RI 8498

Bureau of Mines Report of Investigations/1980

MASTER

Dewatering of Industrial Clay Wastes

By Annie G. Smelley, Bernard J. Scheiner,
and Jalna R. Zatko

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8498

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UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

BUREAU OF MINES
Lindsay D. Norman, Director

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the Bureau of Mines, U.S. Department of the Interior, and The University of Alabama.

This publication has been cataloged as follows:

Smelley, Annie G

Dewatering of industrial clay wastes.

(Report of investigations - United States, Bureau of Mines ; 8498)
Bibliography: p. 13.

1. Clay industries—Waste disposal. 2. Flocculation. 3. Polyethylene glycols. I. Scheiner, Bernard J., joint author. II. Zatko, Jalna R., joint author. III. Title. IV. Series: United States. Bureau of Mines. Report of investigations ; 8498.

TN23.U43 [TD899.C57] 622s [622'.5] 80-607955

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DEWATERING OF INDUSTRIAL CLAY WASTES

by

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ABSTRACT

As a part of research conducted in its mission to effect pollution abatement, the Bureau of Mines, U.S. Department of the Interior, is developing a dewatering technique that allows for disposal of clay wastes, for reuse of water now lost with clays, and for reclamation of mined land. The technique utilizes a high-molecular-weight nonionic polyethylene oxide polymer (PEO) that has the ability to flocculate and dewater materials containing clay wastes. In laboratory experiments, coal-clay waste, potash-clay brine slurry, phosphatic clay waste, uranium tailings, and talc tailings were successfully consolidated. Coal-clay waste was consolidated from 3.6 to 57 percent; potash-clay brine slurry was consolidated from 3.8 to 35 percent; phosphatic clay waste from 15.6 to 49 percent; uranium tailings from 15.4 to 67 percent; tailings from talc production from 9.7 to 53 percent; and an acidic TiO_2 slurr slurry from 1.68 to 30 percent.

INTRODUCTION

The processing of ores for the recovery of minerals such as phosphate (6),[3] potash (3), alumina (4), and coal (1) generally results in the production of ultrafine waste materials, which respond poorly to conventional physical separation and dewatering techniques. In many cases these ultrafine waste materials contain mineral values that represent a major loss of natural resources. Current mineral practices usually dispose of these fine-particle wastes by impoundment in settling ponds because current technology, in most cases, can recover neither ultrafine mineral values nor the water associated with these wastes. The settling ponds not only cover large land areas that are difficult to reclaim but also present a potential environmental hazard. The tremendous losses in resources--minerals, water, and land--plus the negative environmental aspects have created the need for an alternative disposal system.

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The Bureau of Mines is developing a dewatering technique for phosphatic clay slime waste (5) produced in Florida phosphate facilities. The technique consists of mixing the slime waste with a flocculant, polyethylene oxide (PEO), and dewatering the resulting agglomerate on a rotary screen. Slimes containing a nominal 3 percent solids have been dewatered to solids contents of 20 to 30 percent. This paper describes a series of laboratory investigations applying the Bureau-developed dewatering technique to a variety of ultrafine waste materials.

MATERIALS AND TEST PROCEDURE

Two different PEO polymers having molecular weights of 5 and 8 million, respectively, were used as flocculants in this study. Polyethylene oxide is a straight-chain, nonionic polymer consisting of repeating (CH_2-CH_2-O) groups. These polymers are available commercially from Union Carbide.[4]

