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REACTOR IRRADIATION OF THORIUM AND URANIUM OXIDE SLURRIES

by

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UNCLASSIFIEDABSTRACT

REACTOR IRRADIATION OF THORIUM AND URANIUM OXIDE SLURRIES

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Thorium and thorium-uranium oxide slurries were irradiated in the Low Intensity Test Reactor (LITR) at temperatures up to 300°C in small stirred autoclaves. Stirring was accomplished by means of an electromagnetically operated plunger. Stirrer operation was monitored using an oscilloscope.

Relative slurry viscosities were determined both in and out-of-pile using calibration curves of apparent viscosity versus stirrer rise time. Post-irradiation examination of selected slurries indicated no gross changes occurred in the particulate properties.

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INTRODUCTION

The utilization of aqueous thorium oxide suspensions in a homogeneous type power reactor necessitates that their properties are not impaired by reactor irradiation to such a degree that they cannot be handled by ordinary engineering equipment or that their use becomes economically unfeasible. It is conceivable that under neutron bombardment and in the highly ionizing radiation present in the reactor that the surface properties of the thorium and the flocculation characteristics of the suspensions may be considerably changed. Atomic displacements will occur in the oxide lattice as a result of heavy particle bombardment. Fission fragments produced by nuclear fission will leave particles which are less than 5 or 10 μ in size, producing a high concentration of ions and of hydrogen peroxide at the immediate surface of the particle. In addition, the fission fragments will in all probability readsorb on the particle surface producing unpredictable changes in surface behavior. It may also be surmized that electrolytic impurities present in the suspension supernatant could undergo changes as a result of the ionizing action of gamma rays which could affect the slurry behavior.

In the following paper are presented the effects observed in apparent slurry viscosity and on selected oxide properties when aqueous slurries of thorium oxide and thorium oxide containing 0.5 mole % of $U^{235}O_3$ were subjected to reactor irradiation. The slurries were irradiated in the Low Intensity Reactor (LITR) at Oak Ridge at a thermal neutron flux of $3 \times 10^{13}/\text{cm}^2/\text{sec}$.

EXPERIMENTAL

Slurry Preparation

Slurries of pure thorium oxide and thorium oxide containing 0.5 mole % uranium oxide were tested. The thorium oxide was prepared by precipitating thorium oxalate from a thorium nitrate solution with

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oxalic acid. The oxalate was then dried and calcined to the oxide in a multistage calcination. Final firing temperatures ranged from 650 to 900°C.

The uranium bearing oxides were prepared by wet autoclaving mixtures of ThO_2 and UO_3 (about 90% enriched uranium) at 300°C or by coprecipitating thorium and uranous oxalates and calcining to the oxide. The autoclaves were loaded with 5 ml of slurry at room temperature which expanded to fill half of the autoclave at 300°C. When uranium bearing slurries were irradiated, either palladium oxide or molybdenum oxide was added to catalyze the recombination of radiolytic hydrogen and oxygen. In some experiments an oxygen overpressure of 200 to 250 psi was added at room temperature.

Equipment

The experiments were carried out in small cylindrical stainless steel autoclaves (Figs. 1 and 2) approximately 7-1/2 in. long with a maximum diameter of 0.8 in. Both ends of the autoclave were closed with high pressure conical fittings. Two thermocouples were welded into the bottom closure and a 20 ml pressure sensing capillary was welded into the top closure. A dash-pot type stirrer of Armco iron clad in stainless steel with a stainless steel stirring head was included in each autoclave. The capacity of the autoclave with stirrer was approximately 14 ml.

The stirrer was made to reciprocate at 3 to 4 cycles per second by alternately energizing two solenoid coils of double glass insulated aluminum wire wrapped around the autoclave body. Aluminum wire was used because of its low activity after neutron irradiation compared to that of copper. Stirrer operation was monitored on the up stroke by a tickler coil connected to an oscilloscope, and on the down stroke by a microphone attached to an amplifier and speaker. If the slurry settled, the sound changed from a metallic click to a dull thud. Temperature and pressure were continuously recorded.

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Fig. 1 Cross-sectional Drawing of In-pile Autoclave

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Fig. 2 Parts and Assembly of In-pile Autoclave

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The stirrer power supply (Fig. 3) was designed and built by the ORNL Instrument Division. The timing unit consists of an elaborate multivibrator circuit whose frequency of oscillation and cycle time division can be controlled by varying resistances in the circuit. The timer unit in turn controls the grids of two pairs of thyratrons which furnish power to the stirrer solenoids. The current to the solenoids is controlled by adjusting the thyatron plate voltage with a variac. Two thyratrons in parallel are required to supply the necessary current to each stirring solenoid.

Irradiation Technique

The radiation facility consists of a double walled aluminum tube $\sim 7/8$ in. i.d. which extends from the top of the LITR through approximately 20 ft of water into the reactor core. The autoclave is lowered into this tube on a bundle of wires containing the electrical leads, thermocouples and pressure capillary. An isolation chamber which fits over the tube at the top of the reactor contains connectors for the electrical and thermocouple leads and a 10,000 psi Baldwin cell for the pressure capillary. From the isolation head, all leads go via cable to the instruments in an adjoining room.

