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Separation of Flue-Gas Scrubber Sludge into Marketable Products

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Abstract

The reduction of sulfur oxides from high sulfur coal burning utility companies has resulted in the production of huge quantities of wet flue-gas desulfurization scrubber sludge. A typical 400 MW power station burning a coal containing 3.5% sulfur by weight and using a limestone absorbent would produce approximately 177,000 tons (dry weight) of scrubber sludge per year. This brownish colored, finely divided material contains calcium sulfite ($CaSO_3 \bullet 1/2H_2O$), calcium sulfate ($CaSO_4 \bullet 2H_2O$), unreacted limestone ($CaCO_3$), and various other impurities such as fly-ash and iron oxide particles. The physical separation of the components of scrubber sludge would result in the re-use of this material. The primary use would be conversion to a highly pure synthetic gypsum. This technical report concentrates on the effect of baffle configuration on the separation of calcium sulfite/sulfate from limestone. The position of the baffles as they related to the feed inlet, and the quantity of the baffles were examined. A clean calcium sulfite/sulfate (less than 2.0% limestone by weight) was achieved with the combination of water-only cyclone and horizontally baffled column.

Table of Contents

Executive Summary

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 ($CaSO_3•0.5H_2O$), gypsum ($CaSO_4•2H_2O$), 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 ($CaSO_3 \bullet 1/2H_2O$). The combined unit operations of water-only cycloning and froth flotation produced material that was clean enough for a synthetic gypsum used by industry. Quarterly report #12 and #13 looked at options to increase the separation efficiency of limestone and silicate impurities from calcium sulfite/sulfate, with the main focus on increasing the weight recovery of valuable product. This led to the construction and development of laboratory scale flotation column tests.

In the current quarter, experimentation with a horizontally baffled laboratory scale flotation column was performed. The test sequence involved determining the baffle configuration that would provide the cleanest product (i.e. less than 2.0% by weight unreacted limestone). The initial results showed that the flotation column with 6 lower baffles provided the cleanest material, while the complete set of baffles provided the best weight recovery.

Introduction

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 Plant A scrubber sludge was used (see Quarterly Report #1 for characterization of this material). 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. 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 would focus on increasing the weight recovery of valuable product (calcium sulfite/sulfate) without effecting the concentration of unreacted limestone in the final product (i.e. less than 2.0% limestone by weight).

Column flotation was explored as a replacement of conventional cell flotation. The recent growth of column flotation has been tremendous. It is currently being used to separate many different types of materials, i.e. iron ore, copper, and coal. The increased use of flotation columns is due to their superior separation efficiency compared to conventional flotation. This increased efficiency can be attributed to: 1) The countercurrent movement of slurry and air bubbles, which increases the probability of bubble / particle attachment. This is accomplished by a larger aerated volume of the cell, a longer concentration gradient between froth and sinks, and the increased time of contact between air bubbles and particles. 2) Froth washing, which provides a secondary upgrading to reduce entrainment of the gangue in the froth. In addition to these there are several other advantages of column flotation: lower power requirements, lower capital cost, smaller floor space than requirements conventional flotation.

Preliminary work on column flotation reported in 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 order to determine if it could out-perform conventional flotation in the removal of unreacted limestone from scrubber sludge. This column was also designed so that horizontal baffles could easily be installed. The increased selectivity of a horizontal baffled column has been shown by the authors for coal flotation (Eisele and Kawatra, 1994a,b).

EXPERIMENTAL

Material

The scrubber sludge that was investigated in this report was Plant A scrubber sludge from Illinois. The characterization of this material is given in Quarterly Report #1. The lack of floatability of this material in its raw state led to the pre-treating of this material with water-only cycloning. The overflow material could then be used as feed material for flotation studies (see Quarterly Report #10 for details of flotation feed material). This material contained approximately 3.0% limestone by weight and had an 80% passing size of 40 microns.

