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1

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CLAYS AS SUSPENDING AGENTS FOR THORIA SLURRIES

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Suspending Agents for ThO₂ Slurries

By virtue of their size, shape, and surface charge, clay particles are readily suspended in water and exhibit varying degrees of suspending power for other materials. Since the clay minerals are composed of elements of relatively low cross section, it seemed of interest to determine their effectiveness as suspending agents for ThO₂ in water. Since this investigation was necessarily limited in scope, the materials used were those known to have the greatest suspending power, per unit used, in normal ceramic slips. The materials selected for use were various brands of attapulgite and montmorillonite (Wyoming Bentonite). On the basis of representative chemical analysis and cross-sections it was calculated that additions of these materials on the order of 5% could be made to the ThO₂ without seriously affecting the slurry. The thoria used was ORL-CYT-1143 and, unless otherwise specified, was calcined at 1600°C for four hours followed by pulverizing in a hammer-mill.

Preliminary tests were made on available attapulgite and montmorillonite materials to determine what order of concentrations could be used. These materials were suspended in water by mixing in a Waring blender. These materials form thixotropic suspensions and were noticeably gelled at concentrations of 4% and above. With respect to settling tendencies, the most promising materials were Volclay (montmorillonite), Permigel (attapulgite), and Zeogel (attapulgite).

Results of settling tests, shown in Table I, indicated that a 2% addition of Permigel (attapulgite) altered the settling tendencies for short time settling while a 4% addition of either Permigel or Volclay (montmorillonite) considerably altered both short and long time settling tendencies. Slurries with Permigel tended to be slightly flocculated while those with Volclay were deflocculated. There was no measurable settling with additive concentrations of 8% but the apparent viscosity of these suspensions was extremely high.

*Summer participant from the University of Illinois.

SETTLING AND pH TESTS OF 1600°C ThO₂
WITH VARIOUS CONCENTRATIONS OF SUSPENDING AGENTS

Suspending Agent	0% ThO ₂ 0 hr Settling	1 Kg ThO ₂ / ℓ H ₂ O	1 Kg ThO ₂ / ℓ H ₂ O	Height of Sediment (1/16-in.) after time shown			Type of Sediment
		1-1 1/2 hr	20 hr	1/2 hr	1 hr	20 hr	
1/2% Permangel	7.50	7.99	7.79	11	11	11	Hard
1% Permangel	7.45	8.02	8.04	8	10	11	Hard
2% Permangel	7.40	7.95	7.95	5	7	11	Soft
4% Permangel	7.25	7.75	7.78	1	1	7	Very Soft
8% Permangel	7.20	7.51	7.60	0	0	0	None
1/2% Volclay	9.05	8.72	8.68	12	12	13	Hard
1% Volclay	8.90	8.68	8.61	11	12	13	Hard
2% Volclay	9.00	8.70	8.75	10	12	13	Very Hard
4% Volclay	9.20	8.60	8.68	2	2	3	Soft
8% Volclay	8.90	8.30	-	0	0	0	None
None	-	7.80	8.40	13	13	14	Hard

The pH of the slurry was noted to have a considerable affect on the nature of the sediment formed in settling (Table II). As the pH increases, the tendency for the thoria to settle independently increases. At high pH the thoria settles rapidly into a hard cake with the fine clay particles settling on top making it very difficult to disperse. At lower pH values the clay particles and ThO_2 tend to settle together yielding a soft, readily dispersed sediment. Slurries prepared from acid washed Permangel and acid washed ThO_2 were very slow settling and formed very soft sediments. The pH of these slurries ranged from 5.7 to 7.7.

An attempt was made to evaluate the effectiveness of the suspending agents by a simple settling test. For this purpose slurries were prepared by milling in a colloid mill. At various times during the settling period, samples were taken from 2-1/2-in. below the surface and the per cent change in particle concentration, as compared to initial concentration, was determined. Results are shown in Table III. Additives in the concentration of one per cent were not effective in preventing the settling of ThO_2 slurries, except that Zeogel (attapulgate) was effective for a short time. Additives in concentrations of three per cent were very effective in preventing settling of the ThO_2 slurry. This concentration resulted in thixotropic suspensions. From the standpoint of settling alone, five per cent additive concentration was extremely effective in preventing settling. Such concentrations yield thixotropic suspensions of high apparent viscosity.

After 100 hr of settling, there was no visible sediment in the slurry containing five per cent Volclay. Slurries containing five per cent Permangel and Zeogel were slightly flocculated as evidenced by clearing of the water above the settle. These slurries were readily dispersed by shaking.

Slurries containing three per cent additives formed a soft, readily dispersed sediment. There was segregation in the Volclay sediment but this was not apparent in either of the other slurries.

In the slurries containing one per cent additive, Volclay and Permangel, the sediment was very difficult to disperse. The sediment for the same concentration of Zeogel additive was readily dispersed. The thoria slurry with no additive formed a very hard sediment that was extremely difficult to disperse.

