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Separation of Flue-Gas Scrubber Sludge into Marketable Products

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Introduction

To reduce their sulfur emissions, many coal-fired electric power plants use wet flue-gas scrubbers. These scrubbers convert sulfur oxides into solid sulfate and sulfite sludge, which must then be disposed of. This sludge is a result of reacting limestone with sulfur dioxide to precipitate calcium sulfite and calcium sulfate. It consists of calcium sulfite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and unreacted limestone (CaCO_3) or lime (Ca(OH)_2), with miscellaneous objectionable impurities such as iron oxides, silicates, and magnesium, sodium, and potassium oxides or salts (Goldstein, 1990). These impurities prevent many sludges from being utilized as a replacement for natural gypsum, and as a result they must be disposed of in landfills, which presents a serious disposal problem (Carnahan, 1993).

Knowledge of scrubber sludge characteristics is necessary for the development of purification technologies which will make it possible to directly utilize scrubber sludges rather than landfilling them. This project is studying the use of minimal-reagent froth flotation as the purification process, using the surface properties of the particles of unreacted limestone to remove them and their associated impurities from the material, leaving a purified calcium sulfite/gypsum product.

The objectives of this project are to:

- 1 Investigate how the surface properties of the scrubber sludge particles change as the conditions in the solution change, and determine the properties of scrubber sludge that will control its behavior in separation processes.
- 2 Examine the ability of various froth-flotation processes to separate the various components based on differences in their surface chemistry.
- 3 Determine methods for accomplishing the separation without adding additional chemical hazards to the environment.

These objectives will be accomplished by analysis of the composition and flotation behavior of scrubber sludges from various sources. This will lead to the development of a novel application of froth flotation to produce a clean separation with a minimum of reagents. Analysis of the sludge will be carried out using both standard analytical techniques and specialized methods developed for this purpose at Michigan Technological University.

Since the surface chemistry of the solid particles in scrubber sludge is not well known, this project will provide a good deal of basic information which is not currently available from any source. This information is critical to both the purification and the effective utilization of the sludge, since seemingly small changes in surface chemistry can have a disproportionate effect on the overall properties of the material.

Quarterly Report #1 described the collection and preparation of sludge samples from three coal-fired power plants, the preparation of these samples for use in the planned studies, and the results of their characterization by X-ray diffraction. In Quarterly Report #2, initial froth flotation studies using conventional flotation equipment were summarized. These flotation studies determined that a good separation of limestone from the sludge could be made using a cationic collector. A reverse flotation process was used, with the sinks

product being the purified material, and the froth product being the rejected impurities. Quarterly report #3 described the results of column flotation of the scrubber sludge. It was determined that the column provided better removal of unreacted limestone than was possible with conventional flotation, due to its inherently higher selectivity. However, limestone content in the useful product was still too high for industrial use. Initial studies of the zeta potentials of the most important components found in scrubber sludge were also described. Quarterly report #4 and report #5 continued the zeta potential studies of the major components in the scrubber sludge. These studies included the effect of the following factors on zeta potential: pH, dissolved salts, collector type, and concentration of collector. Quarterly report #6 investigated the optimum frother type and frother dosages to use for the flotation of limestone. This optimization was needed because previous flotation tests were unable to provide a clean enough product for industrial use. Several frothers were studied: DF200, DF250, DF400, and DF1012. DF200 proved to be the most selective of the frothers studied for the removal of limestone. Quarterly report #7 continued the optimization of operating parameters for the flotation of unreacted limestone, CaCO_3 . Along with the investigation of a new collector, S 701, developed by Dow Chemical Company, Midland, MI, a gypsum depressant was also investigated. The gypsum depressant used was gelatin, a water soluble protein (Sutherland and Wark, 1955). A new two-inch cyclone test rig was also designed and constructed during this quarter, to be used for pre-treating the sludge before flotation. Quarterly report #8 investigated the effect of different flotation collectors on the surface charge of the main components of wet flue-gas scrubber sludge. These components were calcium sulfite, calcium sulfate (gypsum) and calcium carbonate (unreacted limestone). Aero 870, a Cytec collector, proved to be the most promising flotation collector studied. Further laboratory work will be done to verify these results. Quarterly report #9 continued the investigation of optimizing a two inch water-only cyclone. The proper vortex finder, spigot diameter, and inlet feed pressure were determined. Quarterly report #10 concluded the water-only cyclone study. Water-only cycloning provided the initial separation step for removing unwanted limestone from the scrubber sludge. The overflow from the cyclone could then be processed by froth flotation to provide a useful calcium sulfite/sulfate product which was within grade requirements for producing commercial gypsum (less than 2.0% limestone by weight). The operating conditions of the water-only cyclone that provided the best material for froth flotation were: vortex finder of 11 mm, spigot diameter of 5 mm, an inlet feed pressure of 45 psi, and weight percent solids of 5.0% for the inlet slurry.

