AIIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

2

DOE/PC/93214--T3

**Separation of Flue-Gas Scrubber Sludge
into Marketable Products**

RECEIVED
JSDOE/PETC

94 JUN 29 AM 9:59

Third Quarterly Technical Progress Report

ACQUISITION & ASSISTANCE DIV.

Performance Period: 3/1/94 to 5/31/94 (Quarter #3)

**Principal Investigators:
S. K. Kawatra and T. C. Eisele**

**Graduate Student:
Kyle Shoop**

**Work Performed Under Contract No.
DE-FG22-93PC93214**

**For the
U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

**By
Michigan Technological University
Department of Metallurgical and Materials Engineering
Michigan Technological University
1400 Townsend Drive
Houghton, Michigan 49931-1295**

**D.O.E. Project Manager:
Robert W. Gross
Morgantown Energy Technology Center**

June, 1994

"U. S. DOE. Patent Clearance is not required prior to the publication of this document."

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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; silica; and magnesium, sodium, and potassium oxides or salts. 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.

This project is studying the characteristics of flue-gas scrubber sludges from several sources, which is necessary for the development of purification technologies which will make it possible to directly utilize scrubber sludges rather than landfilling them. 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 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 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 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, which selectively adsorbs on limestone surfaces. A

reverse flotation process was used, with the sinks product being the purified material, and the froth product being the rejected impurities.

In the third quarter, the objectives were to determine how the separation by column flotation differs from the separation by conventional flotation, and to begin studies of the surface chemistries of the individual chemical components found in the sludge samples. The column was found to produce a superior-quality product compared to conventional flotation with the same reagents, showing that a significant improvement in performance can be achieved through equipment improvement. However, the recovery of clean product with the column was less than the recovery using conventional flotation. Studies of the surface chemistries of the individual sludge components were also begun, using measurements of the Zeta potential. These measurements are initially being made on chemically pure calcium sulfite, calcium carbonate, and gypsum, to establish a baseline for comparison for the actual sludge samples. To date, these studies have found that calcium carbonate surfaces in alkaline solution become more strongly negatively charged than either calcium sulfite or gypsum surfaces do under the same conditions. The details of these studies are presented in the following sections.

Progress During the Third Quarter

Column Flotation Experiments

Column flotation represents a significant improvement over conventional flotation for many applications. This improvement consists of increased selectivity between hydrophobic and hydrophilic particles, which allows the column to produce higher-purity products. A schematic of the column used is given in Figure 1.

The basic procedure for the flotation column experiments was as follows:

- 500 grams of the sludge from Plant A (prepared as described in the Second Quarterly Report) was suspended at 40% solids in distilled water, to produce 1600 ml of slurry. Reagents were added, and the slurry was agitated vigorously for 1 minute.
- Frother was added to all of the water to be added to the column, at a rate of 0.03 grams/liter (approximately 0.4 kilograms per metric ton, Kg/mt). The frother used was Dowfroth 200 (a mixture of polypropylene glycol methyl ethers, with a mean molecular weight of 200).
- The column was started, all of the water flowrates were set as desired, and the drain valve was closed. As soon as the water level had reached the base of the feed inlet tube (approximately 1 minute after closing the drain valve), the 1600 ml feed slurry was added over a 15 second interval. This allowed the feed to be added to the column with a minimum of disturbance to the froth layer, and without causing either surging of the pulp level or large losses to the sinks product.
- Flotation was carried out for 9 minutes after closing the drain valve. Froth and sinks products were collected, filtered, dried at 45°C, weighed, and analyzed by thermogravimetric analysis.

Figure 1: Schematic of the flotation column (3" diameter, 5' tall) used in this study. Baffles are installed both above and below the feed inlet, to improve the performance. Air is injected using a water-operated aspirator, consuming 5 liters/min of water at 20 psi. Washwater is added at a rate of 1.3 liters/min.

Experiments conducted with the column in the third quarter used reagent dosages that had already been used in the previous conventional flotation experiments. These results are given in Figure 2, along with the conventional flotation results using the same reagents. It is readily seen that, when no collector is added, the column produces a product that is of markedly higher purity than that produced by conventional flotation. The addition of oleic acid collector to the column feed is not able to produce any further improvement in product quality, and only results in a loss of product recovery.

Zeta Potential Studies

When a particle is suspended in water, it generally develops an electrical charge on its surface. This charge is due to differential adsorption of ions from solution, and its sign and magnitude under various conditions is an indication of the surface chemical properties of the particle. This charge on the particles results in an electrical potential when there is relative motion between the

Effect of oleic acid and frother dosage

Figure 2: Comparison of column flotation with conventional flotation, using either no collector, or oleic acid as collector. This is a reverse-flotation process, with the purified product reporting to the sinks while the impurities are removed in the froth. The feed to the flotation process was from Plant A, and was prepared by water-only cycloning as described in the second quarterly progress report. It contained 4.4% CaCO₃ by weight. Flotation was carried out at a pH of 8, and a temperature of 21°C. Oleic acid was used as a collector to determine whether the column could reverse the poor selectivity of the oleic acid in conventional flotation. The conventional flotation test procedure and conditions were given in the second quarterly report, and the column flotation conditions are given above. The frother dosage was held constant at 0.4 kg/mt for the flotation column tests, while the frother dosage was varied in the conventional tests. Results with a higher % weight recovery, and a lower %CaCO₃ content, are superior. The column produces a much higher-grade product than conventional flotation, and in the absence of oleic acid the combined grade/recovery performance is superior to that produced using conventional flotation. However, the recovery by the column is less than the recovery using conventional flotation. Adding collector in the column produces no further improvement in the grade, and causes a large additional loss in recovery.

particles and the fluid. This is called the "Zeta potential." This parameter can be measured reasonably easily, and is a useful measure of the surface charge on the particles.

