DOE/PC/93214--T7

Separation of Flue-Gas Scrubber Sludge into Marketable Products

Third Year, First Quarterly Technical Progress Report

Performance Period: 9/1/95 to 11/30/95 (Quarter #9)

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

December, 1995

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

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, proven to be the most promising flotation collector studied. Further laboratory work will be done to verify these results.

In the current quarter, further investigation of hydrocycloning was continued. As mentioned in quarterly report # 7, froth flotation was much more effective if scrubber sludge was first processed through a hydrocyclone. This allowed for the coarser limestone and ball mill chips to be removed. Hydrocycloning also helped to scrub the surface of the limestone, which produced a clean surface that was suitable for preferential adsorption of the flotation collector. Therefore the focus of this quarter was to determine the best parameters for removing impurities from wet flue gas scrubber sludge using a two-inch water-only cyclone.

Progress During the Eighth 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 which 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 recovery 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.

Before further froth flotation studies were carried out, it was necessary to optimize the hydrocycloning stage. As stated in an earlier progress report, a water-only cyclone was used. This type of cyclone was selected because it separates largely based on the particle density whereas conventional hydrocyclones separate primarily on the basis of particle size. As Table 1 shows, calcium carbonate (unreacted limestone) and the other impurities (silicates and iron oxides) have a higher density and should report to the underflow product from the cyclone. The less dense material (calcium sulfite and calcium sulfate (gypsum)) and the smallest particles should report to the overflow. This overflow material is the material that is used as flotation feed.

Table 1: Properties of the major components in the scrubber sludge investigated.

Component	Specific Gravity (g/cm^3)	Percent Weight	Solubility in Water (g/L)
Calcium Sulfite ($CaSO_3 \bullet 1/2H_2O$)	2.52	~77.0	0.04
Calcium Sulfate ($CaSO_4 \bullet 2H_2O$)	2.32	~14.0	3.2
Calcium Carbonate ($CaCO_3$)	2.73	~5.6	0.013
Silicate	2.6-2.9	1.5-2.5	Insoluble
Iron Oxides	7.8	0.5-1.5	Insoluble

Experimental

The hydrocyclone test rig used in this study was constructed during the seventh quarter (see Quarterly Report # 7 for details). This test rig was set up to run either a two-inch water-only cyclone or a two-inch conventional hydrocyclone. The dimensions of these hydrocyclones are shown Figure 1. The water-only cyclone was the only one used for this study. Water-only cyclones differentiate between particles largely based on their density, whereas conventional hydrocyclones differentiate based on the size of the particles. Due to the higher density of the impurities in scrubber sludge and the overlapping size distribution of the gypsum and the impurities, water-only cycloning was the logical type of hydrocyclone to use.

During cyclone operations the more dense material reports to the underflow portion of the cyclone, whereas the less dense material (in this case, the calcium sulfite and gypsum product) would report to the overflow. The overflow material would then be used for froth flotation. Therefore the objective of this study was twofold. The first was to determine the optimum vortex finder and spigot diameter for the two inch water-only cyclone. The optimum configuration was considered to be the one that produced a high concentration of unreacted limestone in the underflow product, while maintaining a high weight recovery of the calcium sulfite and gypsum to the overflow product. The second objective was to determine the optimum operating conditions (feed percent solids and operating pressure) for the optimum water-only cyclone configuration. The following tests were used to achieve these objectives.

Water-Only Cyclone Test Procedure

The procedure for the water-only cyclone experiments was as follows:

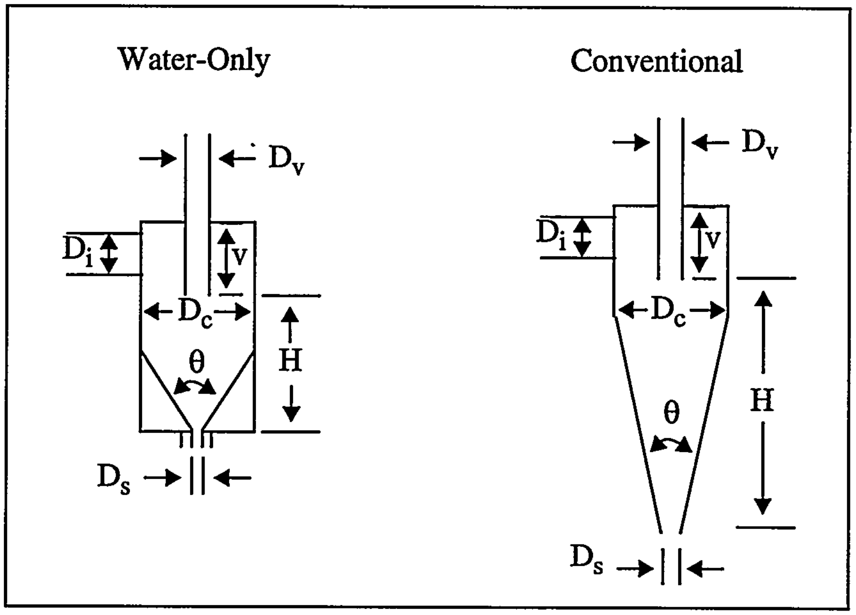
- The water-only cyclone test rig was thoroughly washed out with water and dried to make sure it was clean before all test work was started

- A 950.0 gram sample of scrubber sludge from Plant A (see First Quarterly report for complete characterization of this scrubber sludge) was suspended in water at 5.0% solids by weight to produce 18 liters of slurry.

- The slurry was then added to the hydrocyclone feed sump and allowed to circulate through the hydrocyclone test rig for at least 15 minutes before samples were taken. This allowed time for the slurry to become thoroughly mixed.

