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Separation of Flue-Gas Scrubber Sludge into Marketable Products

Second Quarterly Technical Progress Report

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Abstract

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 ($\text{CaSO}_3 \bullet 0.5\text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$), and unreacted limestone (CaCO_3) or lime (Ca(OH)_2), with miscellaneous objectionable impurities such as iron oxides; silica; and magnesium, sodium, and potassium oxides or salts. Currently, the only market for scrubber sludge is for manufacture of gypsum products, such as wallboard and plaster, and for cement. However, the quality of the raw sludge is often not high enough or consistent enough to satisfy manufacturers, and so the material is difficult to sell. In particular, the presence of calcium sulfite, salts, and lime or limestone in the sludge can make the material completely unsuitable for gypsum products, because they prevent plaster made from it from setting properly. Other markets, such as paper manufacture and plastics fillers, have even more stringent quality requirements and will not accept raw sludge at all.

This project is developing a process that can produce a high-quality calcium sulfite or gypsum product while keeping process costs low enough that the material produced will be competitive with that from other, more conventional sources. This purification will consist of minimal-reagent froth flotation, using the surface properties of the particles of unreacted limestone to remove them and their associated impurities from the material, leaving a purified gypsum or calcium sulfite product. The separated limestone will be a useful by-product, as it can be recycled to the scrubber, thus boosting the limestone utilization and improving process efficiency. Calcium sulfite will then be oxidized to gypsum, or separated as a salable product in its own right from sludges where it is present in sufficient quantity. The main product of the process will be either gypsum or calcium sulfite, depending on the characteristics of the sludge being processed. These products will be sufficiently pure to be easily marketed, rather than being landfilled.

Experiments to date have shown that up to 38.6% of the unreacted limestone could be removed from the sludge with no reagents other than a frothing agent, using only its natural hydrophobicity. However, this was accompanied by a loss of 21.1% of the total sludge weight, showing the need for improved flotation selectivity.

Several reagents have been examined to determine their ability to selectively improve the flotation of the limestone away from calcium sulfite and gypsum. The most successful have been those using a cationic collector, American Cyanamid's Aero 870. Being cationic, this reagent appears to be interacting with the anions rather than with the cations in the sludge particles, and so is exhibiting greater selectivity than the other reagents examined. Using the Aero 870, 46.7% of the limestone could be removed from the sludge while only losing 18.5% of the total weight to the reject. This is a significant improvement over the selectivity with no collector, or with anionic collectors. Experiments are now underway to determine how this reagent reacts with pure limestone that has not been through a flue-gas scrubber, which will show whether the surface chemistry of the limestone is significantly altered by the environment in the scrubber.

Background

Power plants which use wet scrubbers to remove sulfur dioxide from their flue gases produce a great deal of scrubber sludge. This sludge is a result of reacting limestone or lime with sulfur dioxide to precipitate calcium sulfite, and calcium sulfate dihydrate (gypsum). For example, a hypothetical 500 Mw power station, burning coal containing 2.5% sulfur, will produce approximately 15 tons (dry basis) of scrubber sludge every hour. At current landfilling costs (approximately \$17/ton), such a plant could be paying as much as \$2.2 million/year for sludge disposal. Currently, sludge disposal costs and limestone costs discourage plants from using flue-gas scrubbers, and instead encourage them to simply switch to low-sulfur coals. Indeed, as U.S. air pollution standards tighten, many plants which already have installed scrubbers will switch to low-sulfur coal to minimize their sludge production. As a result, the high costs of scrubber operation and sludge disposal are causing the problem of high-sulfur coal utilization to be pushed into the indefinite future, rather than being solved.

