DOE/PC/93214--T8

Separation of Flue-Gas Scrubber Sludge into Marketable Products

Second Year, Second Quarterly Technical Progress Report

Performance Period: 12/1/94 to 2/28/95 (Quarter #6)

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

For the
U. S. Department of Energy
Pittsburgh Energy Technology Center
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March, 1995

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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 ($CaSO_3 \bullet 0.5H_2O$), gypsum ($CaSO_4 \bullet 2H_2O$), and unreacted limestone ($CaCO_3$) or lime ($Ca(OH)_2$), with miscellaneous objectionable impurities such as iron oxides, 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 the 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. 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. Initial studies of the zeta potentials of the most important species found in scrubber sludge were also described. Quarterly report #4 continued the zeta potential studies of the major components in the scrubber sludge. These studies included the effect on zeta potential when the following factors were varied: pH, dissolved salts, and concentration of collector dosage. Quarterly report #5 finished preliminary zeta potential work. This investigation included the determination of the point of zero discharge for all the major components in scrubber sludge (Calcium Sulfite, Calcium Sulfate, and Calcium Carbonate).

In the sixth quarter, the optimization of flotation reagents was begun. The first type of flotation reagents that were investigated were frothers. The frothers that were investigated are common industrially used frothers produced by Dow Chemical Co. These frothers have varying degrees of selectivity and strength characteristics. Initial results show that a week frother that is very selective provides the best results. It was also observed from the results that the hydrophobicity of $CaCO_3$ is minimal or depending on the freshness of the surface.

In addition to optimization of flotation reagents a literature review was also begun on the methods of oxidation of calcium sulfite to calcium sulfate (gypsum). The details of these studies are presented in the following section.

Progress During the Sixth Quarter

There are several types of flotation reagents each with their own function. The main two types of flotation reagents are frothers and collectors. Frothers were designed to stabilize the air bubbles so a froth layer can be obtained. Collectors are chemicals that react with the surface of a selected particle to make the surface of that particle hydrophobic, so that an air bubble will adhere to its surface. The surface charge of the particles determines which type of flotation reagents will perform well, and the pH that would produce the optimum separation. Due to the natural hydrophobic tendencies of $CaCO_3$, which makes it possible to separate it without adding a collecting reagent the optimization of a frother was investigated first.

Initially the three types of frother that were investigated at the slurries natural pH were DF 200, DF 250, and DF 1012. All of these frothers are polyproylene glycol methyl ethers with varying strengths and selectivities. Their chemical structure and approximate molecular weights are given in Table 1.

Table 1: Physical characteristic of the frothers used in determining the best frother type for this froth flotation process. Dow froth frothers are manufactured by Dow Chemical Co.

Frother	Approximate Molecular Wt.	Structure
Dow Froth 200	200	$CH_3\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_3\text{-}H$
Dow Froth 250	250	$CH_3\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_{4.5}\text{-}H$
Dow Froth 1012	400	$CH_3\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_{5.5}\text{-}H$

Froth Flotation Experiments

A conventional flotation cell was used for these flotation studies because of its ease of use. The flotation cell was fitted with motorized paddles to remove the froth, as shown in Figure 1. This method of froth removal was used instead of more conventional removal of froth by hand because the performance of the mechanical paddles is more consistent from test to test. The cell was also designed to maintain a consistent slurry level inside the flotation cell.

The basic procedure for each flotation experiment was as follows:

- Add the proper dosage of flotation reagents to 10 liters of saturated scrubber sludge water. Saturated scrubber sludge water was used to prevent any losses by dissolution of the test material. The temperature of the water was then recorded. This water was the allowed to flow into the flotation cell.
- Approximately 115 grams of Plant A Scrubber Sludge was then added to the flotation cell and conditioned for 2 minutes. The particle size and chemical composition of the Plant A Scrubber Sludge can be seen in a previous progress report.
- The air and froth removal paddles were then turned on. The timer was started when the first froth hit the collection pans, and the test was run for 5 minutes. The time interval of 5 minutes was selected to make sure that all the material that could float would have enough time to do so.

- The pH of the slurry was then measured shortly after the test was over.
- The products of the flotation test were weighed and filtered. They were then placed into the drying oven at 40°C for 24 hours.
- After the material was dried, a chemical analysis was performed to determine the composition of the flotation products. The procedure for determining the composition of the components of a scrubber sludge has already been given in a previous progress report.

Results of Flotation Experiments

The initial results of optimizing the type and dosage of frother can be seen in Table 2. The best results were obtain when the lowest amount of DF 200 were used. This was due to this reagent being a week highly selective frother. The material used in these experiments was untreated raw sludge, and it can be seen that the $CaCO_3$ from this material was not highly floatable. This is in contrast to the feed which was used in previous experiments, which had been pre-treated by hydrocyclone separation to remove coarse particles, and which showed significant flotation of the $CaCO_3$. Investigations are underway to determine the reasons for the different flotation behavior of the two feeds.

Plans for the Seventh Quarter

Optimization of the types and dosages of frothers will be continued, along with a further study of the hydrophobicity of $CaCO_3$. An investigation of collector optimization will also be started. The continuous paddle flotation cell will also be used in this phase of the project. The results of the earlier zeta potential work will help to determine the surface environment for optimum separation, and to select the best collector type and dosages.

