirrer degraded particles larger than 1 to 2 microns, making the postirradiation particle size data difficult to interpret. Since, however, in some of the cases control experiments were run and since mechanical degradation did not proceed much below a micron, qualitative interpretation of the data appeared permissible. Some particle damage was indicated in most experiments, resistance to damage increased with increasing oxide firing temperature, and no relation was observed between irradiation dose and apparent damage.

Atmosphere seemed not to have a measurable effect (except possibly on the subsequent particle size analyses; see below), but, since the stirrer introduced considerable corrosion products, it is entirely possible that most irradiations were actually carried out with a reducing atmosphere. Several attempts to sample the residual gas at the completion of an irradiation were unsuccessful. In only one experiment, LITR-52, was a significant quantity of radiolytic gas observed. In this experiment about 300 psi of radiolytic gas was indicated at the temperature of the experiment.

The bulk of the fission product activity and the corrosion products were found associated with the irradiated solids. Corrosion product pickup appeared enhanced by irradiation only in the presence of sulfate.

3.1 Particle Damage

The size distribution curves obtained on the various unirradiated and irradiated slurries by a neutron-activation-sedimentation method (24) appear in the appendix. From these the information in Tables 2 and 3 were taken. Only those experiments in which material recovery was good and the particle size analyses were reasonably self consistent were used in the analysis of particle size effects. While the tables list the average particle sizes of the unirradiated and irradiated materials, probably the most important information is the increase in the size fraction less than 0.7 μ since degradation in the absence of irradiation probably does not proceed much below this point (see particle distribution curves from LITR-27 in the appendix).

The data of Table 2 indicate that thorium oxide fired at 650-800°C is less resistant to particle damage by reactor irradiation than thorium oxide fired at 900-1600°C. Little particle damage was observed in two experiments with 1600°C fired ThO_2 as a result of the 200 and 300 hr irradiation to which they were subjected.

The mixed oxides appeared to suffer more damage than the pure oxides (Table 3), but were subjected to considerably higher exposure. No correlation

was observed between the dose received and the amount of damage. Hence the observed damage may reflect an effect of preparation method rather than irradiation. The exposures given all the slurries was much less than they would receive in a blanket, and therefore it is not possible to predict whether the materials that show the least damage (i.e., 1600°C-fired ThO_2; 1300°C-fired Th-0.4% U-235 oxide) are in fact suitable blanket materials.

Besides the increase in the fine fraction less than 0.7 μ, radiation damage was indicated by the marked change in the size-distribution curves of nearly all the irradiated samples when compared with those of the original materials (see size distribution curves in the appendix). In general, where the size-distribution curve was much steeper and agglomeration had apparently occurred, it was believed that particle damage had taken place. The apparent discrepancies in Tables 2 and 3 in which a large increase in the fraction of material less than 0.7 μ is accompanied by little or no change, and sometimes even an increase, in average size result from such agglomeration. There is some evidence that treating a slurry in a reducing atmosphere will affect the results of the subsequent particle-size analysis such that particle growth will appear to have occurred. This may account for some of the agglomeration seen in the irradiated materials, many of which were irradiated under reducing conditions.

3.2 Fission Product Distribution

Fission product distribution was determined for most of the irradiated slurries. In the preparation of Table 4, however, only the data obtained from slurries that were poured from the irradiation autoclave were considered. Where solids were removed by rinsing with water or had gone to dryness before recovery, the distribution data were not believed to reliably indicate the distribution obtaining under irradiation.

Only cesium, strontium, and iodine were found in appreciable amounts in the supernatants (Table 4). With a few exceptions, nearly all the zirconium, niobium, rare earths, and protactinium were associated with the solid phase. The addition of 0.02 m sulfate did not appear to significantly affect the distributions.

3.3 Corrosion Products

The stirrer introduced a considerable amount of corrosion products, tending to obscure somewhat any effect of radiation on the corrosion. Table 5 shows some typical data obtained in some irradiation and control experiments. Only in the presence of sulfate did there appear to be a significant enhancement of corrosion by irradiation. Nearly all the iron and aluminum were found associated with the slurry solids. Only the nickel was found in the supernatant in significant amounts.