In the current quarter, research was focused on verifying the zeta potential results which predicted that an Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) would be the best flotation collector to separate unreacted limestone (CaCO_3) from calcium sulfite ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$). This froth flotation study investigated the behavior of two types of feed materials. The first feed was raw scrubber sludge, which had not been pre-treated and which was found to show poor flotation characteristics. The second feed was scrubber sludge which had been pre-treated by water-only cycloning, which removed a portion of the calcium carbonate, and also improved the flotation characteristics of the feed.

Progress During the Eleventh Quarter

One of the goals of this project was to separate the impurities (calcium carbonate and silicates) from wet flue-gas desulfurization scrubber sludge and to use the end products, calcium sulfite (easily oxidized to gypsum) and calcium sulfate (gypsum), as raw materials for the wallboard or plaster industries. Froth flotation was selected as the purification method because it works well for the separation of small particles and is a proven technology that has been commercially successful in other applications (Roe, 1983). However, froth flotation was unable to provide a suitable separation when raw Duck Creek scrubber sludge was used. There were several possible reasons for the lack of a suitable separation, as follows:

- Large particle size of some of the impurities, which made them difficult to recover by froth flotation.
- Lack of a clean surface on the calcium carbonate (unreacted limestone). Flotation is based on the surface properties, not the bulk properties. In order for a separation to occur, the particles being separated must have surfaces that are chemically distinct from the other particle types.

These two possibilities led to the decision to pre-treat the sludge by hydrocycloning before flotation. Hydrocycloning would easily remove the larger, more dense calcium carbonate (unreacted limestone) and ball mill chips, and also provide a scrubbing effect which would provide new, clean surfaces on the remaining calcium carbonate (unreacted limestone). This would improve preferential adsorption of collecting reagents onto unreacted limestone particles. This two stage separation method (water-only cycloning and froth flotation) was capable of producing a useful calcium sulfite/sulfate product with below 2.0% limestone by weight. The first part of this report reviews the effect of floating raw scrubber sludge with a cationic collector and the second part investigates the effect of froth flotation on scrubber sludge that has been pre-treated by water-only cycloning.

Experimental

Materials

The scrubber sludge investigated in this work was from a natural-oxidized scrubber, Plant A. A complete characterization of this scrubber sludge can be seen in Quarterly Report #1. This plant was selected for two reasons. The first was that there are a larger number of flue-gas scrubbers which use natural-oxidation of the sludge than there are that use force-oxidation. The second was that the presence of calcium sulfite in the natural-oxidized scrubber was expected to hinder the separation process for removing unreacted limestone. Therefore, if a clean product could be obtained from a natural-oxidized scrubber, a clean product could certainly be obtained from a forced-oxidized scrubber.

Two different types of feed material were investigated to determine which would lead to the highest-quality product after processing, with the goal being to obtain a product containing less than 2.0% limestone by weight. The first material investigated was raw, unprocessed scrubber sludge from the plant, with the size distribution shown in Figure 1. The limestone grade was 5.6 +/- 0.30% by weight. The second material investigated was scrubber sludge from the same

source, but which had been pre-treated by water-only cycloning prior to flotation, and had the size distribution shown in Figure 2. The limestone grade of this material was 2.89 +/- 0.10%, with a weight recovery of 75.6% by weight from the cyclone.

Figure 1: Size distributions of raw scrubber sludge, and of the fine limestone which was added to the scrubber before it was reacted with sulfur oxides. Size distributions were determined by Microtrac size analysis (laser diffraction).

Figure 2: The size distribution of the products of water-only cycloning, where the underflow is the limestone-rich waste product. These size distributions were determined by Microtrac size analysis. The overflow material was further processed with froth flotation to remove the remaining limestone impurities.

Froth Flotation Test Procedure

The procedure for conventional froth flotation experiments was as follows:

- The laboratory scale Denver flotation machine and 2.5 liter working volume cell were thoroughly washed out with water and dried.
- 2.5 liters of scrubber sludge-saturated water (to minimize dissolution) was added to the flotation cell.
- A 115 gram sample was then added to the cell as the impeller was running. The suspension was allowed to condition for 2 minutes. The impeller speed was set at 1250 rpm.
- The appropriate amount of collector was added and the suspension was conditioned for another 2 minutes.
- Frother was then added and conditioning continued for 15 seconds.
- The air valve was opened to start flotation by allowing air bubbles to enter the pulp. The material was hand scrapped into a tared pan until the test was finished, 5 minutes for these experiments.
- The floated material was then weighed, and a sample of the slurry was taken for pH and temperature measurements.
- The flotation products were then filtered, dried at 40°C, and prepared for chemical analysis.
- Each test condition was repeated in order to calculate an average and standard deviation.

