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DPST-84-101-TL

Project S-1780

LP No. 10159

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RHEOLOGY OF NON-RADIOACTIVE SIMULANT
OF CONCENTRATED TETRAPHENYLBORATE PRECIPITATE

The attached memorandum by M. A. McLain and I. D. Goren summarizes the ETF study to characterize the rheological behavior of the concentrated tetraphenylborate precipitate. The rheograms most closely resembled the Bingham plastic model. The experimental results indicated that the yield stress, as well as the plastic viscosity, is directly related to the concentration of insoluble solids.

The results of this study will be included in the Acid Hydrolysis Process Technical Data Summary and the Precipitation Process Technical Data Summary. Meanwhile SRL recommends for design, use of a yield stress of 300 dynes/cm² and a plastic viscosity of 50 cp in conjunction with the current material balance development basis of 10 wt% insoluble solids.

Any questions should be directed to I. D. Goren on extension 6353.

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DPST-84-401
Project S-1780
LP No. 10159

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March 30, 1984

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RHEOLOGY OF NON-RADIOACTIVE SIMULANT OF
CONCENTRATED TETRAPHENYLBORATE PRECIPITATE

Introduction

The high level waste stored in tanks at SRP consists of sludge and salt. The In-Tank Salt Decontamination Process uses sodium tetraphenylborate (NaTPB) to precipitate Cesium-137 and uses sodium titanate ($\text{NaTi}_2\text{O}_5\text{H}$) to precipitate Strontium-90 from the radioactive salt solution. Potassium is also precipitated, forming KTPB which is a major solid component of the slurry. There are approximately 50 molecules of KTPB formed for every one molecule of CsTPB. The decontaminated supernate is separated from the radioactive solids by crossflow filtration. The resultant concentrated precipitate is 7-15 wt% insoluble solids. After removal of the phenyl groups by the Acid Hydrolysis process, the precipitate will be incorporated into borosilicate glass.

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Since the slurry must be pumped during the Precipitation Process and also from H to S Area, it is important to know the flow characteristics of the precipitate. This report presents rheological information on a simulated non-radioactive concentrated tetraphenylborate (TPB) precipitate.

Summary

Simulated washed and unwashed samples of concentrated TPB precipitate were prepared and rheological properties were analyzed. Five concentrations of the unwashed slurry ranging from 4.1 to 19.5 wt% insoluble solids (IS) and three concentrations of the washed precipitate ranging from 8.8 to 12.9 wt% IS were analyzed. The unwashed samples contained between 32 and 46 wt% total solids. The washed precipitate samples contained only 11.8 to 17.3 wt% total solids.

The concentrated precipitates behave similarly to a Bingham plastic. The yield stress was found to be directly proportional to the concentration of insoluble solids over the range of concentrations studied. Yield stresses ranged from 32 (dynes/cm²) for the 4.1% IS sample to 646 (dynes/cm²) for the 19.5% IS sample. The plastic viscosity was also found to be a linear function over the same concentration range. Plastic viscosities ranged from 10 (cp) for the 4.1% IS sample to 110 (cp) for the 19.5% IS sample. Neither the yield stress nor the plastic viscosity were observed to be significantly affected by the presence of the soluble salts in the unwashed samples. In addition, the presence of sodium titanate was not found to affect the rheology of the precipitate.

Equipment and Procedures

The composition of the simulated unwashed precipitate used for testing is given in Table 1. Five concentrations - 4.1, 7.2, 10.3, 13.4, and 19.5 wt% insoluble solids (IS) - were used to determine how the concentration affects the rheology of the precipitate. The composition of the simulated fully washed precipitate is in Table 2. Three concentrations - 8.8, 10.8, and 12.9 wt% IS - were analyzed. All samples were prepared by mixing the chemicals listed in Tables 1 and 2 in a beaker and stirring with a mechanical stirrer for a minimum of 15 minutes. The TPB was added as NaTPB and stoichiometric amounts of the salts were added as K⁺ salts. The NaTPB reacts with the K⁺ salts to give KTPB and the Na⁺ salts as listed.