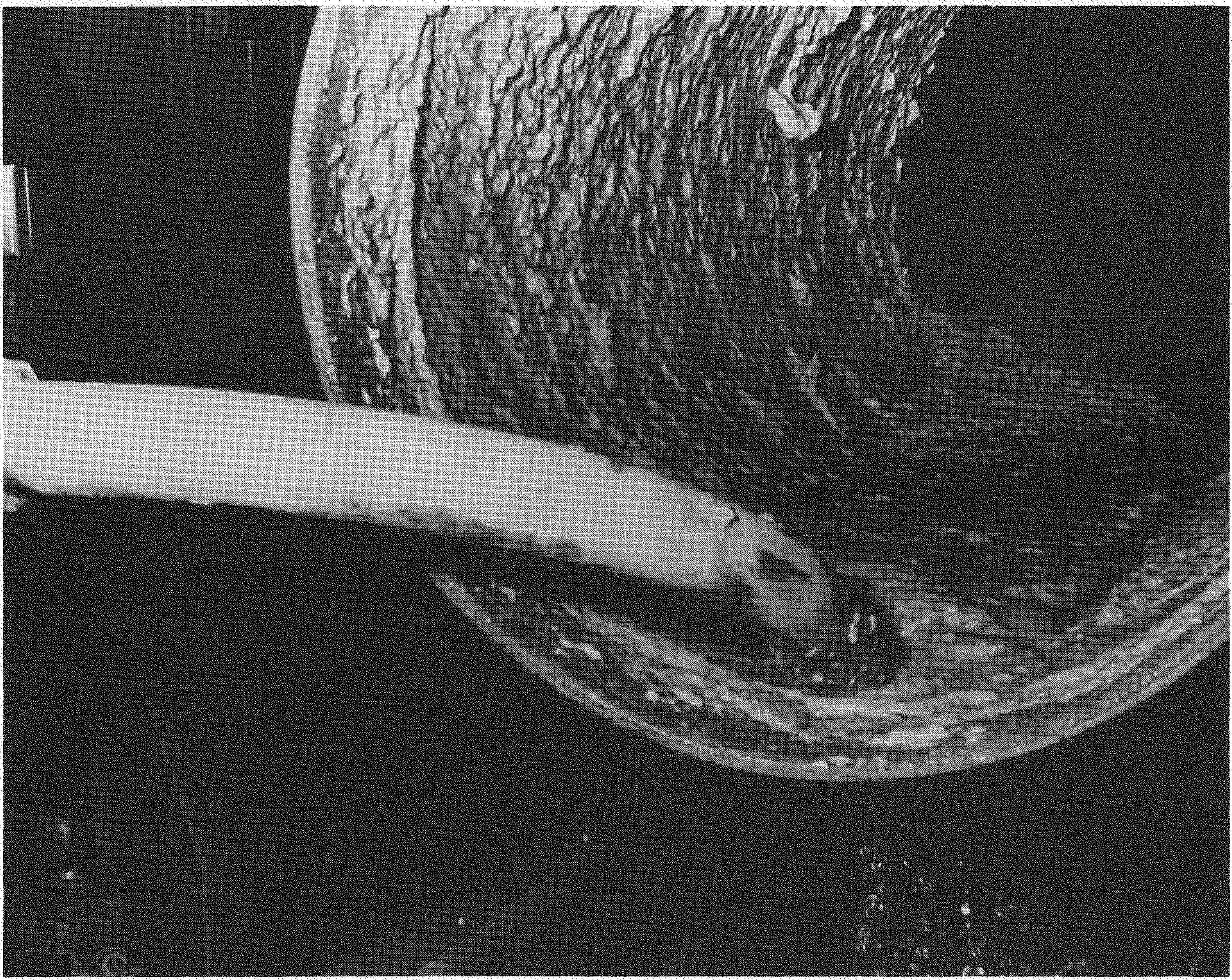

FIGURE 1. - Flocculated clay waste discharged from mixer through pipe into rotating screen.

[4]Reference to specific equipment or trade names does not imply endorsement by the Bureau of Mines.

When PEO is mixed with clay material in the proper manner, strong flocs are formed and water is released. If the released water is removed, the flocs will continue to agglomerate, and conversely, if the released water is not removed, the flocs will disintegrate within a few minutes. To accomplish the water removal quickly in continuous tests, the Bureau has developed a rotary screen method for use after batch tests have been conducted successfully on a clay waste. The rotary screen presently is being evaluated in large-scale experiments on Florida phosphatic clay waste. The flocced material flows onto the screen, as shown in figure 1, where the flocs initially move with the rotation of the screen. However, water is lost immediately, and the consolidated material forms a roll that proceeds down the screen and continues to dewater. In figure 3, the roll of dewatered material is being discharged from the rotary screen and pumped to disposal sites. The quality of water recovered from the clay waste also is evident in figure 2.

FIGURE 2. - Dewatered product discharged from rotating screen. Bottom of picture shows recovered water.