4.0 REFERENCES

1. A. R. Jones et al., "HRP Quar. Prog. Rep. for Period Ending July 31, 1955," ORNL-1943, p. 175.

2. Ibid., for Oct. 31, 1955, ORNL-2004, p. 167.

3. Ibid., for Jan. 31, 1956, ORNL-2057, p. 109.

4. Ibid., for April 30, 1956, ORNL-2096, p. 107.

5. N. A. Krohn et al., "HRP Quar. Prog. Rep. for Period Ending July 31, 1956," ORNL-2148, p. 123.

6. D. E. Ferguson et al., "HRP Quar. Prog. Rep. for Period Ending Oct. 31, 1956," ORNL-2222, p. 145.

7. Ibid., for Jan. 31, 1957, ORNL-2272, p. 144.

8. J. P. McBride et al., "HRP Quar. Prog. Rep. for Period Ending July 31, 1957," ORNL-2379, p. 145.

9. Ibid., for Oct. 31, 1957, ORNL-2432, p. 153.

10. Ibid., for Jan. 31, 1958, ORNL-2561, p. 279.

11. Ibid., for April 30 and July 31, 1958, ORNL-2561, p. 279.

12. Ibid., for Oct. 31, 1958, ORNL-2654, p. 202.

13. Ibid., for Jan. 31, 1959, ORNL-2696, p. 177.

14. Ibid., for April 30, 1959, ORNL-2743, p. 204.

15. J. P. McBride and N. A. Krohn,"HRP Quar. Prog. Rep. for Period Ending May 1-Oct. 31, 1959,"ORNL-2879, p. 168.

16. Ibid., "Chemical Technology Division Monthly Progress Report, March 1957," ORNL-2307, p. 75.

17. V. D. Allred, S. R. Buxton and J. P. McBride, J. Phys. Chem., 61:117 (1957); (also in ORNL-1943, p. 181).

18. W. H. Carr, "Pilot Plant Preparation of Thorium Oxide," ORNL-CF-56-1-50 (1956) (also in ORNL-1943, p. 198).

19. R. L. Pearson et al., "Preparation of ThO_2 for Homogeneous Reactor Blanket Use," ORNL-2509 (May 1958).

20. A. R. Jones et al., op. cit., ORNL-2057, p. 112.

21. J. P. McBride et al., op. cit., ORNL-2654, p. 211.

22. L. E. Morse, "Catalyst for Recombination of Radiolytic Gases over Thorium Oxide Slurries," ORNL-CF-57-1-117 (Jan. 1957).

23. D. E. Byrnes and W. O. Fletcher, "PAR Quar. Prog. Rep. May 31, 1958," WCAP-900, p. 51.

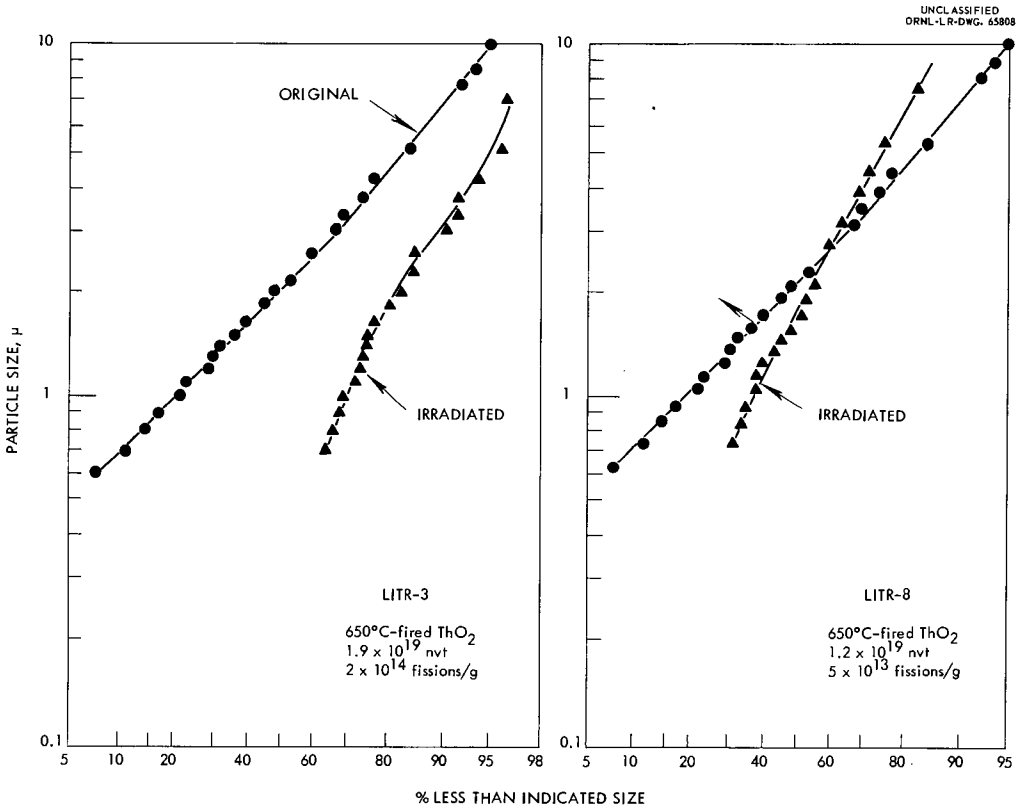
24. G. W. Leddicotte and H. H. Miller,"Anal. Chem. Semiannual Prog. Rep., Oct. 20, 1954,"ORNL-1788, p. 21.