- The speed of the pump was then adjusted to obtain the desired hydrocyclone pressure. All hydrocyclone results were based on the feed pressure to the hydrocyclone.

- Samples of the overflow and underflow were then taken simultaneously and the time taken to collect the samples was recorded. The collected samples were weighed as wet slurries, and the temperature and pH of the samples were measured. Samples were then filtered and placed in a drying oven, and dried at 35 - 40 °C. Once the samples were dry they were weighed and prepared for chemical analysis. See previous reports for the procedure for chemical analysis.



Type of Hydrocyclone	Dimensions of Hydrocyclones in mm						
	D_i	D_c	D_v	D_s	V	H	θ (deg.)
Water-Only Cyclone	6 x 10	51	14	6	25	27	90
	6 x 8	51	11	5	25	29	90
	6 x 6	51	8	3	22	30	90
Conventional Hydrocyclone	same as above	51	same as above	10	same as above	311	6.6

Figure 1. Cross sectional view of two inch water-only and conventional hydrocyclone with there corresponding dimensions.

Results and Discussion

Three different sizes of water-only cyclones were examined. The results can be seen in Table 2. The largest water-only cyclone (vortex finder = 14 mm and spigot diameter = 6 mm) investigated produced the best weight recovery. However, this water-only cyclone also produced an overflow product that was higher in limestone than that produced using the other configurations. The middle-size water-only cyclone (vortex finder = 11 mm and spigot diameter = 5 mm) provided the cleanliest material and still maintained a reasonable weight recovery. The smallest water-only cyclone (vortex finder =8 mm and spigot diameter = 5 mm) proved to be the worst condition for this separation. The grade of the overflow product was not improved, and the weight recovery decreased compared to the middle-size cyclone at the same pressure. In this case the optimum size two inch-water-only cyclone was the middle-size one. Therefore further studies were continued with this cyclone to determine the best operating condition to use.

Table 2: Results of determining the optimum size two inch water-only cyclone for removing the more dense impurities (unreacted limestone and silicates) from the less dense useful product (gypsum and calcium sulfite). Feed material to the water-only cyclone contained 5.6 +/- 0.3% unreacted limestone.

Dimensions of Water-Only Cyclone	Pressure (psi)	Percentage of Unreacted Limestone in Gypsum Product	Percent Weight. Recovery of the Gypsum Product
Vortex Finder = 14 mm Spigot Diameter = 6 mm	5	4.03 +/- 0.07	93.8
	10	3.88 +/- 0.08	93.0
	20	3.71 +/- 0.11	92.6
Vortex Finder = 11 mm Spigot Diameter = 5 mm	5	3.45 +/- 0.10	84.1
	10	3.36 +/- 0.10	81.1
	20	3.21 +/- 0.11	78.2
Vortex Finder = 8 mm Spigot Diameter = 3 mm	20	3.31 +/- 0.06	71.0

As the pressure is increased the amount of kinetic energy of the particles is also increased. This should theoretically produce a better separation. Therefore, several additional tests were performed at higher pressure. The results can be seen in Table 3. As was expected, the overflow product became cleaner at higher pressures. This was accompanied by a loss in the weight recovery of useful product, but the loss was considered acceptable for this work. Higher pressures were not investigated because the physical limits of the hydrocyclone and test rig were being approached, and because further decrease in impurity level would have been accompanied by an unacceptably large decrease in weight recovery.

Table 3: Results for determining the optimum operating condition for the two-inch water-only cyclone with a vortex finder of 11 mm and a spigot diameter of 5 mm. Feed material to the water-only cyclone contained 5.6 +/- 0.3% unreacted limestone.

Dimension of Water-Only Cyclone	Pressure (psi)	Percentage of Unreacted Limestone in Gypsum Product	Percent Weight Recovery of the Gypsum Product
Vortex Finder = 11 mm Spigot Diameter = 5 mm	5	3.45 +/- 0.10	84.1
	10	3.36 +/- 0.11	81.1
	20	3.21 +/- 0.11	78.2
	25	3.03 +/- 0.09	78.1
	35	3.00 +/- 0.11	76.5
	45	2.89 +/- 0.10	75.6

Conclusions

Water-only hydrocycloning was able to remove nearly 50% of the unwanted limestone from the scrubber sludge. The separation performance was best when a water-only cyclone was used that had a vortex finder of 11mm and a spigot diameter of 5mm. Cyclone feed pressures as high as 45 psi could still provide a suitable weight recovery and reduce the overflow (useful) product to as little as 2.89% unreacted limestone.

Plans for the Ninth Quarter

Laboratory scale froth flotation work will begin, using as feed the overflow product from the water-only cyclone. The primary flotation collector that will be investigated is AERO 870, a cationic collector from Cytec, Inc. This collector was shown to have better selective adsorbtion properties than the other collectors studied (see progress report #8 for details). Work will also be done to investigate the surface characteristics of the calcium carbonate (unreacted limestone) to determine what effect hydrocycloning has on the surface of the calcium carbonate that makes it more amenable to froth flotation. This characterization will be carried out with the aid of a scanning electron microscope (SEM).

This SEM study has two major objectives. The first is to study the morphology of scrubber sludge to see if it will provide a clue to methods for obtaining a more effective separation. Newly developed flotation reagents use the crystal shape of particles to perform a separation, and therefore a better understanding of the morphology might prove useful. The second objective is to determine the nature of the possible surface layer on the calcium impurities, which prevents efficient flotation separation unless the sludge is treated by cyclone processing.

References

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

Goldstein, G., 1990. "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.

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