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Separation of Flue-Gas Scrubber Sludge into Marketable Products

Fourth Year, First Quarterly Technical Progress Report

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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 ($CaSO_3$•$0.5H_2O$), 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 looked at options to increase the separation efficiency of recovering limestone and silicate impurities from calcium sulfite/sulfate, with the main focus on increasing the weight recovery of valuable product. This led to the installation of a 344.2 cm high by 7.6 cm inside diameter laboratory scale flotation column.

In this quarter, preliminary experimentation of the laboratory scale flotation column was performed. The test sequence involved two types of feed material. The first was raw scrubber sludge feed that had poor floatability characteristics. The second was scrubber sludge that was pre-treated with water-only cycloning. The initial results showed that the flotation column provided comparable removal of unreacted limestone as conventional froth flotation, but an increase in the weight recovery of valuable product.

In addition to this, the review and investigation of a horizontal baffled flotation column was initiated. It has been shown that column flotation can be improved by the addition of horizontal baffles in the column (Eisele and Kawatra, 1994 a,b).

Progress During the Thirteenth 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 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. below a 2.0% by weight limestone). 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. Along with performing experiments with the laboratory scale column, a new type of column design will be discussed. This is the horizontal baffled column designed by Kawatra and Eisele at Michigan Technological University.

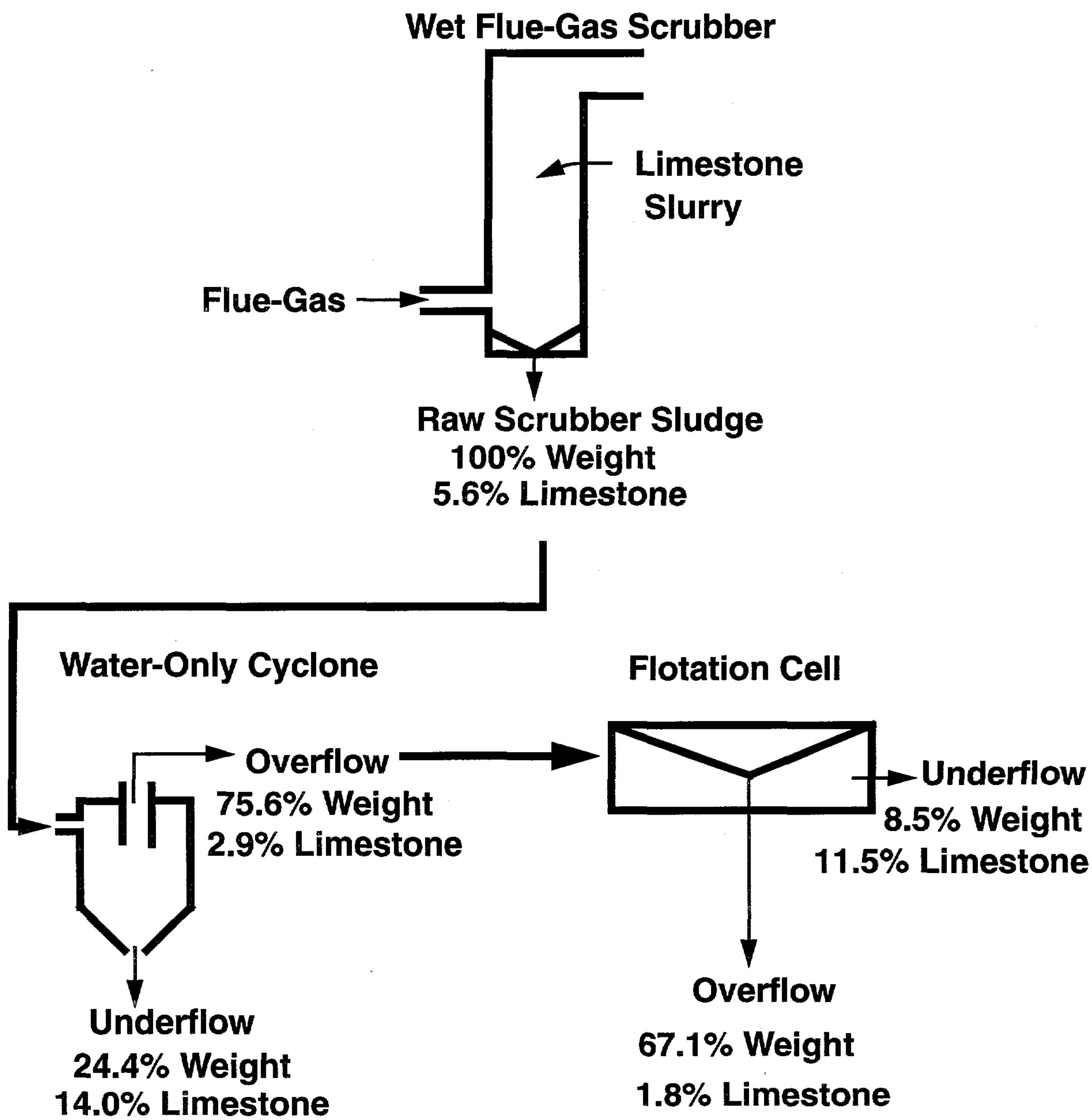

Figure 1: Schematic of the flowsheet which was capable of removing enough of the impurities to provide a clean sulfite/sulfate product.

Column Flotation

In recent years the 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, and it requires less floor space than conventional flotation.

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. Two different feed types were tested in this quarter. The first was raw scrubber sludge as received from the power plant. This material showed poor floatability characteristics in previous experiments (see Quarterly Report #11). This was due to the large particle size of the unreacted limestone. However, it was expected that the advantages of column flotation might produce a desired product (below 2.0% by weight limestone). This would simplify the flow sheet by removing water-only cycloning as a pre-treatment to flotation. The second material investigated was overflow material from the water-only cyclone, see Quarterly Report # 10 for details on this material. This material has been proven to respond to flotation and produce a useful product (see Quarterly Report # 12). However, a higher overall weight recovery of useful material would be desirable.

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 2). 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.

Flotation Reagents

The collector used was an Ethoxylated Octadecyclamine Octadecylguanidine Complex (Aero 870) which was developed by Cytec Industries, Inc. This collector was chosen by surface chemistry studies of scrubber sludge (see Quarterly Report # 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.