Horizontal Baffled Laboratory Column Design

The laboratory-scale flotation column used had an inside diameter of 7.6 cm and a height of 344.2 cm (see Figure 1). This unit uses two bubble generators, which were a standard type manufactured by Deister Concentration Co. The bubble generators were designed to inject a mixture of approximately equal volumes of air and water into the column, and were located at depths of 170 cm and 324 cm below the froth overflow lip. The feed was introduced at 104.8 cm below the froth overflow lip, and the column level control was set to give a froth depth of 43.2 cm. The washwater spray ring was immersed 5 cm below the froth surface, and the washwater flowrate was 0.95 liters/min. Frother was added to the froth washwater and to the bubble generator water using a diaphragm-type reagent pump, and feed was pumped into the column using a peristaltic pump. The horizontal baffles were designed to be an easy retrofit into the column. The open area of baffles was 40%. The holes in the baffles were at 1.3 cm in diameter. This was done to prevent plugging of the column.

Flotation Reagents

The collector used was an Ethoxylated Octadecyclamine Octadecylguanidine Complex (Aero 870) which was developed by Cytec Industries, Inc. This collector was selected by an intensive surface chemistry study. This study involved the determination of the surface charge of pure components of the scrubber sludge and how the surface charge was effected by dissolved species, pH and collector concentration (see Quarterly Reports #4, #5, and # 8). The verification of the effectiveness of this collector can be seen in Quarterly Report # 11. The frother used in this study was Dowfroth 200, which is a PPG-based frother produced by Dow Chemical Company.

Test procedure

Column flotation had been shown to be an effective method for separating calcium sulfite/sulfate from limestone. The installation of horizontal baffles into the column was expected to further increase the performance of column flotation. The experimental design for this quarter involved