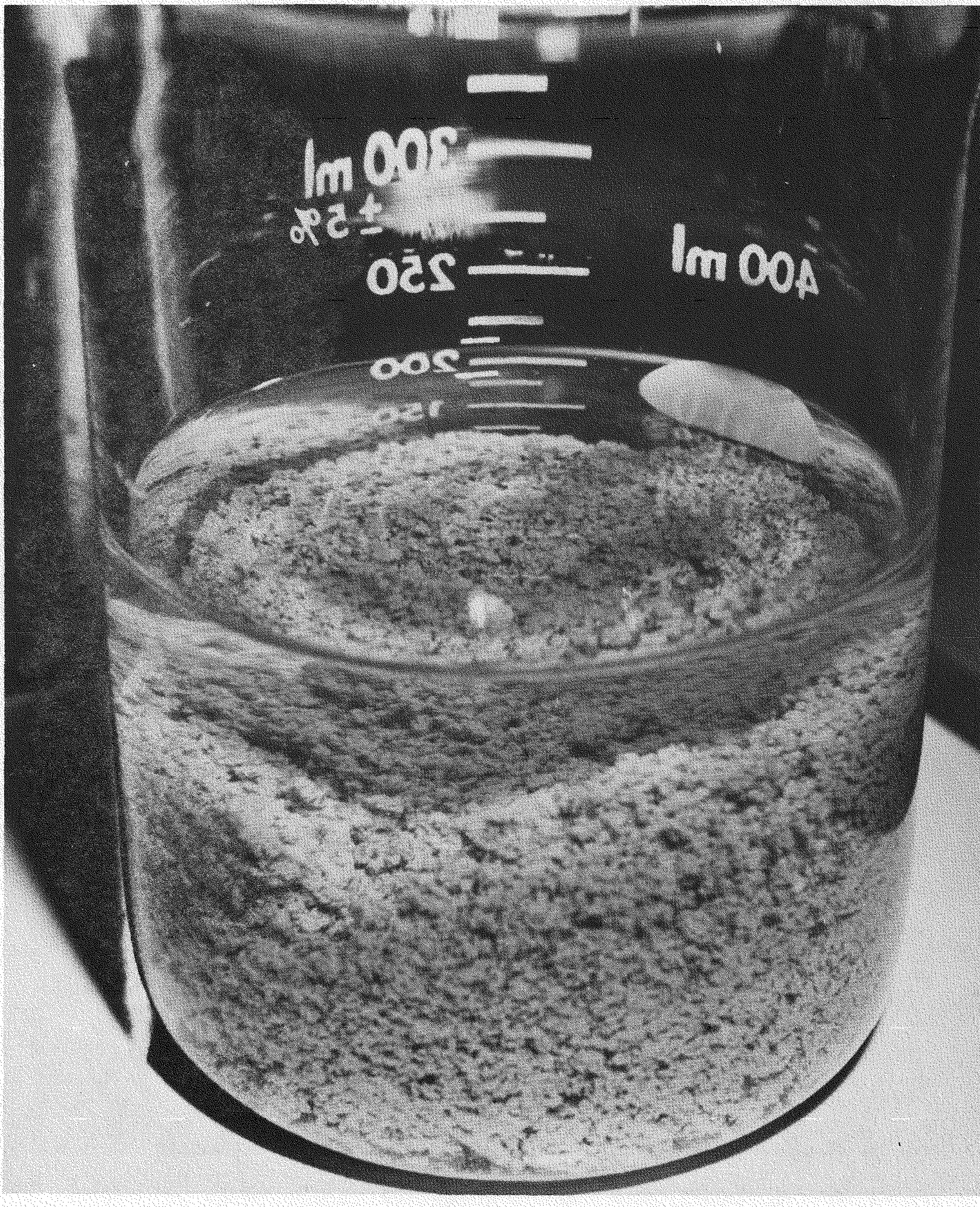

FIGURE 3. - Appearance of flocculated clay waste at completion of PEO addition.

Laboratory batch dewatering tests used for this study were conducted in the following manner: A slime sample of 200 ml was measured into a 400-ml beaker to which an appropriate amount of PEO was added. The mixture was stirred using a magnetic stirring bar, 1.25 to 1.5 in long, turning 500 to 550 rpm to create a vortex approximately 1 in deep. The PEO solution was added from a 10-ml burette at the rate of 1 drop per second. When consolidation of flocs began, both stirring and PEO addition were stopped momentarily at intervals, and the flocs were observed carefully as stirring was resumed. With continued PEO addition, flocculation reached the point where the individual flocs consolidated as shown in figure 3 and moved in the beaker as one mass. This was considered the end point. The supernatant water was decanted until the solid mass could be handled. Then it was picked up by the operator and squeezed until water no longer dripped from the mass. The released water was measured, and the solids content of the mass was determined. The burette was read to determine the amount of PEO used for calculation of dosage by the formula,

$$\text{Dosage, lb/ton} = \frac{\text{volume PEO, ml} \times \text{concentration PEO, g/ml} \times 2{,}000\ \text{lb/ton}}{\text{volume slime, ml} \times \text{density of slime, g/ml} \times \text{solids content of slime, g/g}}$$

The test procedure was varied slightly for the various waste materials. For instance, the potash-clay waste tests were conducted at 61° C to maintain the solubility equilibrium of the various salts in the brine solution.