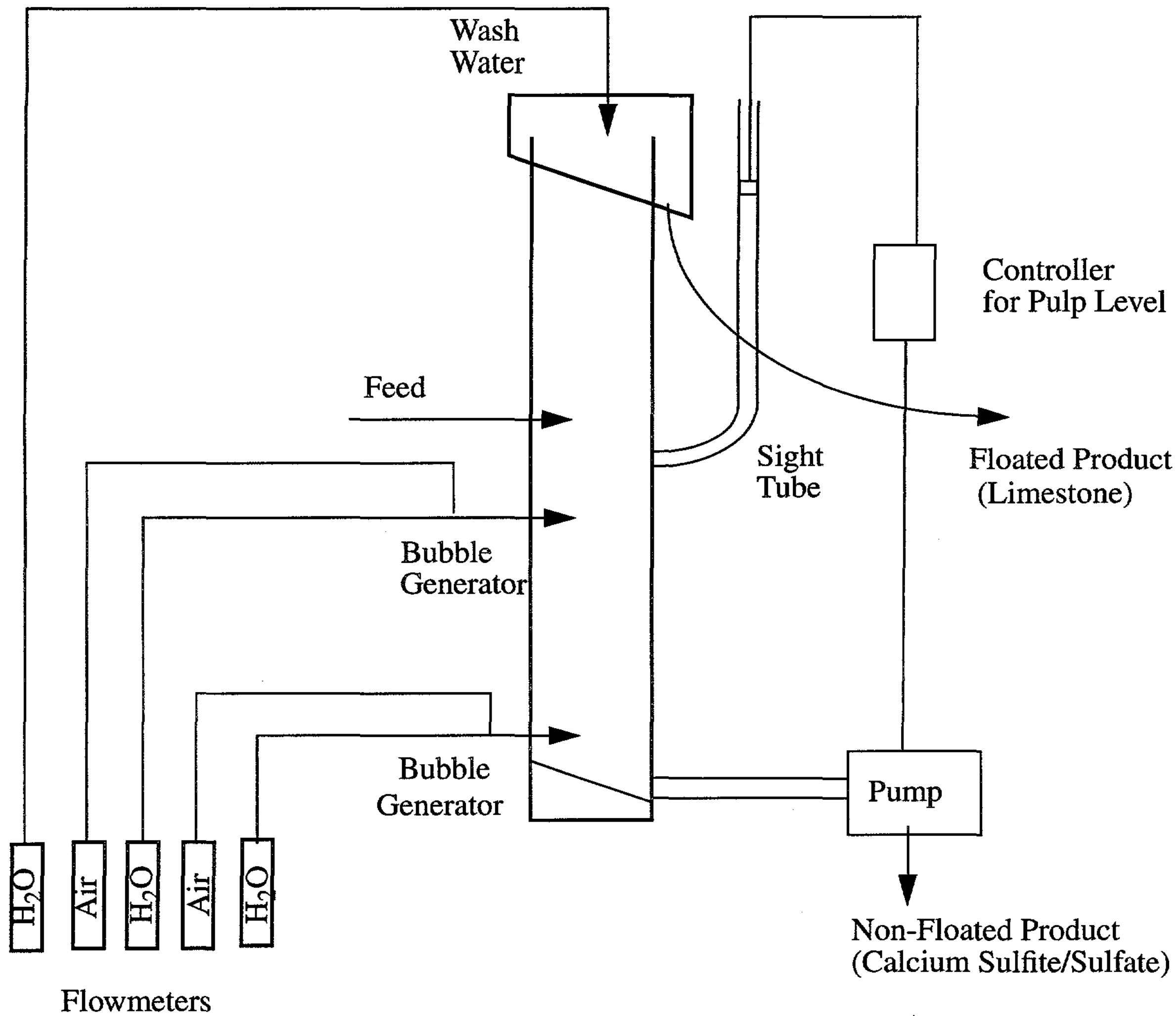

Figure 2: Schematic of the laboratory-scale flotation column (7.6 cm inside diameter and 344.2 cm high) used in this study.

Test procedure

The procedure for the 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 13 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

Preliminary results of laboratory column flotation tests showed an increase in the weight recovery of both test materials (Figure 3). The first material tested was raw scrubber sludge that contained 5.6% limestone by weight. Column flotation reduced the amount of limestone to 4.26% by weight with a 87.2% weight recovery of valuable product. This material was not considered usable for industrial standards. The standard for industrial use is less than 2.0% limestone by weight. However, it did demonstrate the superior performance of column flotation compared to conventional cell flotation.

The second material tested was scrubber sludge that had first been pre-treated with the water-only cyclone. This material contained approximately 3.0% limestone by weight and had been shown to provide a useful industrial product after further purification with conventional cell flotation. However, the overall weight recovery of treating scrubber sludge with water-only cycloning and conventional cell flotation was low. Column flotation was also able to produce a useful industrial product, but with a better weight recovery than obtained with convention cell flotation (Figure 3).