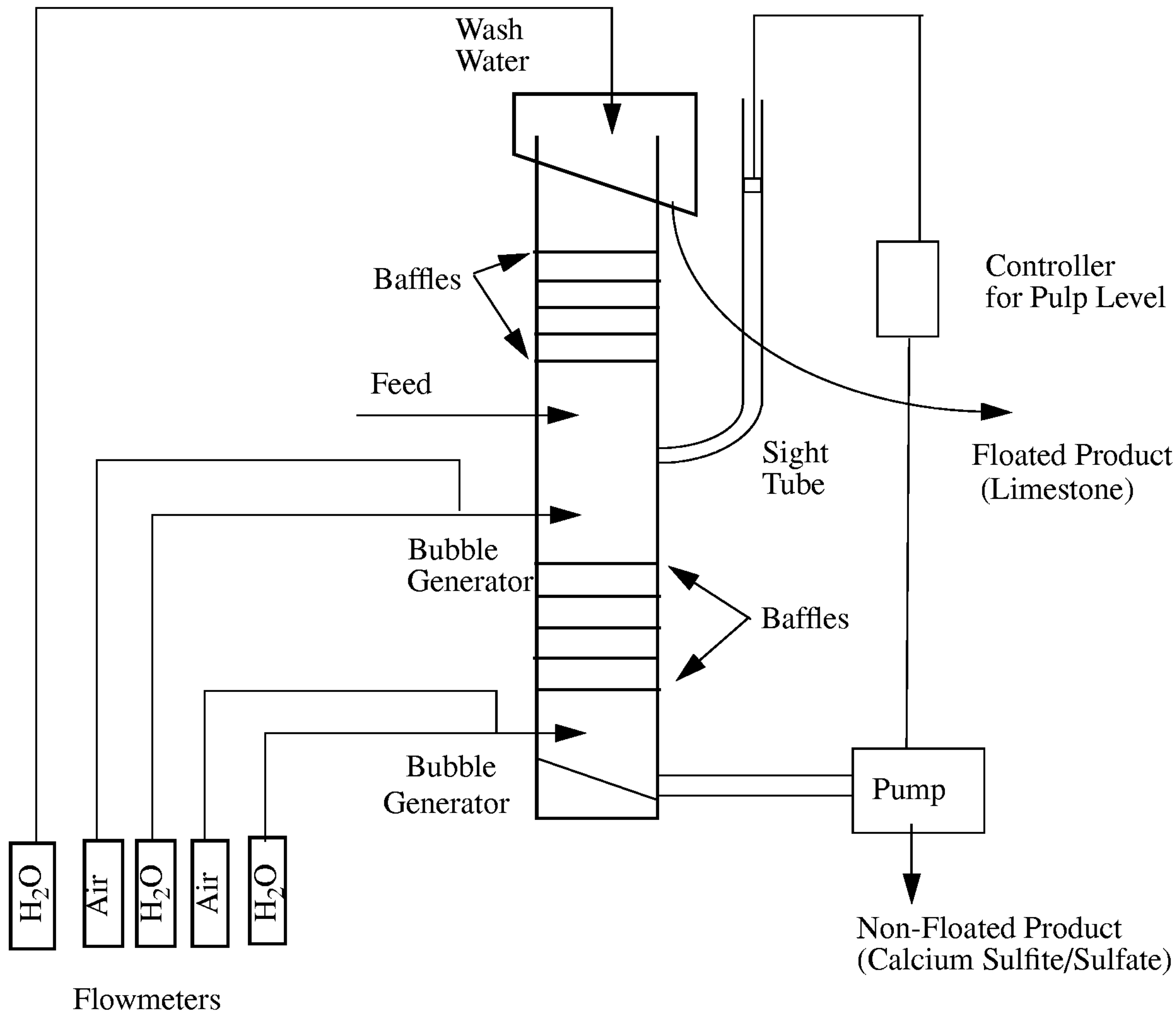


Figure 1: Schematic of the horizontally baffled laboratory-scale flotation column (7.6 cm inside diameter and 344.2 cm high) used in this study.

the performing of a baseline test. This test would be performed with no baffles. Then baffles would be added to determine their effect on the separation performance. Two parameters were of interest. The first was the position of the baffles. There are two areas for the baffles: above and below the feed inlet of the column. This could lead to three combinations: lower baffles, upper baffles, or both upper and lower baffles. Because this is a reverse flotation (i.e. the valuable product is not being floated) only conditions of lower baffles and a full set of baffles were examined. The second parameter investigated was the effect of separation performance based on the number of baffles in the column. The procedure for the horizontally baffled laboratory-scale flotation column tests used in this quarter was as follows:

- Dilute a 500 gram feed sample to 5.0% solids by weight and put in a mixer at 1200 rpm.

- Calculate desired frother and collector concentrations for the feed and the desired frother concentration for the make up water to the column.

- Turn on the frother make up pump and make sure all air bubbles are removed from the water lines. Then turn on water and air and set to desired level.

- Turn on controller for froth level control and set to a level which provides continuous removal of tails.

- Turn on feed pump and set to desired level

- Collect overflow and underflow samples. After feed is stopped the column is run for an additional 15 minutes in order to collect the material still in the column.