During reactor shutdowns the autoclaves were maintained at 300°C by heat generated by the stirring coils. Heat was removed during reactor operation by air which flowed down the tube, over the autoclave, back up through the annulus provided by the double-walled tube and to the reactor off-gas system. Temperature control was automatic, and suitable safety circuits were provided.

At the end of the radiation period which was limited because of other LITR operations requiring the removal of the tank cover, the autoclave was cooled, raised out of the core region, and allowed to decay at least 24 hr. The autoclave could then be pulled into a lead shield and after additional cooling was opened and the slurry recovered for examination.

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Fig. 3 Instruments for Operating In-pile Autoclave

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TECHNIQUE OF SLURRY VISCOSITY MEASUREMENT

The versatility of the timing device described above made possible the measurement of relative slurry viscosity both in and out-of-pile. It was found that the time it takes the stirrer to reach its maximum height for a fixed solenoid current is dependent on the viscosity of the autoclave contents. The "rise time" is determined by adjusting the frequency and load division so that the upper solenoid is deenergized the instant the oscilloscope indicates the stirrer has reached the top of its travel. Figures 4 and 5 show the oscilloscope trace before and after adjustment. The rise time in seconds is then obtained by dividing the load division by the frequency.

Calibration curves of rise time versus viscosity were made using a silicone oil of known viscosity at various temperatures. Low viscosity points were obtained using water and air. Calibration curves for 8 and 10 amp solenoid currents are shown in Fig. 6.

To determine the apparent viscosity of a slurry, the rise time of the stirrer was measured and a value obtained from the calibration curve. It should be pointed out that because of density differences and the non-Newtonian nature of these slurries that the number obtained is useful for comparison only and cannot be related at this time to viscosities or shear diagrams obtained by other methods.

SLURRY VISCOSITY MEASUREMENTS

Measurements were made at slurry concentrations from 250 g Th/kg H_2O to 1250 g Th/kg H_2O and at temperatures up to 300°C.

Typical results are shown in Figs. 7 and 8. The viscosity increases markedly with slurry concentration as expected. Variations with temperature are small in most cases as shown in Fig. 9.

No effect of pile radiation has been noted (Fig. 10) for operating times as long as 400 hr and power densities up to 7 watts per gram of ThO_2 .

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Fig. 4 Oscilloscope Trace of Stirrer Operation

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Fig. 5 Oscilloscope Trace Adjusted for Viscosity Measurements

Fig. 6 Viscosity Calibration Curves

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Fig. 7 VISCOSITY OF ThO₂ SLURRIES

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Fig. 8 VISCOSITY OF MIXED OXIDE SLURRIES

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Fig. 9 The Effect of Temperature on Slurry Viscosity

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Fig. 10 IN-PILE BEHAVIOR OF THORIUM-URANIUM OXIDE SLURRIES

CONDITIONS: TEMPERATURE, 300°C; FLUX, 3×10^{13} n/cm²·sec

OXIDE	CONC. (g Th/kg H ₂ O)	IRRADIATION TIME (hr)	TIME OF STIRRING IN-PILE	VISCOSITY (centistokes)	
				Before Irradiation	During Irradiation
900°C; ThO ₂ - 0.5% Net, UO ₃ (AUTOCLAVED)	1000	151	77*	7	
	1000	68	72*	7	
	1000	172	264	7	
	1000	200	171*	7	
900°C; ThO ₂ - 0.5% ENRICHED UO ₃ (COPRECIPITATED)	500	85	111	4	4
	750	168	211	7	5
	750	92	121	5	5
	750	192	219	4	45

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POST-IRRADIATION EXAMINATION OF SELECTED SLURRIES

The post-irradiation examination consisted of visual examination for color changes and caking, and measurement of the settled volume, crystallite size and particle size distribution. Results of these measurements are given in Fig. 11. No significant changes in particle size or settled density were noted. Crystallite size as measured by x-ray diffraction line broadening appeared to change in a few cases. No coloration of the thorium was observed, and no tendency toward caking was found even on samples irradiated in the settled condition for 10 days.

CONCLUSIONS

No gross effect of radiation has been found that would affect the use of a thorium slurry in a properly engineered reactor system.

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Fig. 11 EFFECT OF LTR IRRADIATION ON THORIUM OXIDE SLURRIES

CONDITIONS: TEMPERATURE, 300°C; FLUX, 3×10^{13} n/cm²·sec

OXIDE	CONC. (g Th/kg H ₂ O)	IRRADIATION TIME (hr)	SETTLED DENSITY		X-RAY CRYSTALLITE SIZE		AVERAGE PARTICLE SIZE OF IRRADIATED OXIDE (μ)
			Control	Irradiated	Original	Irradiated	
650°C; D-16	500	258	1000	1500	200	195	1
	500	66		1600			
	500	165				260	2
900°C; D-16	500	175	1100	1400	474	285	1
900°C; D-30 (PUMPED)	500	200	800	1100	450	200	0.6
900°C; ThO ₂ 0.5% UO ₃ (AUTOCLAVED)	1000	151	1025	1600	350		1
	1000	68	1010	1600	350	330	3
	1000	172	1020	1740	350	350	3

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