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Density and % total solids were determined for each sample. Weight measurements for unwashed precipitate samples were made with Sartorius 3862 MP scale. A Sartorius 1602 MP balance was used to weigh washed samples and the NaTPB was weighed on a Ohaus triple beam balance. Rheograms were obtained using a Haake Rotovisco RV3. The coaxial cylinder sensor systems MVI and NV were used.¹ The MK50 measuring head was used for the more dilute solutions, while the MK500 was used on the more concentrated samples. During testing, the shear rate was increased from 0 to 300 sec⁻¹ and was held constant for approximately 2 minutes before it was decreased back to zero. All flow curves were obtained at 25°C.

Discussion of Results

The % total solids for each solution are given in Table 3. Total solids ranged from 32 to 46 wt% for the unwashed samples. The total solids were determined to be between 11.8 and 17.3 wt% for the washed samples. The washed samples simulate 19, 16, and 13 wt% IS samples that have been washed with water. The resultant slurries contain 1/15 of the soluble salts in the unwashed samples and the same quantities of KTPB and NaTi₂O₅H.

The solubility of the NaTPB is dependent upon the Na⁺ concentration of the solution. The amount of soluble NaTPB can be determined by the following equation:

$$\text{NaTPB} = (.4186)(^{\circ}\text{C})(X+2.5)^{-4.814} + (1.128 \text{ E}25)(X+15)^{-21.347}$$

where X = [Na⁺] from other salts in the solution.² From this equation, the NaTPB is found to be essentially insoluble (>90%) in the unwashed samples and completely soluble in the washed precipitate. Therefore, NaTPB, KTPB, and NaTi₂O₅H are considered insoluble solids in the unwashed precipitate samples while only the KTPB and NaTi₂O₅H are considered insoluble solids in the washed samples.

Density measurements were made by weighing a known volume of solution. The tendency of the slurries to foam made it difficult to read the exact volume. Because of this, difficulties were encountered in obtaining reproducible values for the density. However, all values fell in the range of 1.0 to 1.3 g/ml.

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Flow curves for the unwashed precipitate samples are shown in Figure 1. The slurries produce curves that closely resemble Bingham plastic behavior. The rheograms show a yield stress, initial force required to get the fluid moving. Once the material is moving, the shear stress is linearly proportional to the shear rate. The 19.5, 13.4, 10.3, 7.2, and 4.1% IS samples showed yield stresses of 646 ± 186 , 326 ± 45 , 308 ± 22 , 186 ± 13 , and 32 ± 28 dynes/cm² (+95% Conf. limits), respectively. These values are for slurries at 25°C. Previous work has suggested that at 45°C these values might be 36% lower and at 70°C they might be 44% lower.⁴ Figure 2 shows that over the range of 4.1 to 19.5 wt% IS the relationship between the yield stress and the concentration of insoluble solids can be approximated by a linear curve. Figure 3 shows the correlation between the data obtained in this study and data from earlier studies.^{5,6} The best curve fit was found by comparing coefficients of determination for various curves (see Appendix). The coefficient of determination indicates the proportion of the total variation in the dependent variable (in this case the yield stress) explained by the regression model.⁷

The slope of the shear stress versus shear rate plot for a Bingham plastic is called the plastic viscosity.⁸ As can be seen in Figure 1, the force required to keep the material flowing is much smaller than the initial force required to start it moving. The yield stress is approximately twice the additional force required to go from a shear rate of 0 to a rate of 300 sec⁻¹. Figure 4 reveals that over the range studied, the plastic viscosity increases linearly with an increase in concentration. The plastic viscosities of the 4.1, 7.2, 10.3, 13.4, and 19.5% IS samples were found to be 10, 33, 47, 55, and 110 (cp), respectively. Figure 5 compares these results with results obtained in previous studies of the concentrated precipitate.^{5,6} The best curve fit was found by comparing coefficients of determination for various curves (see Appendix).