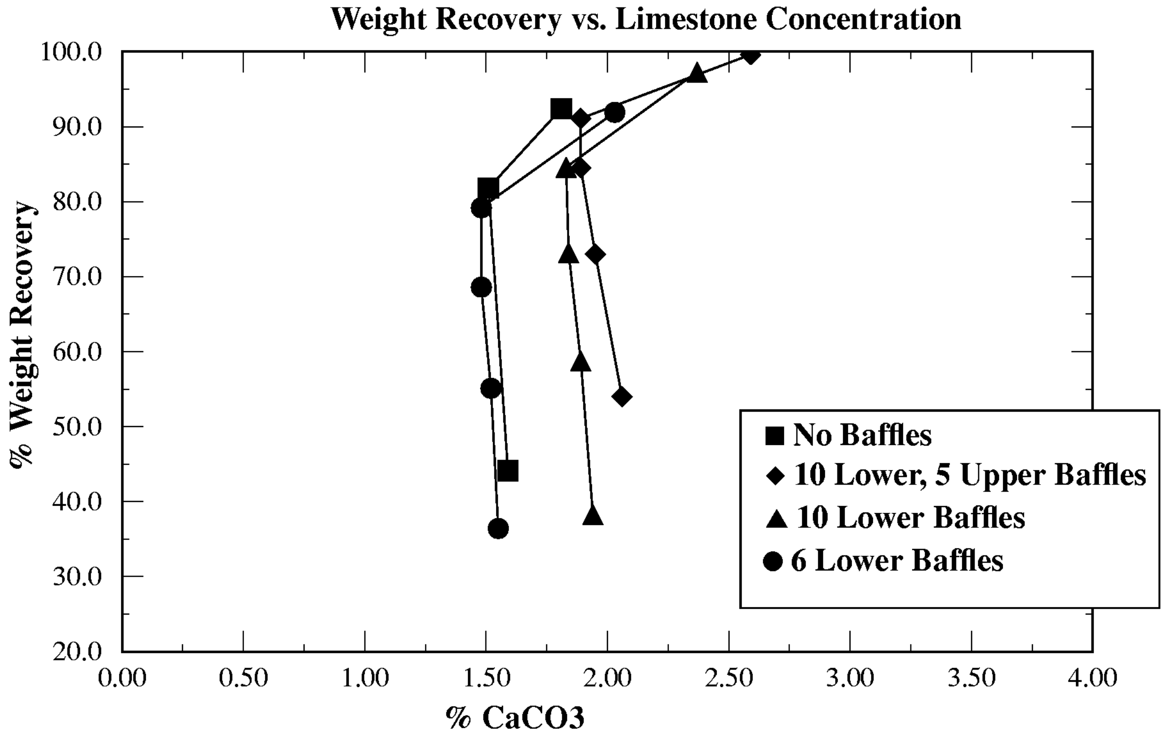
- Measure pH and temperature of the products. Then filter products, dry at 35°C, and prepare for analysis.

RESULTS AND DISCUSSION

Results to date of horizontal baffled column flotation tests showed that the position and the quantity of baffles in the column had an effect on the separation performance The base line test (no baffles) provides an 81% weight recovery of calcium sulfite/sulfate at a grade of 1.51% limestone by weight. This material is considered clean enough for the conversion of synthetic gypsum for industrial use. This value does not include the hold-up value which is the last point on the grade-recovery curves (Figure 2). The hold-up value is the material which was the left inside the column after the test. In all tests performed this material was high in limestone (4.10 to 10.15% limestone by weight). This was due to the limestone product that was in the froth layer when the column was drained. This material was unable to be removed from the column because of the low percent solids in the froth layer at the end of the test. In a fully continuous operation there would be no hold-up fraction.

A full set of baffles (5 upper and 10 lower) provided an increase in weight recovery (91.1% by weight), but a decrease in grade (1.89% limestone by weight). However this is still acceptable quantity. The removal of upper baffles resulted in a decrease in weight recovery (84.6% for 10 lower baffles, and 79.2% for 6 lower baffles) with grades of 1.83% and 1.48% by weight respectively.

Horizontal baffles did have an effect on column performance by either increasing the weight recovery or decreasing the limestone quantity in the calcium sulfite/sulfate product.



Finger 2: Results of baffles configuration on the production of a clean calcium sulfite/sulfate material. The feed material contained 3.0% limestone by weight.

Plans for the Fifteenth Quarter

Experimentation with the horizontal baffled laboratory-scale flotation column will be continued. The experimental design for the upcoming tests will investigate the following factors: (1) effect of horizontal baffles on the separation efficiency of the column as the amount of upper and lower baffles along with the open area of the baffles are altered, (3) vary the limestone concentration of the feed. This will determine the condition that the water-only cyclone should be operated at in order to provide the best overall weight recovery of the combined purification system (i.e water-only cycloning and froth flotation).

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