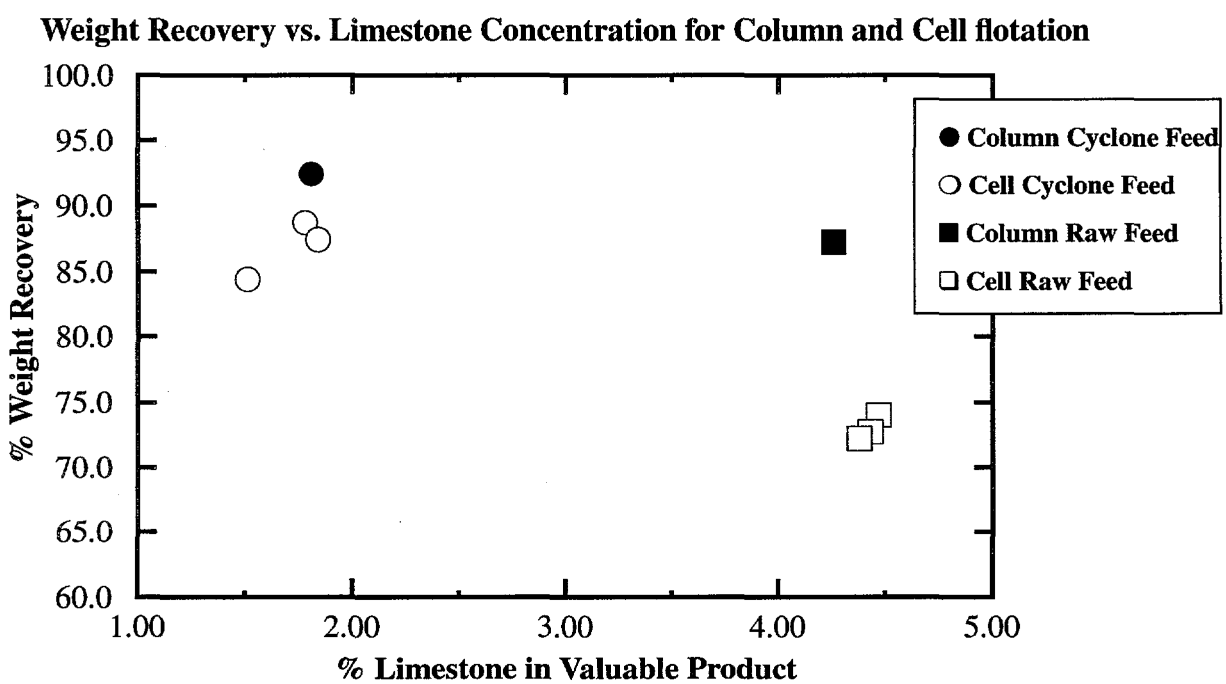

Figure 3: Comparison of column and conventional cell flotation. The collector concentration was the same in all tests (2.0 Kg/mt of Aero 870). Column flotation provided an increase in weight recovery for both materials tested.

Horizontal Baffled Flotation Column

The improved performance of column flotation over conventional flotation has been demonstrated in the previous work. However, column flotation is not without draw backs. These will be reviewed and the alternatives will be discussed.

It is well known that axial mixing and coalescence of air bubbles results in a decrease in efficiency of separation in flotation columns (Finch and Dobby, 1990; Rubinstein, 1995). Axial mixing is the vertical mixing which occurs along the axis of the column (see Figure 4). The results of this axial mixing are two-fold: 1) Upward movement of slurry in the center of the column carries gangue minerals up to the froth, which tends to increase entrainment of ash; and 2) Downward flow of slurry along the outside wall of the column carries small bubbles and coal particles downward, resulting in a loss of valuable material. Axial mixing will increase if the column is not vertical or non-uniform aeration develops. Several investigators have developed methods of reducing this axial mixing (Dell, 1976, Yang, 1988; Eisele and Kawatra, 1994 a,b).

Coalescence of air bubbles can also degrade performance of a column. As bubbles rise, they can merge with other bubbles, which results in larger, faster-rising bubbles. The hydrostatic pressure in the column also decreases as the bubbles rise, which causes them to enlarge. These large bubbles are less able to contact the finer coal particles, and have less surface area available for particles to attach, and so coarser bubbles lead to lower capacity. If the bubbles become too large, they can also disrupt the froth layer, which interferes with froth washing and leads to a higher-ash froth product.

