Separation of Flue-Gas Scrubber Sludge into Marketable Products

Second Year, Fourth Quarterly Technical Progress Report

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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 (CaSO₃•0.5H₂O), gypsum (CaSO₄•2H₂O), and unreacted limestone (CaCO₃) or lime (Ca(OH)₂), with miscellaneous objectionable impurities such as iron oxides, silica, 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 properties of scrubber sludge that will control its behavior in separation processes, and determine how the surface properties of the sludge particles change as the conditions in the solution change.

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 species 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, and concentration of collector. Quarterly report #6 investigated the optimum frother 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, CaCO₃. 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 hydrocyclone test rig was also designed and constructed during this quarter.

In the current quarter, zeta potential measurements were used to optimize the operating parameters for the flotation of unreacted limestone. Several different types of collectors were selected for study based on the observed characteristics of the scrubber sludge and discussions with industrial researchers. These collectors included anionic, non-ionic and cationic collectors. The goal of this quarter was use zeta potential measurements to determine which collector would have the highest affinity for unreacted limestone.

**Progress During the Eighth 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 which has been commercially successful (Roe, 1983). Before froth flotation work could begin, it was necessary to perform zeta potential measurements under various conditions to select the best reagents and their optimum dosage level. These measurements were performed on calcium sulfite and calcium carbonate, both of which were obtained as reagent-grade powders. Calcium carbonate was investigated because it is the most significant impurity by weight in the flue-gas scrubber sludge. Calcium sulfite was also investigated because it makes up approximately 80% of flue-gas scrubber sludge material. Reagent-grade powders were selected because they were free of contaminants that would tend to obscure the results. Each powder was tested at several different collector concentrations.
Experimental

Measurement Procedure:
Calcium sulfite (CaSO₃·0.5H₂O), calcium sulfate (CaSO₄·2H₂O) and calcium carbonate (CaCO₃) were purchased from Pfaltz and Bauer Chemicals as reagent-grade powders, and the silica was obtained from the U.S. Silica Company (Table 1). Suspensions were prepared by mixing distilled water and collector to give the desired concentration, then suspending 0.1 grams of the desired powder in 140 ml of each solution. The suspensions were allowed to stand for 2 hours to equilibrate completely. The pH and zeta potentials for each solution were then measured. All the pH measurements were between 6.8 and 7.6, which corresponds to the natural pH of the scrubber sludge. All zeta potential measurements for this study were made using a microelectrophoresis zeta meter. Zeta potential measurements were repeated by filling the zeta-meter cell with a suspension, measuring the zeta potential twice, draining the cell, refilling with the same suspension, and measuring the zeta potential two more times, for a total of four measurements.

Table 1: Description of the reagent grade powders used for zeta potential studies

<table>
<thead>
<tr>
<th>Type of Powder</th>
<th>Chemical Supplier</th>
<th>Particle Size, 80% Passing Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Sulfite</td>
<td>Pfaltz &amp; Bauer, Waterbury, CT</td>
<td>82 microns</td>
</tr>
<tr>
<td>Calcium Sulfate</td>
<td>Pfaltz &amp; Bauer, Waterbury, CT</td>
<td>84 microns</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>Pfaltz &amp; Bauer, Waterbury, CT</td>
<td>20 microns</td>
</tr>
<tr>
<td>Silica</td>
<td>U.S. Silica Co., Ottawa, IL</td>
<td>47 microns</td>
</tr>
</tbody>
</table>

Types of Collectors

For this study, anionic, non-ionic and cationic collectors were selected to determine which type of collector would be best suited for scrubber sludge purification (Table 2). The collector types and concentrations were selected based on the results of our earlier zeta potential studies and on technical discussions with various scientist in industry. Collector concentrations tested were at 0.0, 0.01, 0.02, 0.05, and 0.10 grams per liter, (0.0, 14.0, 28.0, 70.0, and 140.0 Kg/mt). These reagent dosages are approximately 100 times higher than would be used in froth flotation, because zeta potential measurements are made at extremely low particle loadings.
Table 2: Characteristics of collectors selected for this study