EXPERIMENTAL RESULTS

Dewatering of Ultrafine Coal-Clay Waste

In the preparation of coal to remove impurities and to lower the ash content, the coal usually is sized by screening to remove the larger pieces of coal and then the finer material is subjected to froth flotation. The tails from the flotation consist of ultrafine material that is difficult to dewater. A typical dewatering system consists of adding 1 to 2 pounds of polymer per ton of solids and consolidating the waste in a thickener, followed by filtration in a leaf filter. As the clay content of the waste increases, dewatering of the material becomes difficult, and the thickener and filter capacities often are not adequate. A sample of flotation tailings was obtained from a West Virginia coal producer for laboratory investigation. Screen analysis of the material is shown in table 1.

TABLE 1. - Screen analysis of coal-clay waste

Size, screen mesh	Size distribution, percent
Plus 35	16.5
Minus 35 plus 65	8.6
Minus 65 plus 100	3.4
Minus 100 plus 150	19.8
Minus 150 plus 200	2.0
Minus 200 plus 270	3.3
Minus 270 plus 325	1.5
Minus 325	44.9
Composite total	100.0

Analysis of the minus 325-mesh fraction showed kaolinite, mica, quartz, and coal as the major constituents, along with minor amounts of chlorite and montmorillonite. Microscopic examination of the plus 325-mesh fraction showed the presence of coal, quartz, mica, and a considerable amount of microcrystalline material that appeared to be shale. The sample was received as a 3.6-percent slurry and was used in this form.

A series of dewatering tests was conducted using both the 5 million and 8 million molecular weight (mol wt) PEO's as flocculants. PEO concentration was varied between 0.05 and 0.25 percent. The results are summarized in table 2.

TABLE 2. - Flocculation dewatering of coal-clay waste

PEO, mol wt	PEO concentration percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6	0.25	1.6	56.2
	.10	2.0	48.9
	.05	1.4	55.3
8×10^6	.25	.6	54.1
	.10	.3	58.0
	.05	.2	56.8

[1]Initial solids content of 3.6 percent.

In the tests PEO dosages of 0.2 to 2.0 lb/ton increased the solids content of the dewatered product to 48.9 to 58.0 percent. The minimum dosages of 0.2 lb/ton for the 8 million mol wt PEO and 1.4 lb/ton for the 5 million mol wt PEO were obtained using the 0.05-percent solutions of PEO. This decrease in PEO dosage with a decrease in PEO concentration is in accord with previously reported research (5). As the PEO solution is diluted, the polymer uncoils and reaches maximum length in solution, therefore is more effective.

Dewatering of Potash-Clay Brine

A sample of potash-clay brine was obtained from a Carlsbad, N. Mex., facility in which potash is recovered by a hot leach sequence followed by liquid-solid separation in a series of thickeners. Typically, only 20 percent solids is obtained. An increase in solids content would increase potash recovery that is now being lost with the thickener underflow. The sample used in dewatering experiments is representative of clay-brine after leaching and prior to treatment in a thickener to separate the brine from the clay waste. Analysis of the slurry is shown in table 3.

TABLE 3. - Chemical analysis of total dissolved solids from potash brine

	Brine, percent
Potassium	14.9
Sodium	19.0
Magnesium	4.2
Sulfate (SO_4)	7.7
Chlorine	47.8
Water	6.4

The solids content of the clay brine of 3.8 percent was a mixture of halide salts and clays. The major clay mineral was montmorillonite. Before dewatering tests were conducted, the sample was heated to 61° C and stirred for 4 hours to simulate the conditions at the potash facility. This temperature was maintained during the dewatering tests by means of a water bath. A series of dewatering tests was conducted in which the PEO concentration was varied from 0.25 to 0.01 percent. A summary of the test results is shown in table 4.

TABLE 4. - Dewatering of potash-clay brine

PEO, mol wt	PEO concentration, percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6	0.25	22.9	40
	.10	6.2	36
	.05	4.5	36
	.01	1.7	35
8×10^6	.25	17.6	39
	.10	5.2	36
	.05	4.0	35
	.01	1.3	35

[1] Initial solids content of 3.8 percent.