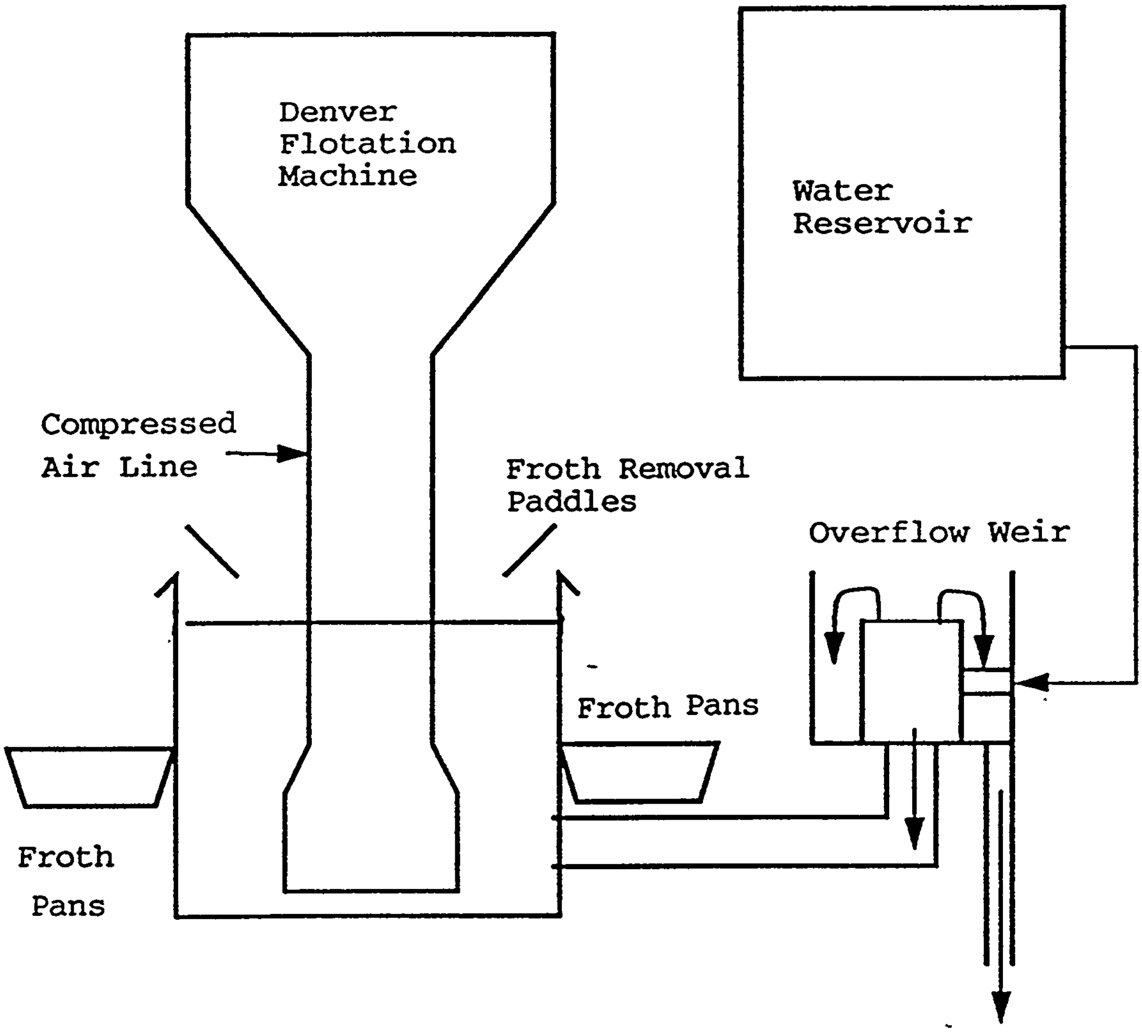

Figure 1. Schematic diagram of the conventional flotation cell showing the motorized froth scrapers and the pulp level control. Froth paddle speed = 19.5 rpm.
Cell volume = 2.75 liters. Impeller speed = 1150 rpm.

Table 2: Flotation Results for Duckcreek Scrubber Sludge using only a frother for flotation reagents. The feed assay was 5.16 +/- 0.09. The temperature of each test was 22°C and the pH was between 8.0 and 8.4. This was a reverse flotation, therefore the cell froth is the reject product. The uncertainties in the weight percent $CaCO_3$ were determined by measuring all of the assays in triplicate.

Frother		% Wt Recovery	% Wt $CaCO_3$ in Concentrate
Type	Dosage (Kg/mt)		
DF 200	0.2	88.98	5.02 +/- 0.13
		87.17	5.04 +/- 0.02
	0.4	49.80	5.86 +/- 0.08
		47.42	6.39 +/- 0.11
	0.6	41.26	6.39 +/- 0.08
		59.61	5.62 +/- 0.12
DF 250	0.1	75.35	5.35 +/- 0.02
		83.63	5.17 +/- 0.07
	0.2	58.70	5.55 +/- 0.14
		51.97	5.33 +/- 0.22
	0.4	32.80	6.57 +/- 0.07
		29.49	6.39 +/- 0.14
DF 1012	0.1	79.89	5.25 +/- 0.29
		83.72	5.10 +/- 0.08
	0.2	62.44	5.28 +/- 0.16

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