Flotation Reagents

Since only a limited amount of information was available to develop a process for floating a limestone material from a calcium sulfite/sulfate material, it was necessary to carry out a detailed zeta potential study to determine which type of collector was best suited for this separation as was described in Quarterly Report #8. Cationic collectors were determined to have a strong attraction for the negative surface of limestone and silica, and a minimal effect on calcium sulfite at a natural pH. This was due to the surface charge being more negative for the impurities (limestone and silica) than the useful products (calcium sulfite/sulfate). Therefore the premise of this separation was that a cationic collector would preferentially adsorb to the surfaces of the limestone first because of the limestone's greater negative surface charge. Zeta potential results predicted that the cationic collector that had the highest probability of preferentially adsorbing to the surfaces of the limestone was an Ethoxylated Octadecylamine-Octadecylguanidine Complex (Aero 870), which is produced by Cytec.

A polypropylene glycol methyl ether (Dow Froth 200) with a molecular weight of approximately 200 was selected as the frother for all experiments. This frother was used because it was a biodegradable reagent that would break down after the material has been removed from the

flotation cell, and because this had been found in previous tests to be the most selective frother for this purpose. The dosage of frother was determined by the minimum amount needed to form a stable froth. A complete list of the test conditions for froth flotation experiments is given in Table 1.

Table 1 List of experimental conditions for froth flotation experiments

Type of Feed Material	Dosage of Frother (Dow Froth 200) Kg/mt	Dosage of Cationic Collector (Aero 870) Kg/mt
Raw Scrubber Sludge with a Limestone Concentration of 5.6 +/- 0.3% by weight.	0.20	0.050
		0.100
		0.200
		0.300
Scrubber Sludge that had been Pre-Treated with Water-Only Cyclone. Limestone Concentrations was 2.9 +/- 0.10.	0.10	0.050
		0.100
		0.200
		0.300

Results and Discussion

Flotation of Raw Scrubber Sludge, with No Pre-Treatment

The results of floating raw scrubber sludge are shown in Figures 3 and 4. The pH in these tests varied from 7.40 to 7.65 and the pulp temperature varied from 20.2 °C to 21.2 °C. The removal of unreacted limestone that was achieved in these tests is shown in Figure 3. The reduction of limestone in the calcium sulfite/sulfate increased as collector dosage was increased. The cleanest product was obtained at a collector dosage of 0.3 Kg/mt, and the limestone content of the product was reduced to 4.30% +/- 0.09 limestone by weight. This reduction in limestone grade was expected because the collector was adsorbing over a progressively larger proportion of the limestone surface as the dosage increased. However, further increases in collector dosage were not practical, because high collector dosage interfered with the properties of the frother. This was observed as a breaking down of the froth layer and the formation of large coalesced bubbles. Figure 4 compares the effect of weight recovery versus collector dosage for these tests. The weight recovery of useful product continued to decrease as collector dosage was increased. This was also expected because of the collector adsorbing to a large quantity of negative surface sites. The weight recovery for the lowest grade (4.30% +/- 0.09 limestone) material was 71.9% +/- 2.4. The theoretical best results for floating raw scrubber sludge would be a grade of 0.0% limestone (a grade of below 2.0% limestone for industrial use) in the useful product and a weight recovery of

94.4% solids by weight of the useful product. The best results obtained from this stage of the investigation was a grade of 4.30% $\pm$ 0.09 limestone in the useful product with a weight recovery of 71.9% $\pm$ 2.4. Further increases in collector dosage were not expected to improve these results.

There were several possible reasons for why the flotation of the raw scrubber sludge did not reduce the limestone content to below 2% by weight:

- Large particle size of some of the impurities, which made them difficult to recover by froth flotation.
- Lack of exposed surfaces of calcium carbonate (limestone). Flotation is based on the surface properties, not the bulk properties. In order for a separation to occur, the particles being separated must have surfaces that are chemically distinct from the other particle types.

Limestone Grade in Calcium Sulfitite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 3: Variation of limestone grade in the valuable product (calcium sulfitite/sulfate) as a function of increasing collector dosage (Aero 870) for raw scrubber sludge feed. Limestone impurity was decreased at higher collector dosages. These results confirm the prediction from the zeta potential results that Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) would be an effective collector for removing unreacted limestone from scrubber sludge.