The obvious solution to the sludge disposal problem is to process it to convert as much as possible to a salable product, not so much to make a profit as simply to save on landfilling costs. One such product is gypsum (calcium sulfate dihydrate), which can be used to make plaster, wallboard, cement, and other construction products. The major barrier to widespread marketing of scrubber sludge is that it contains a number of impurities, and is of uneven quality, which makes it unattractive for most purposes in its raw form. Potential users are therefore not eager to purchase the material, even with significant price breaks (Ellison and Hammer, 1988). If the power companies are to sell the sludge, a low-cost means is first needed to improve its quality enough that customers will be willing to take it.

Typical quality requirements for gypsum for use in wallboard manufacture are given in Table 1. For the gypsum to be salable, it must meet or exceed these requirements.

Table 1: Impurity limits for gypsum for use in plaster or wallboard manufacture (Van der Bruggen and Koppins-Odink, 1989)

Impurity	Maximum % by weight
Fe ₂ O ₃	1.5
SiO ₂	1.0
MgO	0.1
K ₂ O	0.1
Na ₂ O	0.04
Cl	0.01
CO ₃	1.5
SO ₂	0.25
Moisture	8.0

Chemistry of Wet Flue-Gas Scrubbing:

Wet flue-gas scrubbers work by contacting a slurry of finely ground limestone (CaCO_3) with the combustion gases from the plant boilers. The sulfur oxides in the gases reacts with the limestone to form solid precipitates of either calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), depending on how completely the sulfur dioxide is oxidized to sulfur trioxide. The solid precipitate is then removed from the slurry, and the water is recycled to the limestone-grinding mill to produce fresh slurry. The finest particles are recycled with the water to act as seed crystals for precipitation of the sulfite and gypsum.

A serious problem occurs in many wet scrubbers if the sulfur dioxide is only partially oxidized to sulfur trioxide. In this case, the main precipitate is calcium sulfite hemihydrate, with up to 15% calcium sulfate in solid solution in the sulfite particles. If more than 15% is as calcium sulfate, then it can no longer precipitate with the sulfite crystals, and instead precipitates as separate crystals of gypsum. However, there is a shortage of gypsum seed crystals in the slurry in this situation, and so much of the gypsum crystallizes on the walls of the scrubber. This can rapidly plug the scrubber, and must be avoided. In recent years, many plants have taken to adding thiosulfate ($\text{S}_2\text{O}_4^{2-}$) as a reducing agent. This prevents the oxidation of sulfur dioxide, and so eliminates the formation of gypsum and the buildup of gypsum scale in the scrubber. As a result, the sludge produced is primarily calcium sulfite hemihydrate. The remainder of the sludge is unreacted absorbent (limestone), grinding media chips from the limestone-grinding mill (iron or iron oxide), and any silicates, salts, clays, or other impurities that were present in the limestone.

Another problem is caused by unreacted limestone or lime in the sludge, which make it difficult to oxidize the sludge to make gypsum. Calcium sulfite hemihydrate can be oxidized to gypsum by lowering the pH below 5 and sparging with air. Under such mildly acidic conditions, the calcium sulfite becomes sufficiently soluble that it can dissolve, oxidize in aqueous solution, and reprecipitate as gypsum. However, unreacted limestone or lime will need to be completely consumed by adding acid before the sludge pH can be made sufficiently acidic, and so if either of these impurities is present in more than trace amounts, the cost of oxidizing the sludge will be too high to be economical.

Contaminants other than the unreacted absorbent will tend to interfere with the use of the sludge to make gypsum-based plasters. Impurities in the sludge will unpredictably affect the plaster setting rates, and can give the product an objectionable color or cause it to have a poor particle size distribution.

The composition of a typical sludge, when thiosulfate is added to prevent gypsum formation, is as follows (Kawatra and Eisele, 1994):

• Calcium Sulfite Hemihydrate:	77%
• Calcium Sulfate (in solid solution):	14%
• Unreacted Limestone:	7%

- Insoluble Silicates: 2%
- Mean Particle Size: 34.7 micrometers

This corresponds to approximately 48% SO_2 , 4.2% CO_3 , and 2% SiO_2 , all of which are in excess of the limits in Table 1. Other impurities are also present, such as small amounts of iron sulfate, and soluble salts, both of which are unacceptable if the products are to be marketed. Depending on how the scrubber is being operated, the composition can obviously change a great deal, and so any process for purifying the sludge must be able to deal with large variations in sludge composition.