Figure 3: Zeta potentials of reagent-grade Calcium Sulfite, Calcium Carbonate, and Gypsum in distilled water, with the pH adjusted using sodium hydroxide. The Calcium Carbonate shows the most negative potential, particularly at alkaline pH.

Initial zeta potential measurements were carried out on pure calcium sulfite, calcium carbonate, and gypsum, which were obtained as reagent-grade powders. These pure powders were selected because they are the most important phases found in the scrubber sludges, and are free of contaminants that would tend to obscure the results. These powders were suspended in distilled water at a concentration of 1 gram/liter, with the pH adjusted by addition of sodium hydroxide. The zeta potentials were measured as a function of pH, using a Pen-Kem microelectrophoresis unit. The results of these measurements are shown in Figure 3, and confirm that the three phases of interest can be made to show significantly different surface behaviors, which can be exploited in a froth flotation process.

Plans for the Fourth Quarter

Zeta potential studies will be continued during the fourth quarter, to determine the variations in zeta potential as the concentrations of the potential-determining ions are varied (Ca^{+2} , Mg^{+2} , SO_4^{-2} , SO_3^{-2} , $\text{S}_2\text{O}_3^{-2}$, and CO_3^{-2}). The effects of cationic and anionic collectors on the zeta potentials of the pure calcium sulfite, gypsum, and calcium carbonate will also be determined.

Once the behavior of the pure compounds has been determined, further tests will be carried out using the actual scrubber sludge samples. This will determine whether the presence of trace components in the sludge cause significant changes in the surface chemistry of the individual components.

These results will be used to plan subsequent flotation experiments for each of the three sludge samples. In particular, they will be used to predict what reagent types and dosages will have the greatest effect, and to determine whether dissolved salts in the water will alter the flotation performance.

References

- Ando, J., 1984. "Status of SO₂ and NO_x Removal in Japan," Proceedings, Eighth Symposium on Flue Gas Desulfurization, New Orleans
- Anonymous, 1988. "TU Electric Pioneers FGD-Gypsum Production for Use in Wallboard," *Power*, April, pp 33-34
- ASTM Standard C22-90, 1991. *Annual Book of ASTM Standards*.
- Baillo, C. R., K. B. Rundman, S. McIntyre, and J. Sandell, 1990. "Market Development Research on Industrial Uses of Spent Foundry Sand," Michigan Technological University Environmental Engineering Center, Internal Report.
- Carnahan, R., 1993. personal communication
- Chemical Marketing Reporter*, April 6, 1992. Schnell Publishing Co.
- CILCO, 1992. "Analysis of flue-gas scrubber sludge for the Central Illinois Light Co. Duck Creek Station," performed 8/18/92.
- Cockren, M., 1992. Manager of Environment for Central Illinois Public Service Co., personal communication.
- Dallmann, W., T. Neesse, V. Menzer, K. Domasch, and K. Muehle, 1989. "Development and Testing of Dewatering Plants for Flue Gas Scrubbers," *Chemische Technik*, vol. 41, no. 8, pp 340-342
- Davis, L. L. 1989. "Gypsum," *Minerals Yearbook*, U.S. Bureau of Mines, pp. 493-501
- Duvel, W. A., W. R. Gallagher, R. G. Knight, C. R. Kolarz, and R. J. McLaren, "State-of-the-Art of FGD Sludge Fixation," Final Report, EPRI-FP-671, vol. 3, NTIS PC A12/MF A01
- Ellison, W., and E.L. Hammer, 1988. "FGD Gypsum Use Penetrates U.S. Wallboard Industry," *Power*, February, pp. 29-33
- Henzel, D. S., and W. Ellison, 1990. "Commercial Utilization of SO₂ Removal Wastes in the Application of New Advanced Control Technology," Proceedings, 1990 SO₂ Control Symposium, New Orleans
- Kawatra, S. K., and T. C. Eisele, 1994. "Separation of Flue-Gas Scrubber Sludge into Marketable Products," to be presented at the AIME Annual Meeting, February, 1994.
- Miller, M. M., 1989. "Lime," *Minerals Yearbook*, U. S. Bureau of Mines, pp. 655-665
- Necker, P., 1990. "Development and Present Status of Flue Gas Desulfurization in Germany," ASME-IEEE Joint Power Generation Conference, Boston, MA, Technical Paper 90-JPGC/EC-7.
- O'Brien, W. E., W. L. Anders, R. L. Dotson, and J. D. Veitch, 1984. "Marketing of By-product Gypsum from Flue Gas Desulfurization," EPA-600/S7-84-019.
- Van der Bruggen, F. W., and J. M. Koppins-Odink, 1989, "Flue Gas Cleaning in Power Stations in the Netherlands," Proceedings: First Combined Flue Gas Desulfurization and Dry SO₂ Control Symposium, Electric Power Research Institute, paper 1-5, pp1-69 to 1-94
- Weiss, N. L. (editor), 1985. *SME Mineral Processing Handbook*, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, pp 5.20 -5.30, 5.72-5.79, 29.11-29.12
- Wirsching, F. and R. Hueller, 1989. "Examination of the Understanding of Flue-Gas Gypsum Quality," *Zement-Kalk-Gips*, Edition B, vol. 42, no. 5, pp. 223-228.

DATE

FILMED

9 / 1 / 94

END