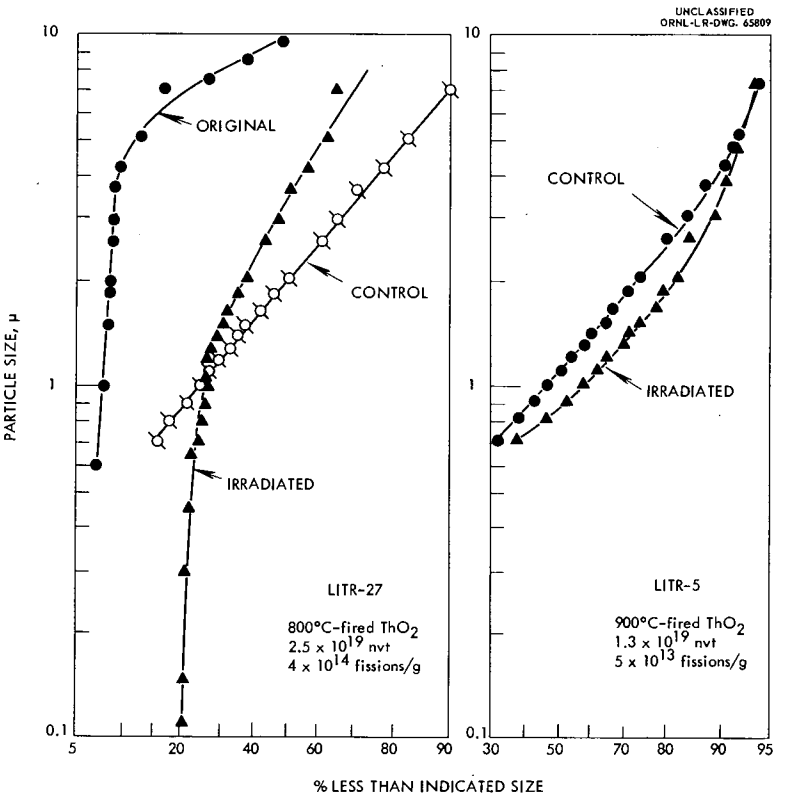
5.0 APPENDIX

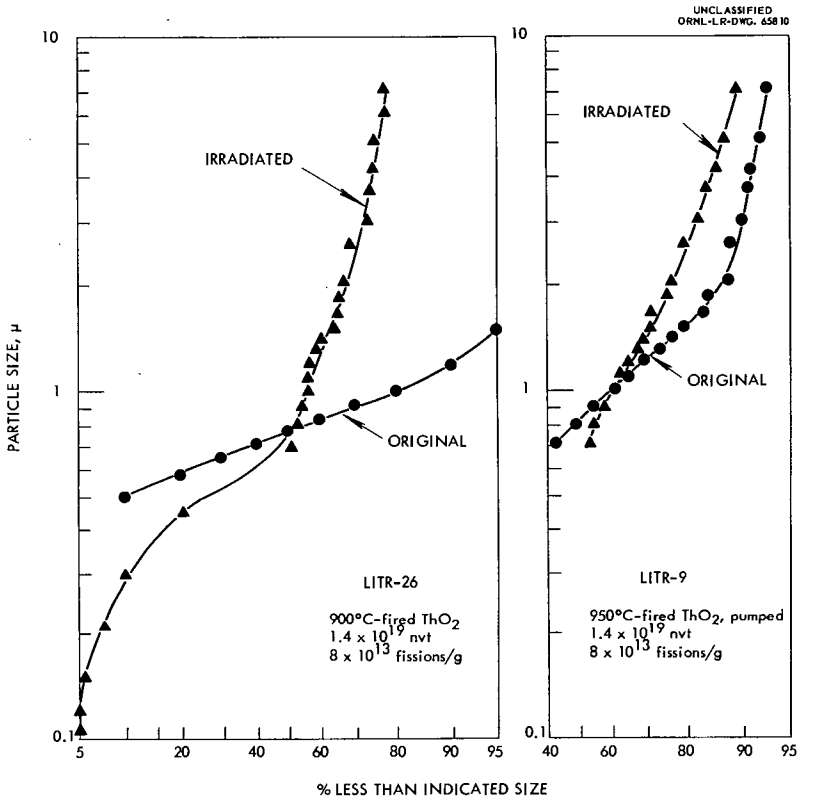
SIZE DISTRIBUTION CURVES FROM OXIDE SLURRY IRRADIATION EXPERIMENTS