Dewatered products of 35 to 40 percent solids were obtained using amounts of PEO ranging from 1.3 to 22.9 lb/ton. The required amount of PEO decreased dramatically as the concentration of PEO was decreased from 0.25 percent to

0.01 percent. A possible explanation for the unusually large decrease in dosage is that the PEO is only sparsely soluble in saturated brine, and diluting the brine reduces the amount of PEO precipitating out of solution. Therefore, more PEO is available to flocculate the clay waste. To determine the effect of dilution of the brine on PEO dosage, a series of experiments was conducted in which water was added to the clay-brine prior to PEO addition. The results are shown in table 5.

TABLE 5. - Effect of dilution on PEO dosage for potash-clay brine

PEO concentration, percent	Solids content after dilution,[1] percent	Dosage,[2] lb/ton	Solids content of dewatered product, percent
0.25	3.8	22.9	40
.25	2.9	19.1	36
.25	2.6	9.9	36
.25	2.2	10.1	36
.10	3.8	6.2	36
.10	3.5	6.4	35
.10	3.1	5.5	32
.10	2.9	4.7	35
.05	3.8	4.5	36
.05	3.5	4.0	33
.05	3.1	3.0	31
.05	2.9	2.8	34

[1] Initial solids of 3.8 percent, diluted with water prior to PEO addition.
[2] The 5 million mol wt PEO used for these experiments.

The PEO dosage decreased as the brine was diluted, while the solids content of the dewatered material remained essentially the same. These data indicate that the dosage required will be directly related to the amount of salts contained in the brine.

Dewatering of Senegal Phosphatic Clay Waste

Phosphatic clay waste containing 15 percent solids was obtained from an operating phosphate company in Senegal through the International Fertilizer Development Center located in Muscle Shoals, Ala. At present, only a small portion of the water is being recovered from the slimes.

X-ray analysis showed that apatite was the major constituent of the sample, which contained minor amounts of quartz, montmorillonite, and kaolinite. A series of experiments was conducted to determine the effect of PEO concentration on PEO dosage requirements. Concentration was varied from 0.25 to 0.01 percent. The results are summarized in table 6.

TABLE 6. - Dewatering of Senegal phosphatic clay waste

PEO, mol wt	PEO concentration, percent	Dosage, lb/ton	Solids content of dewatered product, percent
5×10^6...........	0.25	1.06	48
	.10	.92	49
	.05	.70	47
	.01	.39	45
8×10^6...........	.25	1.60	48
	.10	1.00	49
	.05	.74	48
	.01	.41	45

The tests showed that decreasing the PEO concentration from 0.25 to 0.01 percent reduced the dosage requirements from 1.06 to 0.39 lb/ton for the 5 million mol wt PEO and from 1.60 to 0.41 lb/ton for the 8 million mol wt PEO. The dewatered product ranged in solids content from 45 to 49 percent, showing little alteration of the results at the lower PEO concentrations. The overall results from this dewatering of the Senegal material were higher than results reported for PEO dewatering of Florida-type phosphatic clay waste (5), which typically dewaters to 35 percent solids in laboratory tests.

Dewatering of Uranium Mill Tailings

A sample of uranium mill tailings from a New Mexico mine was furnished by the Colorado School of Mines Research Institute (CSMRI). The material had been cycloned to remove the sand friction prior to dewatering experiments. The resulting material had a solids content of 15.4 percent and was 66 percent minus 325 mesh. The analysis showed 60 percent quartz, 20 percent plagioclase, 15 percent orthoclase, and 5 percent unidentified. A series of dewatering experiments was conducted, and the results are summarized in table 7.

TABLE 7. - Effect of PEO concentration on PEO dosage for uranium tailings

PEO, mol wt	PEO concentration, percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6...........	0.25	1.13	46
	.10	.46	49
	.05	.35	47
	.01	.39	42
8×10^6...........	.25	1.02	64
	.10	.50	60
	.05	.48	62
	.01	.18	67

[1]Initial solids content of 15.4 percent.

Decreasing the PEO concentration from 0.25 to 0.01 percent reduced the dosage from 1.13 to 0.39 lb/ton for the 5 million mol wt PEO with little ill effect on the dewatered product, and from 1.02 to 0.18 lb/ton for the 8 million mol wt PEO with increased solids content at 0.18 lb/ton. The results indicate that the uranium tailings are easy to consolidate, especially with the higher molecular weight polymer, since 67 percent solids was obtained with a PEO dosage of only 0.18 lb/ton.

