DOE/PC/93214--T12

RECEIVED
USDOE/PETC
96 OCT -3 AM 10:08
ACQUISITION & ASSISTANCE DIV.

Separation of Flue-Gas Scrubber Sludge into Marketable Products

Third Year, Fourth Quarterly Technical Progress Report

Performance Period: 6/1/96 to 8/30/96 (Quarter #12)

RECEIVED
NOV 2 5 1996
OSTI

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
1400 Townsend Drive
Houghton, Michigan 49931-1295

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

September, 1996

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

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 ($CaSO_3 \bullet 0.5H_2O$), gypsum ($CaSO_4 \bullet 2H_2O$), and unreacted limestone ($CaCO_3$) or lime ($Ca(OH)_2$), 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. Quarterly report #10 concluded the water-only cyclone study. Water-only cycloning provided the initial separation step for removing unwanted limestone from the scrubber sludge. The overflow from the cyclone could then be processed by froth flotation to provide a useful calcium sulfite/sulfate product. Quarterly report #11verified the zeta potential results which predicted that an Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) would be the best flotation collector to separate unreacted limestone ($CaCO_3$) from calcium sulfite ($CaSO_3 \bullet 1/2H_2O$)l. This froth flotation study investigated the effect of two types of feed materials. The first was raw scrubber sludge feed which had poor floatability characteristics. The second was with scrubber sludge which was pre-treated with water-only cycloning.

In this quarter, the installation of a laboratory-scale flotation column was completed. This column has the option to be operated as a batch or continuous stream column. This adds to the diversity of the experiments that can be performed. A pulp level controller was also installed to this column. This provides the capability of monitoring the froth/slurry interface, which is crucial for proper column operation.

In addition to the installation of the flotation column, research on the determination of the surface properties of the components of the scrubber sludge was continued. Auger electron spectroscopy (AES) was investigated as a method for determining the composition of the first few monolayers of unreacted limestone and calcium sulfite/sulfate particles.

Progress During the Twelfth 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. This two stage separation method (water-only cycloning and froth flotation) was capable of producing a useful calcium sulfite/sulfate product with below 2.0% limestone by weight, see Figure 1. Progress reports #9, #10, and #11 can be reviewed for more information on the selection of the water-only cyclone and conventional froth flotation parameters.

The next phase of this study was to improve the efficiency of this separation process. This was accomplished by beginning preliminary work on column flotation. Quarterly report #3 indicated that column flotation could be used to provide a cleaner product than conventional froth flotation. Therefore a laboratory scale flotation column was installed in ordered to determine if it could out perform conventional flotation in the removal of unreacted limestone from scrubber sludge.

The surface composition of the scrubber sludge needs to be better understood in order to help increase the efficiency of separation. Therefore, Auger electron spectroscopy (AES) samples were constructed. The difficulty in sample preparation has led to unsuccessful results in determining the surface composition.

Column Flotation

The installation of a laboratory-scale column was extensive and involved many man hours. The column consists of four stainless steel sections and two clear acrylic sections with a 3- inch inside diameter. The total height of the column is 11.5 feet. It contains two internal sparge bubble generators. One's located at the base of the column and the second is located just below the feed inlet. The wash water and bubble generators are controlled by rotometers. The height of the froth/slurry interface can be controlled by the pulp level controller. There is a float mechanism inside the sight tube, which acts as a switch for the discharge pump. A schematic of the laboratory-scale flotation column is in Figure 2.

