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Separation of Flue-Gas Scrubber Sludge into Marketable Products

Third Year, Second 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 ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and unreacted limestone (CaCO_3) or lime ($\text{Ca}(\text{OH})_2$), 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, 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, 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.

In the current quarter, research was focused on two different areas. The first part of this quarter the optimization of the feed slurry percent solids for the two inch water-only cyclone was completed. The optimization of the vortex finder, spigot diameter and inlet feed pressure was completed in the previous quarter (Quarterly report #9).

The second part of this quarter began the investigation of why water-only cycloning helps froth flotation performance. The hypothesis is that water-only cycloning scrubs the surface of the unreacted limestone. This scrubbing effect provides a clean calcium carbonate surface, which results in better flotation reagent adsorption. This study used the scanning electron microscope to investigate the surface of the unreacted limestone particles.

Progress During the Tenth 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 (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.

Experimental

The details of the experimental set-up and the procedure for operating a water-only cyclone can be seen in the last progress report (Quarterly Report #9).

Results and Discussion

The bulk of the work on optimizing the water-only cyclone was done in the last progress report (see Quarterly Report #9). The analysis of the data of that quarter has shown that the most efficient separation occurred with an 11mm vortex finder, 5mm spigot diameter, and an inlet feed pressure of 45 psi. These operating parameters were able to remove nearly 50% of the unwanted limestone and maintain a weight recovery of approximately 76% of the valuable product.

The final operating variable investigated was the weight percent solids of the feed slurry. It has been reported in literature that an increase in weight percent solids would increase the specific gravity of separation with a slight decrease in efficiency of the water-only cyclone (Weiss, 1985). Our work proves just the opposite as illustrated in the Table 1. The feed weight percent solids selected were 3.0%, 5.0%, 10.0% and 20.0%. The remaining cyclone parameters were set at their optimum conditions which were determined from previous work and described in the earlier progress reports. An improvement in weight recovery at higher percent solids was observed, but with no improvement in grade. This might be allowable if froth flotation can still provide an acceptable grade.

Table 1: Effect of feed percent solids for determining the optimum percent solids for the two-inch water-only cyclone with a 11 mm vortex finder and a 5 mm spigot diameters. Feed material contained 5.6+/-0.3% unreacted limestone.

Dimension of Water-Only Cyclone	Feed Pressure (psi)	Percent Solids by Weight	Percentage of Unreacted Limestone in Overflow	Percent Weight Recovery of the Overflow
Vortex Finder = 11 mm Spigot Diameter = 5 mm	45	3.0	3.00+/-0.10	69.3
	45	5.0	2.89+/-0.10	75.6
	45	10.0	3.26+/-0.04	79.8
	45	20.0	3.90+/-0.20	86.8

The second half of this quarter was devoted to determining if water-only cycloning does scrub the surface of the unreacted limestone particles. Preliminary flotation work on raw Duckcreek scrubber sludge was unable to provide an efficient separation, even though the particle size of the sludge was within the particle size limits of froth flotation. However, scrubber sludge which had been treated by water-only cyclone separation was seen to be much more amenable to froth flotation. This has led to the hypothesis that the unreacted limestone has a sulfur based surface layer present due to the incomplete dissolution of limestone in the scrubber. In the initial investigation of the surface properties of the unreacted limestone, SEM analysis was used. SEM was selected for several reasons, including: higher resolution and better depth of field than an optical microscope, and it provides elemental composition of submicron scale particles.

Experimental

A list of the samples that were prepared for SEM analysis can be seen in Table 2. These samples were selected because they would represent the input and output of every product in the separation process. The preparation of non-conductive particulates needs special consideration when analyzed with SEM, because of sample preservation, charging effect, and topographical difficulties.

The procedure for sample preparation is given as follows and can be seen in figure 1.

- Bakelite slugs with 1.25 inch diameter were made. These were used as mounting stages for the scrubber sludge samples.
- A layer of carbon paint was applied to the bakelite slug. Carbon paint has two main functions. The first is to act as a glue to secure the particles, as the SEM requires the samples to be kept in vacuum, and care must be taken to keep the particles from being lost which the air is

pumped out of the chamber. The second is to act as a pathway to prevent electrical charging on the surface of the samples.

- A representative sample of scrubber sludge, see Table 2 for list of samples, was applied to the wet carbon paint and allowed to dry for 24 hours.
- The samples were then carefully dusted off with compressed air to remove any of the excess particles.
- A thin layer of carbon was then deposited on the surface of the scrubber sludge. This was done to prevent charging on the surface of the particles. Finally, the samples were covered with dust covers until they could be analyzed.