The apparent viscosity represents the viscosity of a Newtonian fluid with the same resistance to flow at a particular shear rate. Graphically, the apparent viscosity is the slope of a line drawn from the origin to a point on the shear stress versus shear rate curve. The apparent viscosities of the unwashed precipitates are shown in Figure 6. As the shear rate approaches zero, the apparent viscosity approaches infinity. As the shear rate approaches infinity, the apparent viscosity approaches the plastic viscosity.⁹

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Rheograms for the washed precipitates are shown in Figure 7. The theoretical %IS for the samples are 12.9, 10.8, and 8.8; however, experimentally the %IS were determined to be 13.6, 11.3, and 8.8 wt%, respectively. Yield stress of 470 ± 66 , 310 ± 116 , and 218 ± 67 dynes/cm² (+95% Conf. limits) were found for the 13.6, 11.3, and 8.8% IS samples, respectively. These values are plotted in Figure 2. The values fall close to the line obtained with unwashed samples. The plastic viscosities of the 13.6, 11.3, and 8.8% IS samples were found to be 68, 47 and 30 (cp), respectively. The plastic viscosity of the washed precipitates appears to show the same relationship to the concentration of insoluble solids as that of the unwashed samples. This can be seen in Figure 4 where the plastic viscosities of the washed precipitates fall close to the line obtained by linear regression on the unwashed values. Thus, no significant effect on the rheology of the precipitate by the presence of the salts was observed. The three washed samples behave similarly to unwashed samples with the same concentration of insoluble solids.

Sodium titanate was present in all samples as an insoluble solid. During an earlier study, a 10 wt% IS precipitate sample which did not contain sodium titanate was determined to have a yield stress of 232 dynes/cm² at 25°C.⁴ Since this is consistent with the results obtained for the samples with sodium titanate, it was concluded that the sodium titanate does not affect the rheology of the precipitate except for the fact that it is an insoluble solid.

Conclusions and Recommendations

For the range of concentrations analyzed, the yield stress and plastic viscosity are directly proportional to the percent of insoluble solids in the concentrated TPB precipitate. The high concentrations of soluble salts in the unwashed samples were not observed to affect the rheology of the precipitate slurries. Also, the presence of sodium titanate was not found to affect the rheology of the precipitate.

Previously, it was determined that the yield stress of the washed precipitate is inversely proportional to the temperature.⁴ Therefore, it is recommended that if the Precipitation Process operating temperature significantly varies from 25°C, the temperature effect on the rheology of the unwashed concentrated precipitate should be studied.

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Quality Assurance

Test results were recorded in E35148, a registered E. I. DuPont de Nemours & Company laboratory notebook. The Haake viscometer was checked for accuracy with standardized oils - see Table 4.

References

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- ✓2. DPST-84-341, "Solubility of Sodium Oxalate and Sodium Tetraphenylborate in DWPF Supernate", L. L. Kilpatrick to M. A. Ebra, February 28, 1984.
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- ✓9. J. R. Van Wazer, J. W. Lyons, K. Y. Kims, and R. E. Colwell, Viscosity and Flow Measurement, Interscience Publishers, New York, 1963.

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TABLE 1

COMPOSITION OF UNWASHED CONCENTRATED PRECIPITATES

COMPOUND	Weight Percent				
	19.5% IS	13.4% IS	10.3% IS	7.2% IS	4.1% IS
H_2O	55.41	59.51	61.56	63.61	65.67
$NaNO_3$	13.23	14.21	14.70	15.19	15.68
$NaNO_2$	3.28	3.52	3.64	3.76	3.88
$NaOH$	2.77	3.18	3.39	3.60	3.82
Na_2CO_3	1.39	1.49	1.55	1.60	1.65
Na_2SO_4	1.59	1.71	1.77	1.82	1.88
$NaCl$	0.11	0.11	0.11	0.11	0.12
$NaAl(OH)_4$	2.69	2.89	2.99	3.10	3.19
$NaTPB^*$	6.64	4.57	3.52	2.46	1.40
$KTPB^*$	12.10	8.28	6.37	4.46	2.55
$NaTi_2O_5H^*$	0.76	0.52	0.40	0.28	0.16

*Insoluble Solids (IS)

TABLE 2.