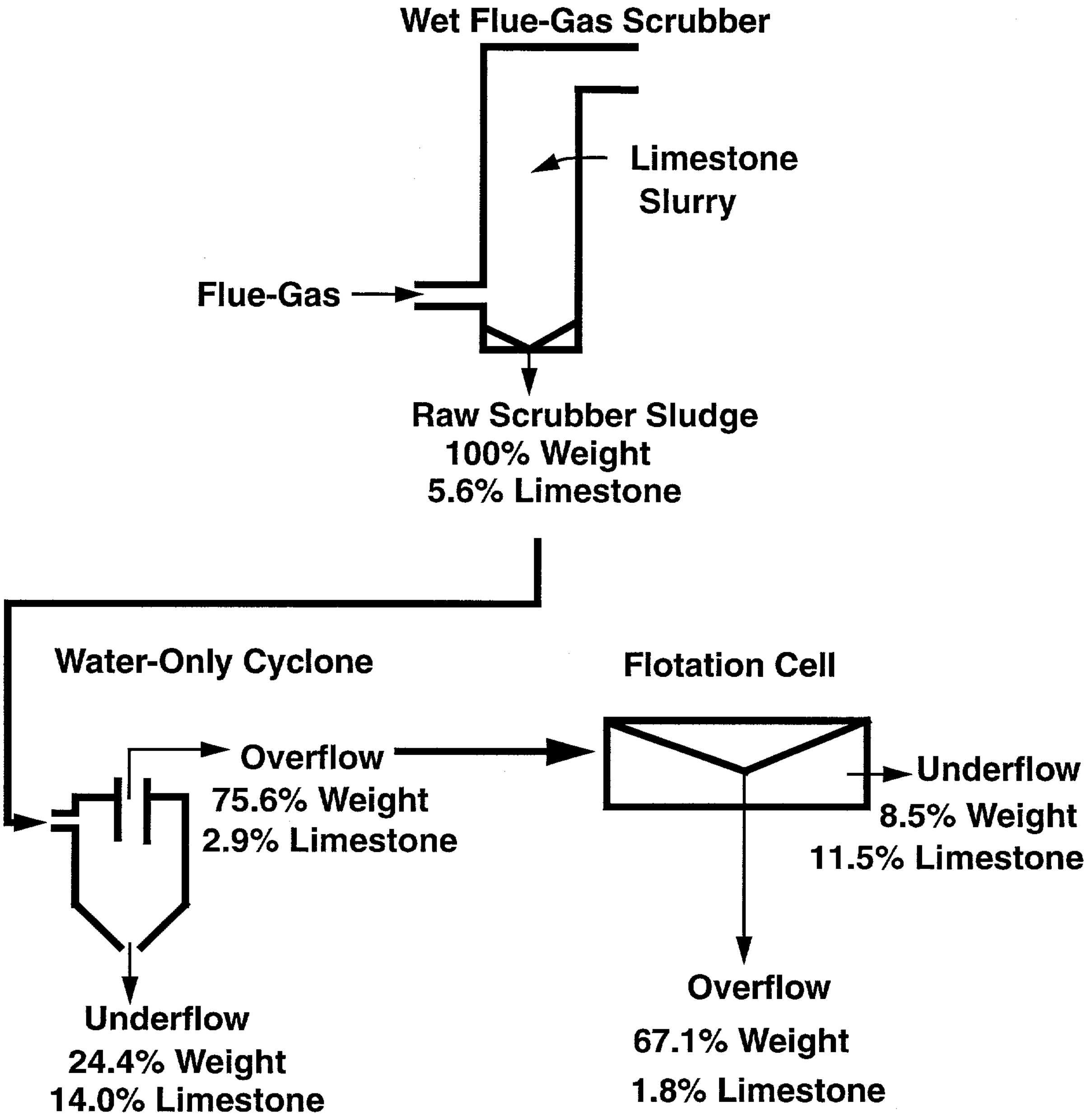

Figure 1: Schematic of the flowsheet which was capable of removing enough of the impurities to provide a clean sulfite/sulfate product.