TABLE II

INFLUENCE OF pH OF SLURRY ON NATURE OF SEDIMENT FORMED
(1 Kg. Th/l H₂O, 2% Permangel)

pH Before Adding ThO ₂	pH 17 hr After Adding ThO ₂	Type of Sediment
5.22	7.00	Very soft, dispersed by inverting sedimentation tube.
6.55	7.78	Very soft, dispersed by inverting sedimentation tube.
7.20	8.11	Soft, readily dispersed by shaking tube.
7.42	8.20	Soft, readily dispersed by shaking tube.
7.45	8.00	Soft, readily dispersed by shaking tube.
8.15	8.42	Soft, readily dispersed by shaking tube.
9.32	9.13	Hard, difficult to disperse by shaking tube.
10.70	10.30	Very hard, not dispersed by shaking alone.
11.50	11.35	Very hard, not dispersed by shaking alone.
11.82	11.75	Very hard, not dispersed by shaking alone.

TABLE III

CHANGE IN PARTICLE CONCENTRATION
IN SETTLING OF 1600°C ThO₂ SLURRIES

Additive	<u>Per Cent Change in Particle Concentration with Time</u>				
	1 hr	3 hr	6 hr	72 hr	pH
None	74	90	94	99	8.70
1% Volclay	78	90	93	98	8.77
1% Zeogel	1	86	100	100	8.55
1% Permangel	73	89	92	98	8.63
3% Volclay	30	32	31	21	8.62
3% Zeogel	0.4	7	29	66	8.51
3% Permangel	33	29	32	39	8.30
5% Volclay	4	3	4	8	8.70
5% Zeogel	10	18	27	45	8.48
5% Permangel	0.1	0.3	2	2	8.09

The addition of Zeogel in amounts of three per cent to five per cent appears to be very effective both in the retardation of settling and in the production of a readily dispersed sediment. There is a possibility that the higher concentration will present pumping problems due to its high viscosity.

Slurries prepared from ThO_2 calcined at various temperatures were compared as to their settling tendencies (Table IV). The 1600°C calcined material appeared to make the best slurry. These materials were compared after receiving the same grinding treatment since time did not permit testing them at equivalent particle sizes. Such a test should be carried out.

Summary

Montmorillonite and attapulgite, in concentrations of three per cent and above, are very effective in the retardation of settling of ThO_2 slurries and in the prevention of hard-caked sediments. Since this work is based upon sedimentation tests only, it will be necessary to do further work to evaluate their usefulness. Of primary interest would be the effect of radiation on the suspending power of these materials. Such information does not seem to be available.

The most useful material found was attapulgite sold under the trade name of Zeogel. Concentrations of three per cent of this material were very effective and five per cent were even more so. Viscosity of the slurry may be prohibitive in concentrations above three per cent. The most desirable pH range appears to be from 7.5-9.0 both from the standpoint of rate of settling and hardness of sediment formed. In the preparation of slurries containing these materials, it is essential that the suspending agent be mixed in the water using a high shear type mixer.

TABLE IV

CHANGE IN PARTICLE CONCENTRATION IN SETTLING
OF SLURRIES CONTAINING 3% ZEOGEL ADDITION +
1 Kg/l·H₂O of ThO₂

ThO ₂ Calcining Temperature	Per Cent Change in Particle Concentration with Times				
	1 hr	3 hr	6 hr	24 hr	pH
1000°C	1.1	3.1	9.7	46.3	8.02
1300	2.2	0.7	6.3	32.6	8.39
1500	1.9	0.8	5.1	24.0	8.70
1600	1.8	0	5.7	29.2	8.88
1700	0.3	5.5	17.3	39.4	9.01
1800	0.3	7.1	23.7	42.8	8.95
				3% Zeogel	8.80

1-8

Table 1 - RESULTS OF INVESTIGATION

Run No.	Date	Voltage Variation	Axial Velocity ft/sec	Degree of Subcooling at Exit °F	Inlet Static Pressure psig	Test Section					x, Exit Quality %	$\left(\frac{P_{FF}}{P_{HA}}\right)\%$	$(q/A_1)_b$, Btu/hr-ft ²
						ID, In.	OD, In.	Heated Length in.	L/D _i	Material			
1	9/27/57	Step Taps	12.1	36	93	0.275	0.300	3.063	11.14	Copper	0.0	0.26	5,940,000
2	10/2/57	Variacs	11.8	0	94	0.275	0.300	3.187	11.60	"	1.24	0.19	8,240,000
3	10/13/57	"	12.35	0	99	0.275	Inlet-0.2875 Exit--0.300	2.875	10.44	"	1.49	0.20	9,690,000
4	10/17/57	"	13.61	72	100	0.250	0.300	1.20	4.80	Inconel	0.0	0.43	10,980,000