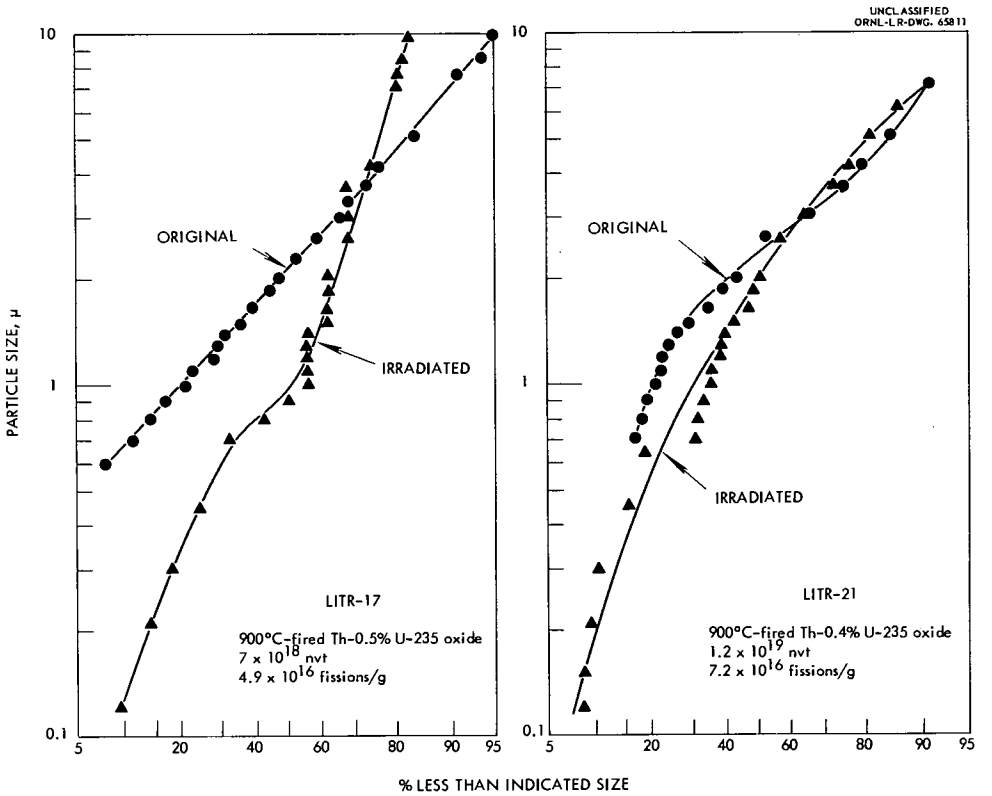
Curves showing particle size distributions of the irradiated oxide and the original oxide and/or the oxide from the control experiments are given as follows:

