Separation of Flue-Gas Scrubber Sludge into Marketable Products

First 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. The quantity of sludge is considerable. For example, a hypothetical 500 Mw power station, burning coal containing 2.5% sulfur, will produce approximately 15 tons (dry weight) of scrubber sludge every hour, or nearly 132,000 tons/year. The vast majority of the sludge is simply landfilled, but with increasing landfilling costs this can cost the plant millions of dollars per year. As a result, this option is rapidly becoming less attractive. Producing marketable materials from the sludge is a far more promising avenue, provided that the products can meet the necessary specifications at a reasonable cost.

Scrubber sludge 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; 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 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 investigating the surface properties of scrubber sludge, particularly of the calcium sulfite, since the surface chemistry of this material has never been studied in detail. Knowledge of these properties is critical for the development of 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.

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 with sulfur dioxide to precipitate calcium sulfite and calcium sulfate. 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.

A typical method for disposing of this sludge is to dewater it to 30-40% moisture, mix it with fly ash, and landfill it (Cockren, 1992). However, suitable landfill space is becoming expensive, especially in populous areas, where landfilling costs can average \$17/ton for bulky, stable, non-toxic wastes (Baillod et al., 1990). The hypothetical power station above would therefore be paying an average of \$255/hour to dispose of their sludge, or \$2.2 million/year. 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.

There are a number of potential markets for the most prominent compounds in scrubber sludge. Gypsum can be used to make plaster, wallboard, and other construction products, while calcium sulfite can be used in paper manufacture, as a vat-sterilant in brewing, as a low-cost reducing agent, and as a cement additive (Merck Index, 1983). 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.

In existing scrubber operations, the main emphasis is on removing as much sulfur dioxide as possible, and on keeping the scrubber operating smoothly. Research work to date has mainly been concerned with ensuring that the limestone has been used as completely as possible, and that the crystals formed were easy to dewater and dispose of. Relatively little attention has been paid to the precise properties of the resulting sludge, or to how it could be treated and utilized for other purposes. In view of the significant cost and environmental benefits of using this sludge for useful purposes, this project will concentrate on determining the precise properties of the scrubber sludge, and on using these properties to improve product quality and marketability.

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_2O_3	1.5
SiO_2	1.0
MgO	0.1
K_2O	0.1
Na_2O	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.

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_2 , 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 Study the surface-chemical effects that can be used to separate the various components.
- 3 Develop processes for efficiently separating the components at low cost, with high enough purity that they can be sold in a variety of markets.
- 4 Recycle unreacted compounds to the scrubber, so that scrubber operating costs can be reduced while simultaneously reducing the total sludge volume.
- 5 Accomplish these benefits without adding additional chemical hazards to the environment.

These objectives will be accomplished by analysis of the composition and surface chemistry 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 First Quarter

Sample Selection and Collection

Following the start of the project in September 1993, coal-fired power plants in the Midwest were surveyed to select a representative set of plants using wet flue-gas scrubbers. It was decided to conduct studies on sludges collected from wet flue-gas scrubbers operated in three different modes: 1. Limestone sorbent, with thiosulfate added to prevent gypsum scaling; 2. Lime sorbent, with magnesium added to enhance the performance; and 3. Forced oxidation of the scrubber sludge to form gypsum outside of the scrubber.

As the samples were received from the selected plants, each was air-dried for two weeks to remove excess water. This was necessary to allow each sample to be mixed to a uniform consistency, so that it could be divided into representative fractions for analysis and experiments. Multiple samples were taken from each sludge, to check the uniformity.

Plant Descriptions

Three plants were selected for this study which fit the specifications given above. The operation of these plants is being studied, and a brief description of their characteristics follows:

- Plant A: This plant is located in Illinois, and uses limestone (CaCO_3) as the sulfur dioxide absorbent. The limestone is ground in a ball mill, and the limestone slurry is injected into the scrubber. Thiosulfate is added at a rate of 600 ppm to prevent premature oxidation of calcium sulfite to gypsum, which would cause scaling problems. The scrubber is operated at a pH of 5.5, and the sludge is withdrawn as a 13% solids slurry. This slurry is then thickened, and the water is recycled to the scrubber while the sludge is landfilled. A suitable sample of 64 kg (dry weight) of raw sludge was collected from this plant as a 50% solids slurry.
- Plant B: This plant is located in Ohio, and uses lime (CaO) as the sulfur dioxide absorbent. The lime is ground and slaked, and the resulting lime slurry is injected into a Magnesium - Enhanced scrubber. Magnesium is added to slow the growth of gypsum crystals and prevent scaling. The plant does not oxidize the sludge to gypsum. Complete details of the plant operations are being studied. A 28 kg (dry weight) sample of raw sludge was collected as a 40% solids slurry.
- Plant C: This plant is located in Indiana, and unlike plants A and B, it uses forced oxidation to convert calcium sulfite to gypsum. We are currently in the process of obtaining samples and operating data from this plant.