COMPOSITION OF WASHED PRECIPITATES

COMPOUND	Weight Percent		
	8.8% IS	10.8% IS	12.9% IS
H_2O	88.82	86.51	84.23
NaNO_3	0.942	0.917	0.867
NaNO_2	0.234	0.227	0.219
NaOH	0.213	0.198	0.214
Na_2CO_3	0.100	0.095	0.092
Na_2SO_4	0.113	0.109	0.107
NaCl	0.308	0.577	0.777
NaAl(OH)_4	0.189	0.189	0.179
NaTPB	0.282	0.358	0.430
KTPB^*	8.28	10.21	12.11
$\text{NaTi}_2\text{O}_5\text{H}^*$	0.519	0.599	0.759

*Insoluble Solid (IS)

TABLE 3
TOTAL SOLIDS OF PRECIPITATES

Condition	% Insoluble Solids	Percent Total Solids		
		Exper.	Theor.	% diff
unwashed	4.1	32.21 ± 0.01	34.33	6.2
unwashed	7.2	33.87 ± 0	36.39	6.9
unwashed	10.3	35.84 ± 0.06	38.44	6.8
unwashed	13.4	37.61 ± 0.04	40.49	7.1
unwashed	19.5	45.83 ± 0.92	44.59	2.8
washed	8.8	11.87 ± 0.01	11.26	5.4
washed	10.8	14.45 ± 0.07	13.49	7.1
washed	12.9	17.30 ± 0.04	15.77	9.7

FIGURE 1

RHEOLOGY OF UNWASHED CONCENTRATED TPB PRECIPITATE

FIGURE 2

YIELD STRESS AS A FUNCTION OF THE CONCENTRATION

*Equation developed using unwashed precipitate.

NOTE: Linear equation developed for concentration range of 4.1 to 19.5%.
Do not extrapolate beyond this region.

FIGURE 3

YIELD STRESS OF CONCENTRATED TPB PRECIPITATE

FIGURE 4

PLASTIC VISCOSITY AS A FUNCTION OF THE CONCENTRATION

*Equation based on unwashed precipitate.

NOTE: Linear equation developed for concentration range of 4.1 to 19.5%.
Do not extrapolate beyond this region.

FIGURE 5

PLASTIC VISCOSITY OF CONCENTRATED TPB PRECIPITATE

FIGURE 6

APPARENT VISCOSITIES OF UNWASHED CONCENTRATED PRECIPITATE

FIGURE 7

RHEOLOGY OF WASHED PRECIPITATE

TABLE 4
VISCOSITY STANDARDS

oil type	Viscosity (cp) at 25°C		
	standard *	exper.	% deviation
Fluid-100	95	91	4.2
Fluid Blend	151	144	4.6
Fluid Blend	151	145	4.0
Fluid 500	490	450	8.2

*Brookfield Viscosity Standard

APPENDIX

CURVE FIT ANALYSIS

FIGURE 2

Linear fit:

$$Y = 37.6X - 109$$

$$*r^2 = 0.97$$

FIGURE 3

Linear fit:

$$Y = 45.5X - 220$$

$$r^2 = 0.84$$

Linear fit:

without pt. (19.7,919)

$$Y = 35.9X - 143$$

$$r^2 = 0.89$$

Power curve:

$$Y = 2.34X^{1.91}$$

$$r^2 = 0.90$$

Best curves

(linear fit was chosen because it was confirmed by the latest study)

Exponential curve:

$$Y = 24.3 e^{.19x}$$

$$r^2 = 0.87$$

FIGURE 4

Linear fit:

$$Y = 6.14X - 15.9$$

$$r^2 = 0.96$$

FIGURE 5

Linear fit:

$$Y = 7.3X - 21.4$$

$$r^2 = 0.78$$

Linear fit:

without pt. (19.7,188)

$$Y = 5.6X - 11$$

$$r^2 = 0.86$$

Exponential curve:

$$Y = 4.44 e^{.19x}$$

$$r^2 = 0.88$$

Best curves

(linear fit was chosen because it was confirmed by the latest study)

Power curve was not considered because it must pass through point (0,0).
This is an impossible condition since viscosity is always >0.

**r² is the coefficient of determination.*