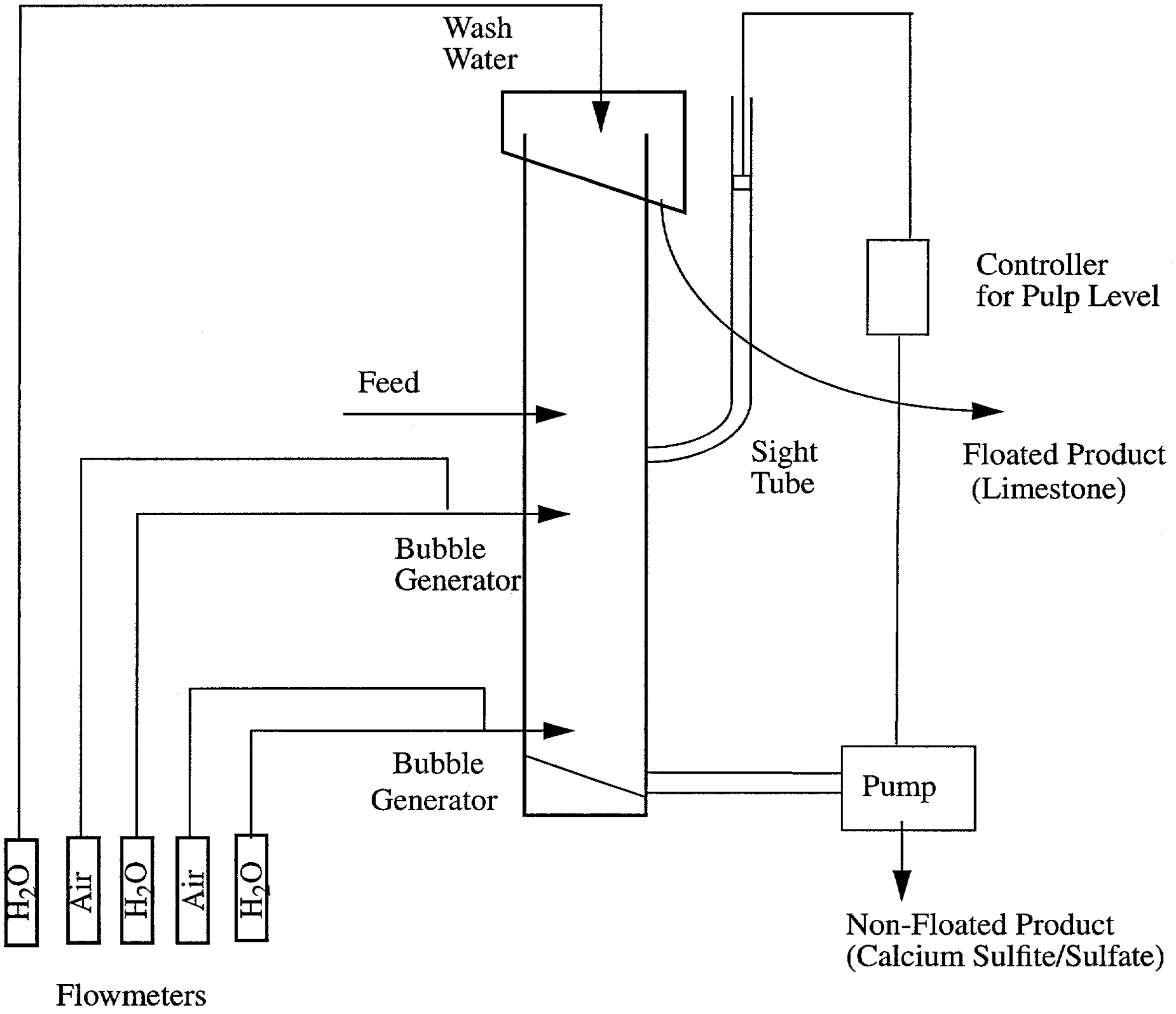

Figure 2: Schematic of the flotation column (3" diameter, 11.5' tall) to be used in this study.

This flotation column can be operated in batch or continuous mode depending on the method of introducing the feed. Initial scrubber sludge tests will have the feed pumped into the flotation column, similar to an actual plant column. The procedure for operating the column and preliminary tests with the column are currently under way and will be reported in the next progress report. Feed material and flotation reagents will be similar to the ones used in quarterly report #11.

Surface Analysis

In addition to developing a process for purifying the calcium sulfite/sulfate content of scrubber sludge by removing the unreacted limestone, the fundamental interaction of these particles is investigated. It has been proposed by this study and the work of others (Gage, C.L. and Rochelle, G.T., 1992) that calcium sulfite plays a role on the dissolution of limestone. Initial work by this study used scanning electron microscopy to investigate the components of scrubber sludge, see quarterly report #10. The results of this study were beneficial in determining the morphology of the particles. Calcium sulfite/sulfate was distinct with its flat plate-like particles, whereas the unreacted limestone particles were rounded. However, the interaction volume of the characteristic x-rays was to large to determine the surface composition of the particles.