Dewatering of Waste From Talc Mine

A sample of tailings from a talc-producing mine located in the Northeastern United States was obtained as a slurry containing 9.7 percent solids. At present, tailings at the talc facility are being impounded in a series of ponds. The overflow from these ponds often contains fine particles. To overcome this problem, a better dewatering sequence is needed.

A series of experiments was conducted to determine the effectiveness of PEO in dewatering this talc waste slurry. The results are summarized in table 8.

TABLE 8. - Dewatering of talc waste slurry

PEO, mol wt	Concentration, percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6..........	0.25	0.31	52
	.10	.12	52
	.05	.11	53
	.01	.03	42
8×10^6..........	.25	.16	53
	.10	.12	53
	.05	.08	50
	.01	.01	50

[1] Initial solids content of 9.7 percent.

The data indicate that only 0.01 lb/ton of the 8 million mol wt PEO was required to produce a consolidated material of 50 percent solids.

Dewatering of TiO_2-HCl-Fe-Cl Slurry

In the conversion of ilmenite to synthetic rutile by acid leaching, TiO_2 is often lost as fine particles with the spent leach liquor (2). This TiO_2 could be recovered if the spent liquor slurry could be dewatered. A sample of this type slurry with a solids content of 1.68 percent was obtained from an operating facility. Analysis of the slurry is shown in table 9.

TABLE 9. - Analysis of TiO_2-HCl-Fe-Cl Slurry

Constituent	Analysis, percent
Iron	10.3
HCl	3.3
Chlorine	12.6
Magnesium	.1
Aluminum	.16
Trace elements[1]	.1
Insolubles[2]	1.68
H_2O	73.7

[1]Nickel, vanadium, zinc, manganese, sodium, potassium, lead, calcium, chromium, and copper.
[2]Suspended particles of TiO_2.

A series of experiments was conducted to determine if PEO could be used to consolidate the TiO_2 particles. The results from these preliminary experiments are summarized in table 10.

TABLE 10. - Dewatering of TiO_2 slurry with PEO

PEO, mol wt	Concentration, percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6	0.25	0.36	5.1
	.05	.34	6.6
	.01	.30	5.7
8×10^6	.25	.36	4.5
	.05	.14	4.9
	.01	.10	5.1

[1]Initial solids content of 1.68 percent.

The flocs formed when the PEO was added were small as compared with other experiments described in this paper. The agglomerated material could be handled, but it contained large amounts of entrained solution. To determine if larger flocs could be produced by adding excess PEO, a second series of experiments was conducted. The results are shown in table 11.

TABLE 11. - Dewatering of TiO_2 slurry with excess PEO

PEO, mol wt	Concentration, percent	Dosage, lb/ton	Solids content of dewatered product,[1] percent
5×10^6..........	0.25	0.81	9.3
	.05	.66	5.8
	.01	.41	5.9
8×10^6..........	.25	.59	12.7
	.05	.33	8.4
	.01	.30	6.8

[1]Initial solids content of 1.68 percent.

The data show that the solids contents increased when compared to experiments using lower dosages of PEO. The best result obtained was 12.7 percent solids using a PEO dosage of 0.59 lb/ton.

The PEO agglomerated material continued to dewater with time. To take advantage of this behavior, TiO_2 slurry was treated with the 8 million mol wt PEO at a dosage of 0.35 lb/ton and the resulting agglomerate placed on a bed of coarse sand. In 24 hours the agglomerate had dewatered to 30 percent solids. The dewatered material had handling characteristics that could be handled by mechanical means, such as with a front-end loader.

CONCLUSIONS

Polyethylene oxide has been successfully used as a flocculant in laboratory scale tests to dewater a variety of clay waste materials:

1. Coal-clay waste from 3.6 to 57 percent.

2. Potash-clay brine from 3.8 to 35 percent.

3. Phosphate clay waste from 15.6 to 49 percent.

4. Uranium tailings from 15.4 to 67 percent.

5. Tailings from talc production from 9.1 to 53 percent.

6. Acid TiO_2 slurry from 1.68 to 30 percent.

In a majority of wastes treated, the 8 million mol wt PEO was superior to the 5 million mol wt PEO. Larger scale experiments will be required to evaluate the commercial potential of the PEO dewatering technique for the various materials tested.

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☆U.S. GOVERNMENT PRINTING OFFICE: 1980-603-102/125

INT.-BU.OF MINES,PGH.,PA. 24922