Some of the detailed information on these plants is proprietary, and is therefore not immediately available. Information on scrubber operations is also being obtained from other sources. The samples from Plant A and Plant B have been prepared, and are currently being analyzed.

X-Ray Diffraction Studies

Initial sample analysis is being carried out by X-ray diffraction. This has the advantage of determining what compounds and crystalline phases are present, and not only the elemental composition. This information is useful for determining which phases can be separated from each other by a physical separation, as opposed to a chemical separation. The X-ray diffraction results for the two sludge samples are given in Figure 1. The compounds which have been identified in

Figure 1: X-ray diffraction results for the two sludge samples. In both cases, the dominant phase is $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$, with the CaCO_3 and Ca(OH)_2 being residual absorbent. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is detectable in the Plant A sludge, but is present at a much lower level in the Plant B sludge. Other phases, listed in Table 2, were identified from the remaining peaks. The diffraction pattern for the CaSO_3 in the Plant B sludge is very close to the theoretical value, while the same compound in the Plant A sludge shows markedly different peak intensities. This is apparently due to preferred orientation of the particles in the Plant A sludge, as a result of its relatively coarse particle size, shown in Figure 2.

each of the two scrubber-sludge samples to date are given in Table 2, and the relative importance of each phase is currently being determined. Quantitative analyses from the X-ray diffraction intensities is currently being carried out.

Table 2: Discrete crystalline phases detected by X-ray diffraction in the scrubber-sludge samples obtained to date. The dolomite in the Plant A sludge is an impurity in the limestone used as an absorbent. Plant B shows calcium hydroxide in the sludge rather than calcium carbonate, because it uses lime as the absorbent rather than limestone.

Plant A - Illinois	Plant B - Ohio
Calcium Sulfite Hydrate, $\text{CaSO}_3 \bullet 0.5\text{H}_2\text{O}$	Calcium Sulfite Hydrate, $\text{CaSO}_3 \bullet 0.5\text{H}_2\text{O}$
Calcium Sulfate Sulfite, $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4$	Calcium Sulfate Sulfite, $\text{Ca}_3(\text{SO}_3)_2\text{SO}_4$
Calcium Carbonate, CaCO_3	Calcium Hydroxide, $\text{Ca}(\text{OH})_2$
Gypsum, $\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$	Gypsum, $\text{CaSO}_4 \bullet 2\text{H}_2\text{O}$
Quartz, SiO_2	Quartz, SiO_2
Dolomite, $\text{CaMg}(\text{CO}_3)_2$	

Particle Size Determination

The particle size distribution of the sludge samples was determined using a laser-diffraction particle size analyzer. This instrument requires that the particles be suspended in water and circulated for a period of several minutes. Since several of the important phases are soluble in water, the particles were suspended in water which had been saturated with the sludge, to prevent dissolution of the finest particles. The results are given in Figure 2. These results show that the sludge from Plant A is significantly coarser than that from Plant B. This is a result of differences in the chemistry of the two plants. The size difference will have a major impact on the physical separation of the components of the sludge, for two reasons:

- 1 The hydrodynamics of smaller particles differ greatly from larger particles, and as a result the separation characteristics will be different. Because small particles are more easily swept along with the water in a separation, the probability of particles being misplaced into the wrong product is increased. As a result, the finer Plant B sludge will require the separation to be more selective in order to produce the desired level of separation.
- 2 Larger particles are more likely to contain inclusions of other components. This "locking" of different types of particles means that the level of separation is restricted unless the particles can be ground to a finer size. The coarser Plant A sludge may therefore need to be treated differently than the finer Plant B sludge in order to deal with coarse, locked particles.

Figure 2: Particle size distributions for the two sludge samples, as determined by laser diffraction. The Plant A sludge is considerably coarser than the Plant B sludge, which is due to magnesium being added to the Plant B absorbent.

Plans for the Second Quarter

The project is proceeding according to the schedule originally proposed. Preliminary X-ray diffraction studies are complete. In the second quarter, collection of sludge samples will be continued. Electron microprobe studies will be conducted to determine the degree of locking between crystals of different phases, and evaluate the potential for their separation. Additional detailed chemical analyses of the sludges will be carried out using wet-chemical techniques, to determine the concentration of trace impurities and salts which may be present in quantities too small to be detected by X-ray diffraction.

Wet-chemical techniques used will include both standard ASTM analytical methods, and a method for determining the quantity of calcium sulfite in sludge from its increase in weight upon oxidation with hydrogen peroxide. Atomic Absorption Spectroscopy will also be used to determine the quantity of magnesium, sodium, potassium, and iron salts in the sludges. Based on these results, surface-chemistry and froth-flotation studies will be planned to determine the best conditions for separating impurity phases such as calcium carbonate, calcium hydroxide, quartz, and dolomite from each of the sludges.

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