Objectives:

The objectives of this project are as follows:

- 1 Investigate properties of scrubber sludge that will control its marketability.
- 2 Develop a froth-flotation process that can be used to separate the various components based on differences in their surface chemistry, with high enough purity that the sludge can be sold as a high-grade gypsum product while recycling unreacted absorbent to the scrubber, so that scrubber operating costs can be reduced while simultaneously reducing the total sludge volume.
- 3 Accomplish these benefits 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 development of a novel application of froth flotation to produce a clean separation with a minimum of reagents, and therefore at a minimal cost. 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.

Progress During the Second Quarter

Samples have been received from three operating plants, and prepared for analysis and flotation studies by air-drying, mixing, and dividing into representative samples. These samples were collected from three types of scrubber. The Plant A scrubber uses limestone as an absorbent, and produces a primarily calcium sulfite sludge. The Plant B scrubber uses magnesium-enhanced lime as the absorbent, and produces a calcium sulfite sludge that has a finer particle size than the Plant A sludge. The Plant C scrubber uses limestone as the absorbent, and uses forced oxidation to produce a sludge that is primarily gypsum. X-ray diffraction has been used to determine the crystalline phases present in each sludge sample, and wet-chemical analysis of the samples is in progress. Calibration standards are being prepared for electron microprobe work, to determine the associations between individual particles of the various types.

In this quarter, flotation experiments were begun using the Plant A scrubber sludge. In an earlier project, sludge from this power plant was treated by water-only cycloning to remove coarse unreacted limestone. It was found that the fine unreacted limestone that remained after cycloning was naturally hydrophobic and could be removed by froth flotation. In the current project, the flotation of limestone and other impurities is being further investigated, to determine the actual mechanism and to improve the separation efficiency. This is being done using sludge samples collected from three power plants, each of which uses a different type of scrubber and therefore produce sludges with different characteristics.

The flotation studies have been being carried out on a 12.2 kg sample of the sludge from Plant A, which was first treated with a water-only cyclone to remove the coarse impurities that would otherwise interfere with flotation. This particular sample of raw sludge contained 4.9% limestone before cycloning, while the cycloned product was reduced to 4.4% limestone, while recovering 83% of the total sludge weight. Flotation experiments with the cycloned sludge were then carried out using the following basic flotation equipment, materials, and procedure:

- Equipment: Denver flotation machine, 1200 ml working volume, operated at 1100 rpm
- Feed: 50 grams of cycloned scrubber sludge
- Water: 1200 ml of sludge-saturated water (to minimize dissolution)
- Reagents (not all reagents are used in every test):

Frother:	Dow DF200 (polyglycol alkylether, mean molecular weight approximately 200)
Collectors:	Oleic Acid (anionic)
	#2 Fuel Oil (nonpolar)
	American Cyanamid Aero 845 (anionic, tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate)
	American Cyanamid Aero 870 (cationic, ethoxylated octadecylamine-octadecylguanidine complex)
Modifier:	Sodium Silicate

- Procedure:

- Add solids and water to flotation cell, condition 2 minutes
- Measure pH and temperature, add modifying reagents (if used)
- Re-measure pH, condition additional 3 minutes
- Add collector (if used), condition 1 minute 45 seconds
- Add frother, condition 15 seconds
- Open air inlet to begin flotation
- Float for three minutes, collecting the froth by hand scraping into a tared pan
- Weigh froth to determine water recovery, dry at 45° C and reweigh
- Carry out chemical analysis of the flotation products

The experiments conducted to date can be divided into three sets. In Series 1, the effect of oleic acid and frother dosage on the flotation grade and recovery was determined. In Series 2, sodium silicate was used to attempt to improve the selectivity of the process. In Series 3, collecting reagents other than oleic acid were studied, to determine whether they had a greater intrinsic selectivity between limestone and calcium sulfite.