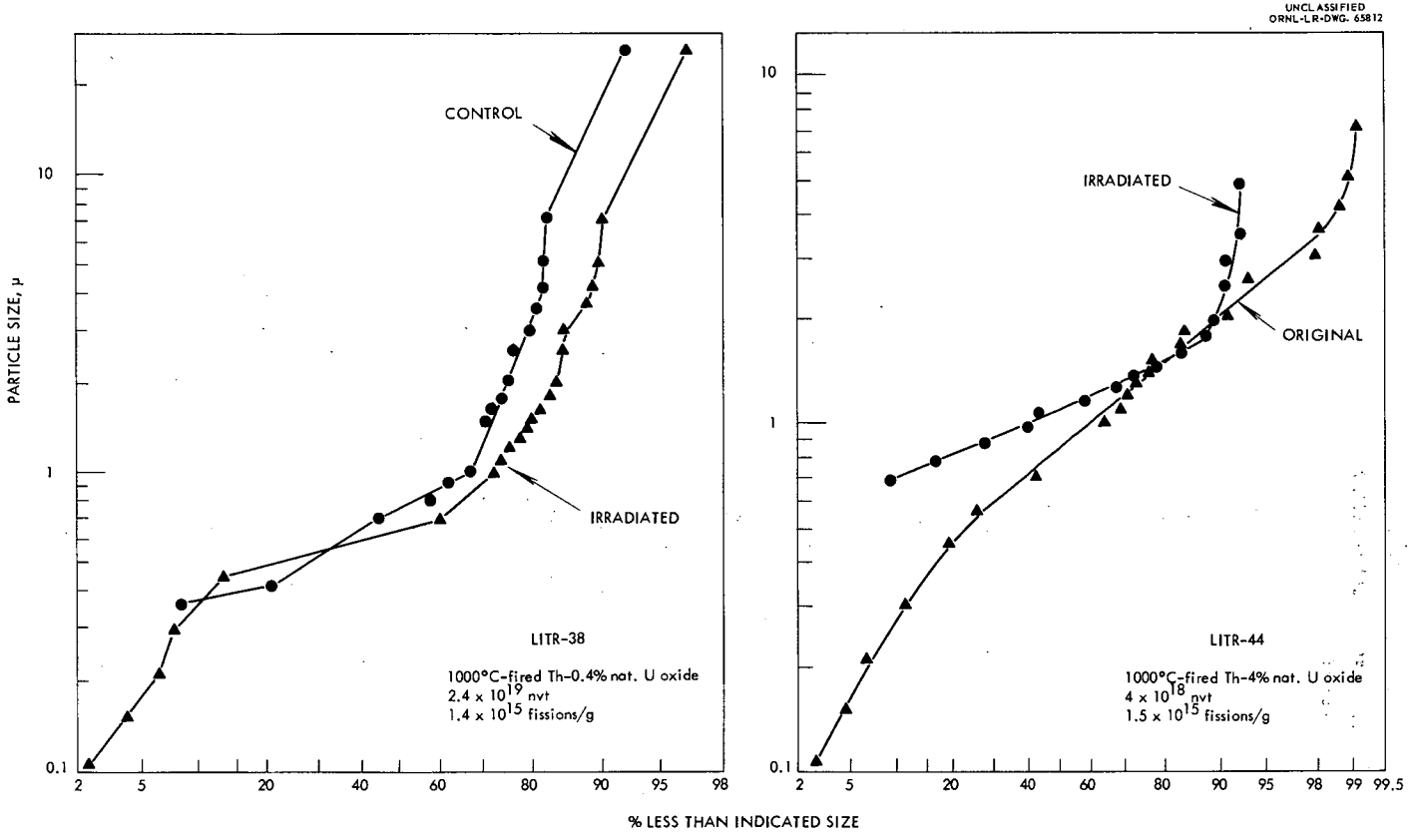
Experiment	Slurry	Page
LITR-3, -8	650°C-fired ThO_2	15
LITR-27	800°C-fired ThO_2	15
LITR-5	900°C-fired ThO_2	15
LITR-26	Same	16
LITR-9	950°C-fired, pumped ThO_2	16
LITR-17, -21	900°C-fired Th-0.4% U-235 oxide	16
LITR-38	1000°C-fired Th-0.4% nat U oxide	17
LITR-44	1000°C-fired Th-4% nat U oxide	17
LITR-46, -47	Same	18
LITR-48, -49	Same	18
LITR-54, -55	1050°C-fired Th-8% nat U oxide	19
LITR-40	1300°C-fired Th-0.4% U-235 oxide	19
LITR-33	1600°C-fired, pumped ThO_2	19