The horizontal baffled column developed by Eisele and Kawatra was designed for improved performance in coal flotation. It has been extensively tested in an industrial setting without showing the negative effects (plugging and reduced capacity) observed in other columns that attempted to reduce axial mixing (Eisele and Kawatra, 1994a,b). The baffles have been designed to be straightforward modifications to existing columns, so they can be installed as a retrofit at reasonable cost. It is also possible to design the baffles to allow trash and foreign objects to pass through, while preventing bubbles from coalescing and becoming large enough to be troublesome.

Baffles were located in two regions of the column, one set above the feed inlet and the other set below the feed inlet. The benefit of the upper baffles in the column was to reduce the coalescence of air bubbles as they rise through the column. This in turn would reduce the axial mixing which would increase the separation efficiency of the column. The benefit of the lower baffles was to increase the retention time of the sinks, to insure that every floatable particle has an opportunity to be recovered.

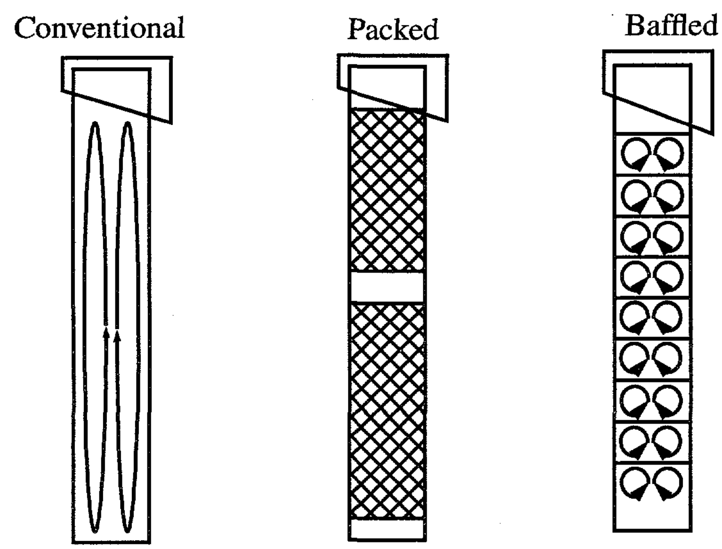

Figure 4: Comparison of flow patterns in conventional, packed, and horizontally baffled columns (Eisele and Kawatra, 1994a).

Previous work by Eisele and Kawatra demonstrated that a horizontal baffled column was superior to a non-baffled column for coal flotation. This work was also verified in a pilot scale test located on the coal cleaning facility (Eisele and Kawatra, 1994b).

Plans for the Fourteenth Quarter

Experimentation with the laboratory-scale flotation column will be continued. The experimental design for the upcoming tests will investigate the following factors. The first is to determine the optimum reagent concentration for the separation of limestone from calcium sulfite/sulfate in this flotation column. The second is to investigate the effect of horizontal baffles on the separation efficiency of the column. The amount of upper and lower baffles along with the open area of the baffles will be investigated. The final condition to be analyzed is too 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).

References

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

Dell, C.C., 1976, Froth Flotation, British Patent No. 1,519,075.

Eisele, T.C., and Kawatra, S.K., 1994a, "Laboratory Baffled-Column Flotation of Mixed Lower / Middle Kittanning Seam Bituminous Coal," 1994 SME Annual Meeting, Albuquerque, NM, Preprint No. 94-22.

Eisele, T.C., and Kawatra, S.K., 1994b, Baffled-Column Flotation of a Coal Plant Fine Waste Stream," 1994 SME Annual Meeting, Albuquerque, NM, Preprint No. 94-21.

Finch, J.A. and Dobby, G.S., 1990, *Column Flotation*, Pergamon Press, Oxford.

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

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

Rubinstein, J.B., 1995, *Column Flotation, Processes, Designs and Practices*, Gordon and Breach Science Publishers S.A., Switzerland.

Yang, D.C., 1988, "A New Packed Column Flotation System," *Column Flotation '88*, K.V.s. Sastry, editor, Society of Mining Engineers, Littleton, CO pp. 257-266.

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