Figure 1: Variation in residual calcium carbonate and clean-product recovery as the oleic acid and DF 200 frother dosage are varied. Increasing either the collector or the frother dosage improved the limestone removal, but both resulted in a large reduction in the total weight recovery.

The results of the first series, given in Figure 1, showed that up to 38.6% of the unreacted limestone could be removed from the sludge with no reagents other than a frothing agent, using only its natural hydrophobicity. However, this was accompanied by a loss of 21.1% of the total sludge weight, showing the need for improved flotation selectivity. It was also found that the amount of residual limestone remaining in the cleaned product could be reduced by increasing the dosage of either collector or frother. However, oleic acid acts as a collector not only for the limestone, but also for the calcium sulfite and gypsum in the sludge. As a result, increases in the collector dosage caused the recovery of clean product to decrease, and it is therefore not a suitable collector for selective removal of limestone. The results of the Series 2 tests, given in Figure 2, show similar results when sodium silicate is added. While the sodium silicate does act as a flotation depressant, it is not selective between the various components of the sludge, and therefore its only effect is to move the results along the same grade-recovery curve as was seen in the tests with oleic acid alone.

Figure 2: Results of flotation experiments using oleic acid as collector, with sodium silicate added to attempt to depress the flotation of calcium sulfite. Frother dosage for this series of tests was held constant at 0.6 kg/mt. These results show that sodium silicate does not provide any systematic improvement in flotation selectivity.

In the third test series, two different collectors were studied. The first, American Cyanamid's Aero 845, was, like the oleic acid, an anionic collector, but its functional group was sulfosuccinamate rather than carboxylate. However, Figure 3 shows that the Aero 845 followed the same grade-recovery curve as was seen in the oleic acid tests, which demonstrates that its selectivity is similar.

In experiments with American Cyanamid's Aero 870, it was found that here the selectivity could be markedly improved. Using the Aero 870, 46.7% of the limestone could be removed from the sludge while only losing 18.5% of the total weight to the reject. This is a significant improvement over the selectivity with no collector, or with either of the anionic collectors. Being cationic, this reagent appears to be interacting with the anions rather than with the cations in the sludge particles, and so is exhibiting greater selectivity. Experiments are now underway to determine how this reagent reacts with pure limestone that has not been through a flue-gas scrubber, which will show whether the flotation characteristics of the limestone are significantly altered by the environment in the scrubber.

Flotation with Cyanamid collectors

Figure 3: Flotation of scrubber sludge with reagents other than oleic acid. In tests using the anionic Aero 845 collector, the results followed the same grade-recovery curve as was seen for the oleic acid experiments. However, the cationic Aero 870 collector showed a much greater ability to remove limestone from the sludge while maintaining a high weight recovery.

Plans for the Third Quarter

The work in the second quarter has given a considerable amount of information about the flotation response of unreacted limestone in the Plant A scrubber sludge, and so further work will concentrate on determining the surface chemistry of the sludge that is responsible for this response.

Experiments have been begun to attempt to duplicate the flotation of limestone, using a pure limestone that has been finely ground, but has not yet been used in a flue-gas scrubber. This will be done using each of the three types of collecting agent that were used for the sludge flotation tests (anionic carboxylate, anionic sulfosuccinamide, and cationic amine/guanidine complex). The response of the limestone to each reagent as a function of particle size will be determined, and compared with the response of the unreacted limestone in the sludge under the same conditions. If the behavior of the pure limestone is found to be different from that of the sludge limestone, then experiments will be conducted to determine what effects in the scrubber are responsible for the differences

Chemical and physical analyses of the sludges will also be continued in the third quarter, both to determine the reasons for the observed performance of the Plant A sludge, and to prepare for flotation studies with the Plant B and C sludges.

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