There are several spectroscopic techniques available for better surface resolution, see Table 1. These techniques have been reviewed by others (Giesekke, E.W., 1993 and Maratini, A.M. et al, 1993). Auger electron spectroscopy (AES) was selected for the analysis of the components of scrubber sludge for several reasons. 1) It is a non-destructive test, therefore samples can be re-analyzed. 2) Sampling depth is of the first several monolayers of the particles, which are the most important for analyzing the interaction between the particles and the flotation reagents. 3) The small size of the scrubber sludge particles. However, Auger electron spectroscopy was not without several disadvantages. The major concern is the high vacuum which is needed for this technique. This resulted in several sample preparation problems. The general nature of the scrubber sludge also enhanced the sample preparation problems. First, scrubber sludge is a non-conductive powder. Therefore it has to be surrounded by a conductive substrate that does not interfere with the surface properties. The second was the relative softness of the scrubber sludge. The initial sample preparation was as follows:

- Split out a representative sample of scrubber sludge (i.e. 0.5 grams)
- Place the scrubber sludge on a thin copper foil. The copper foil was used as a conductive substrate, which would prevent the charging to the surface of the scrubber sludge.
- Use a LECO hand press to push the scrubber sludge into the copper foil. This would prevent the particles from be dislodged in the high vacuum chamber of the AES.

This procedure proved to be successful in preventing charging and keeping the particle in place. However, the pressing of the particles in the copper foil caused major distortion of the particles. This prevented any accurate surface analysis from being done. An alternative solution which has not been investigated is to use a fine mesh screen as the conductive substrate. This would eliminate the distortion of the particles caused by pressing of the particles.

Table 1: Comparison of spectroscopic techniques available in mineral processing studies (Marabini, A.M, ET AL, 1993)

Spectroscopic Techniques	Destructive (D) or not destructive (ND)	Sampling Depth (monolayers)	Spatial resolution	Chemical information	Depth profile
Air Techniques					
IRS	ND	--------	1 cm^2	yes	no
Transmission					
Emission	ND	2-4	1 cm^2	yes	no
Air	ND	20	1 cm^2	yes	no
PAS	ND	10^2	1 cm^2	yes	yes
Vacuum Techniques					
UPS, XPS	ND	2-6	100 μm	yes	yes
Auger, AES	ND	2-6	0.2 μm	yes	yes
SIMS					
Static	D	2	1 mm	no	no
Dynamic	D	40	1 μm	no	yes
REELS	ND	2	0.2 mm	yes	no
SEXAFS	ND	2-6	100 μm	no	no

Plans for the Thirteenth Quarter

Extensive experiments will be performed with the laboratory-scale column. The feed material will consist of raw scrubber sludge and material that had been pre-treated with water-only cyclone. The flotation reagents used will be the ones that proved to be successful in conventional froth flotation. However the dosages will be optimized for the flotation column. The goal of this study will be to increase the efficiency of the current separation process If time permits in the next quarter new samples will be prepared for Auger electron spectroscopic analysis.

References

Carnahan, R.,1993, Personal communication, U.S Gypsum.

Gage, C.L. and Rochelle, G.T., 1992, "Limestone Dissolution in Flue-Gas Scrubbing; Effect of Sulfite," Journal of Air Waste Management, vol 42 pp. 926-935.

Giesekke, E.W., 1983, "A Review of Spectroscopic Techniques Applied to the Study of Interactions between Minerals and Reagents in Flotation Systems," International Journal of Mineral Processing, vol 11, pp. 19-56.

Goldstein, G., 199,. "Scrubbing Coal for Emission Control," *Mechanical Engineering* Vol. 112, pp. 60-65.

Marabini, A.M., Contini, G., and Cozza, C., 1993, "Surface Spectroscopic Techniques Applied to the Study of Mineral Processing," International Journal of Mineral Processing, vol 38, pp.1-20

Roe, L.A., 1983, *Industrial Waste Flotation*, published by Roeco, Inc., Illinois, pg. 1.

Sutherland, K.L. and Wark, I.W., 1955. *Principles of Flotation*, Australasian Institute of Mining and Metallurgy, Inc., Melbourne, pg. 41.

Weiss, N.L. (editor), 1985, SME Mineral Processing Handbook, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, pp. 4-25.