Table 2: List of the samples prepared for SEM study

Sample Description	Sample Number	Type of Carbon Coat
Scrubber Sludge Raw Feed Sample	1	SPI Carbon Coater
Scrubber Sludge Raw Feed Sample	1-A	Denton DV-502 Evaporator
Cyclone Underflow V.F.=11mm, S.D.= 5mm Pressure 45 psi	2	SPI Carbon Coater
Cyclone Underflow, same conditions as above	2-B	Denton DV-502 Evaporator
Cyclone Overflow, same conditions as above	3	Denton DV-502 Evaporator
Flotation Sinks, 0.2Kg/mt of Aero 870 and 0.1Kg/mt of DowFroth 200	4	Denton DV-502 Evaporator
Flotation Conc., same conditions as above	5	Denton DV-502 Evaporator
Ground Limestone Feed	6	Denton DV-502 Evaporator

Two different carbon coaters were investigated, which both operate under similar principles, but apply different carbon layer thickness. For each device, a carbon source (a rope for the SPI Carbon Coater and a carbon rod for the Denton DV-502 Evaporator) is placed between two electrodes. The sample and the carbon source were then placed under a vacuum. The current between the electrodes was then increased until the carbon source began to evaporate, followed by redeposition of a carbon layer onto the sample surface. The SPI Carbon Coater was easier to operate but the thickness of the carbon coat is difficult to control, resulting in a thick carbon coat, see Figure 2. The Denton DV-502 Evaporator operates under a much higher vacuum and has a greater operator control. This resulted in a better and more controllable carbon coat. This coating process was much more time consuming but provides for a better secondary electron image (SEI), see Figure 3.

Figure 1. Procedure used to prepare samples for SEM study. The thickness of the carbon coat depends on the method used.

Results and Discussion

The scanning electron microscope allowed the characterizations of the scrubber sludge on a sub micron level. The benefits of using a SEM were two-fold. The first was the characterization of the morphology of the scrubber sludge. The distinct difference in the particle's shape can be seen in Figure 2, which was a raw Duckcreek scrubber sludge sample which was prepared using an SPI Carbon Coat. This carbon coater was selected because of ease of use and short coating times. The upper image is a back scattered image which is used for elemental composition data. The square plate-like particles in the image were determined to be calcium sulfite/sulfate particles because of high calcium and sulfur peaks that were associated with these particles. The rounded particle was determined to be an unreacted limestone particle because only a strong calcium peak was present. The bottom image of Figure 2 is a secondary electron image of the same particles in the upper image. Secondary electron imaging (SEI) provides topographical information about the particles. It appears that the surface of the particles were rough or covered with bumps. This was later discovered to be caused by the SPI Carbon Coat, and this method of carbon coating was therefore discarded. Figure 3 shows raw Duckcreek scrubber sludge with the carbon coat applied with the Denton DV-502 Evaporator. The true topographical information can now be viewed. The upper image in Figure 3 shows the shape of the calcium sulfite/sulfate particles, which tends to be smooth, thin plates. The bottom image of Figure 3 shows the diversity of this material. Along with the flat plate-like structure of the calcium sulfite/sulfate, there is a large rounded particle of unreacted limestone in the bottom center of the image. The spherical shaped particle in the upper center of this image is a fly-ash particle, which is considered another impurity.

The difference in particle shape between calcium sulfite/sulfate and the unreacted limestone can also be beneficial in the separation process. Newly developed flotation reagents by Dow Chemical Co. separate particles based on their shape instead of their surface chemistry. These reagents will be explored in further detail in the next quarter.

The second benefit of SEM was its EDS system which allows elemental compositions to be determined. The investigation of scrubber sludge samples using EDS is still in its initial stages, and will be discussed in more detail in the next progress report.

Figure 2: Raw scrubber sludge sample (sample no. 1). Top photograph is a back-scattered image, whereas the bottom photograph is a secondary electron image (SEI). The square plates are calcium sulfite/sulfate particles. The round particle in the middle of the photograph is an unreacted limestone particle. The rough surface of the particles in the SEI photograph was due to a very thick carbon coat.

Figure 3: Raw scrubber sludge sample (sample no. 1-A). These two SEI photographs continue to define the characteristics of the raw scrubber sludge feed. The top photograph shows the thickness of a calcium sulfite/sulfate particle. The bottom photograph shows the diversity of the components of the scrubber sludge. Along with the unreacted limestone particles present, the round sphere of a fly-ash particle can be seen.

Conclusions

Water-only hydrocycloning was able to remove nearly 50% of the unwanted limestone from the scrubber sludge. The separation performance was best when a water-only cyclone was used that had a vortex finder of 11mm, a spigot diameter of 5mm, an inlet feed pressure of 45 psi, and weight percent solids of 5.0%.

A distinct difference was observed in the morphology of the main components in scrubber sludge. The bulk of the material was flat, plate-like material which contained high calcium and sulfur peaks, and was characterized as calcium sulfite/sulfate. The more rounded, blocky particles were determined to contain high levels of calcium and were also associated with Mg, Cl, Fe, and S peaks, and were characterized as unreacted limestone.

Plans for the Eleventh Quarter

Work will continue on the determination of whether there is a sulfur based layer on unreacted limestone particles. This will be done with SEM and also X-ray diffraction (XRD). XRD samples that will be investigated include raw scrubber sludge, cyclone overflow, cyclone underflow, and a reconstituted feed sample. The reconstituted feed sample will be a sample that will represent the feed sample but will be made up from the water-only products. The goal of this study is to see if there is a variation in the amount of unreacted limestone present. The hypothesis is that if hydrocycloning scrubs the surface of the unreacted limestone, then a higher XRD intensity peak for the limestone will occur. If there is a difference in the peak intensity between the different samples this will strengthen the hypothesis that a sulfur layer is present.

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