Weight Recovery of Calcium Sulfite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 4: Weight recovery of valuable product (calcium sulfite/sulfate) compared with collector dosage for raw scrubber sludge feed. The continues decrease in weight recovery at higher collector dosage was expected due the collector adsorbing to a larger quantity of unwanted limestone particles and also to highly charged calcium sulfite/sulfate particles.

Effect of Floating Scrubber Sludge After Cyclone Pre-Treatment

The results of water-only cycloning of the scrubber sludge were reported in Quarterly Reports #9 and #10. Water-only cycloning was beneficial in reducing the raw scrubber sludge from a limestone grade of 5.6% to 2.9% by weight in the overflow product of the cyclone. Water-only cyclones separate based on the difference in specific gravity of the particle, and to some degree by the difference in size of the particles. They therefore remove the largest, highest specific gravity particles from the scrubber sludge which tend to be unreacted limestone particles. The second possible benefit was the scrubbing of the limestone particles. It has been hypothesized by this research that during the wet flue-gas desulfurization process a calcium sulfite coating can occur on the surface of the limestone, preventing complete dissolution of the limestone. This layer would have a detrimental effect on flotation efficiency if it was not removed.

The results of floating scrubber sludge that had been previously treated with a water-only cyclone are given in Figure 5 and 6. The pH in these tests varied from 7.00 to 7.37, and the pulp temperature varied from 20.5°C to 20.9°C. Successful results were obtained as the collector

dosage was increased. The optimum reduction in limestone impurity (~1.70% limestone by weight in the valuable calcium sulfite/sulfate product) occurred at collector dosage of 0.20 Kg/mt. This met the target value of less than 2% limestone by weight, and provides a method for producing a clean calcium sulfite/sulfate product, which could be used for the production of wallboard. Figure 6 shows the effect of weight recovery verse collector dosage. As the collector dosage was increased, a decreased in weight recovery of useful product was observed. This was similar to the effect seen in the flotation of raw scrubber sludge. However, at a collector dosage of 0.30 Kg/mt, an increase in weight recovery was observed. This was due to the high collector concentration reacting with the frother, and reducing the stability of the froth layer. This resulted in more material falling out of the froth back into the flotation cell.

Limestone Grade in Calcium Sulfite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 5: Limestone content remaining in the valuable product (calcium sulfite/sulfate) as a function of collector dosage, for scrubber sludge that had been previously treated with a water-only cyclone before flotation. Limestone impurity decreased as collector dosage increased until a minimum limestone grade (~1.70% limestone by weight) was achieved at a collector dosage of ~0.20 Kg/mt. The combined separation strategy of water-only cycloning and froth flotation produced a calcium sulfite/sulfate that was clean enough to be use as a synthetic gypsum.

Weight Recovery of Calcium Sulfite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 6: Weight recovery of valuable product (calcium sulfite/sulfate) as a function of collector dosage, for scrubber sludge that had been processed through a water-only cyclone prior to froth flotation. Weight recovery decreased as collector dosage was increased until a minimum weight recovery (~87.0% by weight) was reached at a collector dosage of approximately 0.20 Kg/mt.

Conclusions

The success of floating raw scrubber sludge verified the results of earlier zeta potential studies, which had predicted that a cationic collector, Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) would be an effective reagent for removing unreacted limestone from scrubber sludge by froth flotation.

The complete removal of limestone (below 2.0% limestone by weight) from raw scrubber sludge was hindered by two factors: 1. The presence of large limestone particles made it impossible to remove all of the limestone by flotation, and 2. The formation of a calcium sulfite layer on the surface of the limestone during the scrubbing process prevented the collector from adsorbing properly on the limestone surfaces.

A clean calcium sulfite/sulfate product could be produced by froth flotation when raw scrubber sludge was processed in a water-only cyclone prior to flotation. The overall grade of the clean product was approximately 1.70% limestone by weight, with a weight recovery of nearly 66%.

Plans for the Twelfth Quarter

Work will continue on determining the surface properties of the limestone, with particular attention to the mechanisms by which cycloning increases the effectiveness of the flotation separation. The understanding of these properties is crucial for the development of an efficient separation of the materials being investigated (limestone, silica, and calcium sulfite/sulfate). This continued investigation of surface properties will be started with a review of spectroscopic techniques used to examine surface properties of minerals. This review will result in the determination of an appropriate method for determining surface properties of limestone in scrubber sludge. After this spectroscopic method has been selected a sample procedure will be developed to examine the scrubber sludge samples.

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