<table>
<thead>
<tr>
<th>Collector</th>
<th>Chemical Structure</th>
<th>Collector Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aero 845</td>
<td>Tetrasodium N-(1,2-dicarboxyethyl-N-octadecyl sulfosuccinamate)</td>
<td>Anionic</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>Fatty Acid</td>
<td>Anionic</td>
</tr>
<tr>
<td>S 701</td>
<td>1-(Ethylthio) Octane Poly(oxy(methyl-1,2-ethanediyl)), α-hydro-o-hydroxy-</td>
<td>Non-Ionic</td>
</tr>
<tr>
<td>Ether Primary Amine</td>
<td>1-Propanamine, 3-(C_{8-10}-alkoxy)</td>
<td>Cationic</td>
</tr>
<tr>
<td>Aero 870</td>
<td>Ethoxylated Octadecylamine-Octadecylguanidine Complex</td>
<td>Cationic</td>
</tr>
</tbody>
</table>

Results and Discussion

When analyzing the zeta potential data with the various collectors two areas were of interest. The first was the degree of adsorption of the collector on the particles. This was determined by analyzing the slope of the zeta potential curve. The adsorption of a collector is indicated by an increase or decrease in the zeta potential. The steeper the slope of the zeta potential curve, the greater the adsorption of the collector on the particle. The second area of interest was the point at which a plateau occurred on the zeta potential curve. This point indicates the maximum amount of collector that needs to be added. The relative positions of the plateaus for a given collector is a measure of the affinity of the collector for a particular particle. Therefore, the distance between the plateaus of the zeta potential curves for calcium carbonate and calcium sulfite should be large if a superior separation is to be achieved.

Effect of Anionic Collectors

Anionic collectors have a negatively-charged polar group. These types of collectors did not have a pronounced effect on the zeta potentials of calcium carbonate and calcium sulfite (Figures 1 and 2). This was due to the negative surface charge of the calcium carbonate and calcium sulfite in distilled water ($\zeta = -24.1$ mV and $\zeta = -10.0$ mV respectively where $\zeta$ is the zeta potential of the particle), which repelled the collector from the particle surface. Because of similar charges (negative) on the particle surfaces and the collector, any adsorption of the collector on the surface of the calcium sulfite and calcium carbonate was by replacement of existing anions, and so little alteration in charge occurred. There was no chemical adsorption of either of these collectors, which would have been seen as an increasingly negative zeta potential at an increasing collector concentration. This was evident because the zeta potential varied only slightly with collector concentration for anionic collectors.
Zeta Potentials in Aero 845 Solutions

Figure 1. Aero 845 is an anionic collector produced by Cytec Industries Inc. (Bountiful, UT). The negative charge of the particles and the collector lead to a condition of repulsion. Therefore, the collector does not readily adsorb on the particles. This is evident by the near zero slope of the zeta potential curves.

Zeta Potentials in Oleic Acid Solutions

Figure 2. Oleic Acid is an anionic collector. Once again the collector is not strongly adsorbed on the particle surface.
Effect of Non-Ionic Collectors

A non-ionic collector was also investigated in this study to determine its potential for separating calcium carbonate from calcium sulfite. This collector had no effect on the surface charge of the calcium carbonate and the calcium sulfite (Figure 3). This was expected because when a non-charged collector adsorbs onto the surface of a particle, a change in the surface charge of the particle does not occur. This is evident by the near zero slope of the zeta potential curves for calcium carbonate and calcium sulfite.

![Zeta Potentials in S 701 Solutions](image)

Figure 3. S 701 is a non-charged collector produced by Mineral Reagents International (Midland, MI). This collector had no effect on the surface charge of the calcium carbonate or the calcium sulfite. This is evident because the curves are parallel to each other and the slopes of the zeta potential curves do not change.