UNCLASSIFIED
ORNL-LR-DWG. 65808
ORIGINAL
IRRADIATED
LITR-3
650°C-fired ThO_2
1.9×10^{19} nvt
2×10^{14} fissions/g
IRRADIATED
LITR-8
650°C-fired ThO_2
1.2×10^{19} nvt
5×10^{13} fissions/g
PARTICLE SIZE, μ
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65809
ORIGINAL
CONTROL
IRRADIATED
LITR-27
800°C-fired ThO_2
2.5×10^{19} nvt
4×10^{14} fissions/g
CONTROL
IRRADIATED
LITR-5
900°C-fired ThO_2
1.3×10^{19} nvt
5×10^{13} fissions/g
PARTICLE SIZE, μ
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65810
PARTICLE SIZE, μ
IRRADIATED
ORIGINAL
LITR-26
900°C-fired ThO2
1.4 x 10^19 nvt
8 x 10^13 fissions/g
LITR-9
950°C-fired ThO2, pumped
1.4 x 10^19 nvt
8 x 10^13 fissions/g
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65811
PARTICLE SIZE, μ
ORIGINAL
IRRADIATED
LITR-17
900°C-fired Th-0.5% U-235 oxide
7 x 10^18 nvt
4.9 x 10^16 fissions/g
LITR-21
900°C-fired Th-0.4% U-235 oxide
1.2 x 10^19 nvt
7.2 x 10^16 fissions/g
% LESS THAN INDICATED SIZE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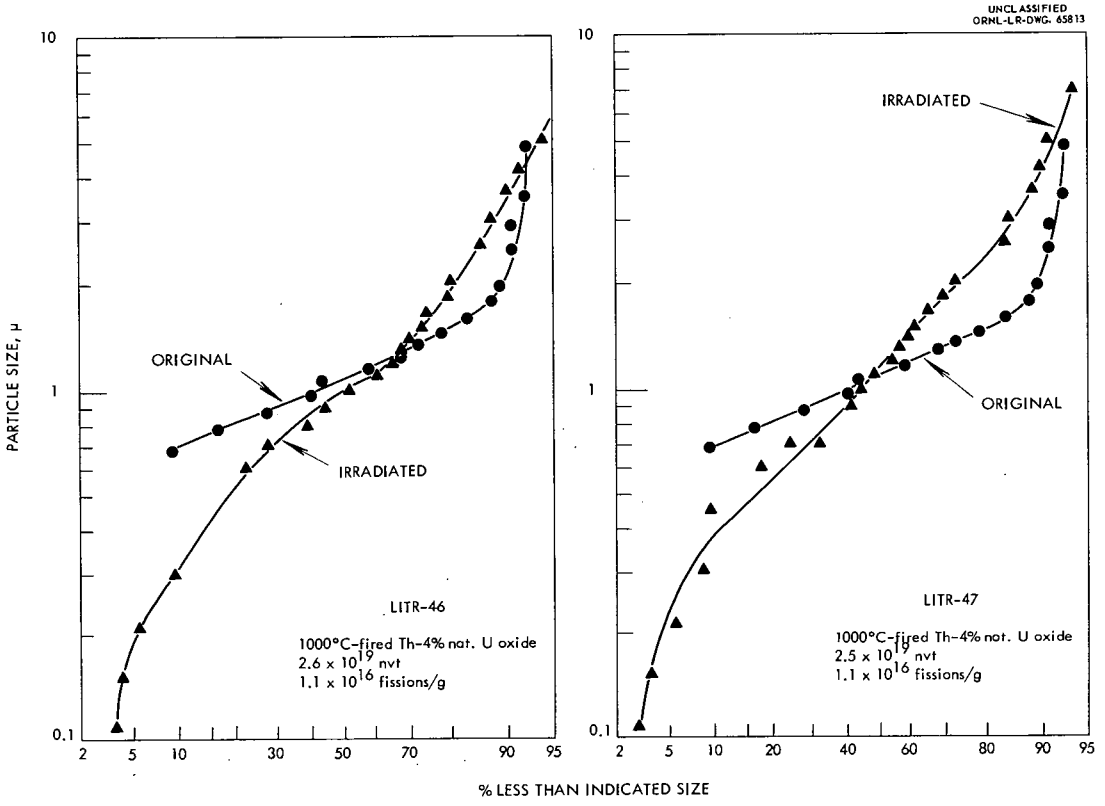
ORNL-LR-DWG. 65812
PARTICLE SIZE, μ
10
1
0.1
CONTROL
IRRADIATED
LITR-38
1000°C-fired Th-0.4% nat. U oxide
2.4 x 10^19 nvt
1.4 x 10^15 fissions/g
IRRADIATED
ORIGINAL
LITR-44
1000°C-fired Th-4% nat. U oxide
4 x 10^18 nvt
1.5 x 10^15 fissions/g
2 5 20 40 60 80 90 95 98 99 99.5
% LESS THAN INDICATED SIZE