Effect of Cationic Collectors

Cationic collectors are those whose polar group has a positive charge. These types of collectors had a much more pronounced effect on the zeta potential of calcium carbonate and calcium sulfite than the anionic and non-ionic collectors did (Figures 4 and 5). This effect would be expected due to the attractive forces between the positive charge of the collector and the negative surface of the particles. Even though both calcium carbonate and calcium sulfite have negative surface charges and would be attracted to the positive charge of the collector, a separation can still be made if the collector has a stronger affinity for one of the particles. This would show up as a large difference in the plateaus of the zeta potential curves of the particles studied. Aero 870, a Cytec collector, was a much better collector for the separation of calcium carbonate than Ether Amine because
Aero 870 adsorbed on the calcium carbonate at a very low concentration. This can be seen by comparing the steepness of the slope of the zeta potential curves for the Aero 870 to the slope of the curves using Ether Amine. Aero 870 also shows a higher affinity for calcium carbonate than for calcium sulfite as is indicated by the difference in the zeta potential plateaus, ($\zeta = 60.0$ mV for calcium carbonate, compared to $\zeta = 23.0$ mV for calcium sulfite). The higher affinity of Aero 870 for calcium carbonate would indicate that this is a suitable collector for separation of calcium carbonate from calcium sulfite by froth flotation.

Zeta Potentials in Ether Amine Solutions

![Zeta Potential Graph](image)

Figure 4. Ether Amine is a cationic collector. The zeta potential curves for calcium sulfite and calcium carbonate are parallel until a concentration of 0.05 g/L is reached. After this point the slope of the calcium carbonate curve becomes steeper than the slope of calcium sulfite curve. The steeper slope indicates that calcium carbonate is preferred over calcium sulfite above this concentration.
Figure 5. Aero 870 is a cationic collector produced by Cytec Industries Inc. (Bountiful, UT), which shows the best potential for aiding a separation between calcium carbonate and calcium sulfite. The higher zeta potential plateau for calcium carbonate over the calcium sulfite indicates that the collector has a higher affinity for calcium carbonate.

**Effect of Cationic Collector on Silica**

Cationic collectors have a better potential for removing calcium carbonate from calcium sulfite than anionic or non-ionic collectors. However, there are other materials that are in flue-gas desulfurization scrubber sludge that must also be removed, such as silica. Therefore zeta potential curves were also determined for silica. Due to the superior nature of Aero 870, the zeta potential curve for silica was determined with this collector (Figure 6). The silica zeta potential curve falls between the zeta potential curves for calcium carbonate and calcium sulfite. This indicates that the collector has a stronger affinity for the calcium carbonate than for silica. The collector also has a higher affinity for silica than for calcium sulfite. Therefore this collector has the potential to remove the majority of the impurities (calcium carbonate and silica) from wet flue-gas desulfurization scrubber sludge.
Figure 6. The zeta potential curve for silica lies between the calcium carbonate and calcium sulfite curves, indicating that both calcium carbonate and silica are preferred over calcium sulfite by the collector. Therefore, Aero 870 can possibly be used to separate calcium carbonate and silica (which are the impurities) from calcium sulfite.

Conclusions

1. Cationic collectors had a larger effect on the calcium carbonate and calcium sulfite zeta potential than the anionic collectors did. This indicates that cationic collectors interact more strongly with the particle surfaces, and are therefore more likely to be useful collectors.

2. A non-ionic collector had no effect on the surface charge of the particle. Therefore this would not be a good collector for a selective separation between calcium carbonate and calcium sulfite.

3. Of the collectors tested, the collector that is likely to provide the best separation between calcium sulfite and the impurities (calcium carbonate and silica) is Aero 870. Its rapid adsorption by calcium carbonate and silica at low concentrations, and its preferential adsorption by these particles compared to calcium sulfite, indicates that it is a selective collector for this application.

4. Even though Aero 870 has the characteristics of a good collector for the separation of calcium carbonate from a flue-gas desulfurization scrubber sludge, further laboratory flotation test work must be done to confirm this.
Plans for the Ninth Quarter

It was found in earlier work that froth flotation of scrubber sludge is more effective when the sludge is pre-treated with hydrocyclone to remove the coarse, non-floatable particles. Cycloning will therefore be used to prepare flotation feed material. Work will begin with a two-inch hydrocyclone with goals of optimizing the separation of calcium carbonate from gypsum. This will be done by varying the parameters of the water-only cyclone. Initial parameter variation will be the pressure of the feed stream and solids by weight of the feed slurry. The pressure will be varied from 5 - 20 psi at 5 psi intervals, and the solids will also be varied from 5 - 20% solids by weight at intervals of 5%. The optimal results from the hydrocyclone test, overflow product with low% CaCO₃ and good recovery, will then be the feed material for froth flotation experiments.

References