UNCLASSIFIED
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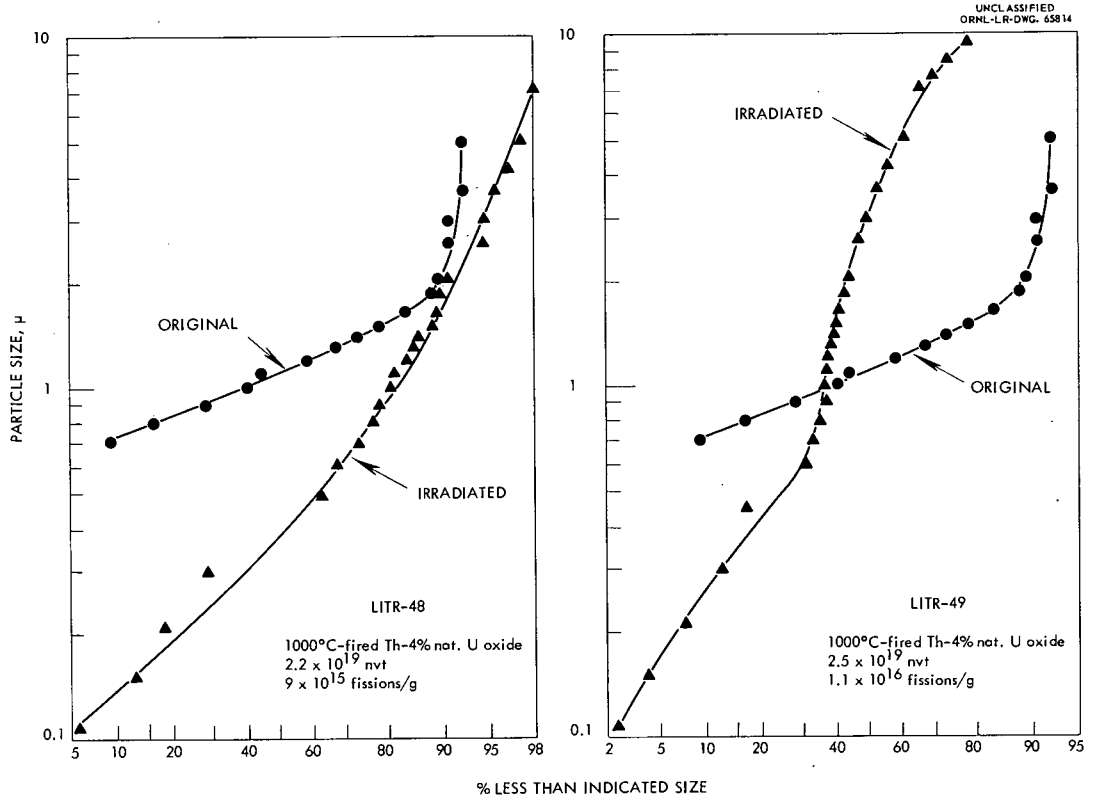
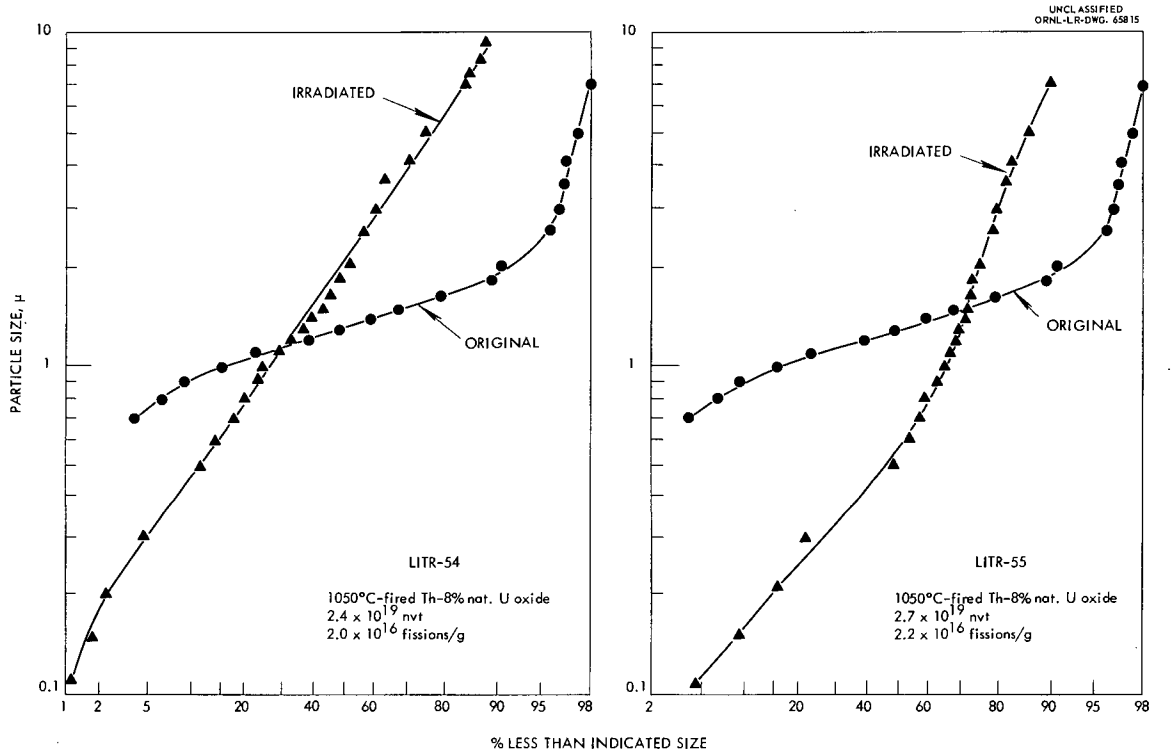
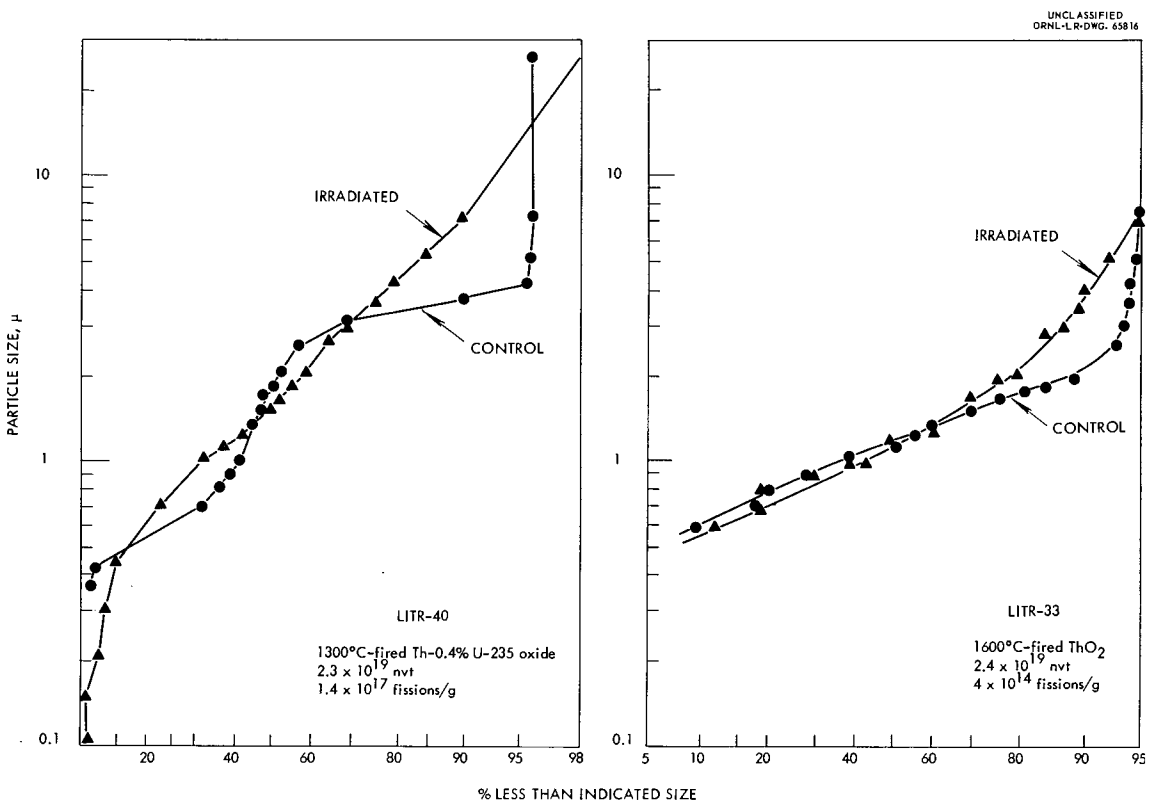
PARTICLE SIZE, μ
ORIGINAL
IRRADIATED
LITR-46
1000°C-fired Th-4% nat. U oxide
2.6 x 10^19 nvt
1.1 x 10^16 fissions/g
IRRADIATED
ORIGINAL
LITR-47
1000°C-fired Th-4% nat. U oxide
2.5 x 10^19 nvt
1.1 x 10^16 fissions/g
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65814
PARTICLE SIZE, μ
ORIGINAL
IRRADIATED
LITR-48
1000°C-fired Th-4% nat. U oxide
2.2 x 10^19 nvt
9 x 10^15 fissions/g
IRRADIATED
ORIGINAL
LITR-49
1000°C-fired Th-4% nat. U oxide
2.5 x 10^19 nvt
1.1 x 10^16 fissions/g
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65815
IRRADIATED
ORIGINAL
LITR-54
1050°C-fired Th-8% nat. U oxide
2.4 x 10^19 nvt
2.0 x 10^16 fissions/g
LITR-55
1050°C-fired Th-8% nat. U oxide
2.7 x 10^19 nvt
2.2 x 10^16 fissions/g
PARTICLE SIZE, μ
% LESS THAN INDICATED SIZE


UNCLASSIFIED
ORNL-LR-DWG. 65816
IRRADIATED
CONTROL
LITR-40
1300°C-fired Th-0.4% U-235 oxide
2.3 x 10^19 nvt
1.4 x 10^17 fissions/g
LITR-33
1600°C-fired ThO2
2.4 x 10^19 nvt
4 x 10^14 fissions/g
PARTICLE SIZE, μ
% LESS THAN INDICATED SIZE

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