Separation of Flue-Gas Scrubber Sludge into Marketable Products

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ABSTRACT

A tremendous amount of wet flue-gas desulfurization scrubber sludge (estimated 20 million metric tons per year in the United States) is currently being landfilled at a huge cost to utility companies. Scrubber sludge is the solid precipitate produced during desulfurization of flue-gas from burning high sulfur coal. The amount of this sludge is expected to increase in the near future due to ever increasing governmental regulation concerning the amount of sulfur emissions. Scrubber sludge is a fine, grey colored powder that contains calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$), calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), limestone (CaCO_3), silicates, and iron oxides.

This material can continue to be landfilled at a steadily increasing cost, or an alternative for utilizing this material can be developed. This study explores the characteristics of a naturally oxidized wet flue-gas desulfurization scrubber sludge and uses these characteristics to develop alternatives for recycling this material.

In order for scrubber sludge to be used as a feed material for various markets, it was necessary to process it to meet the specifications of these markets. A physical separation process was therefore needed to separate the components of this sludge into useful products at a low cost. There are several physical separation techniques available to separate fine particulates. These techniques can be divided into four major groups: magnetic separation, electrostatic separation, physico-chemical separation, and density-based separation. The properties of this material indicated that two methods of separation were feasible: water-only cycloning (density-based separation), and froth flotation (physico-chemical separation). These processes could be used either separately, or in combination. The goal of this study was to reduce the limestone impurity in this scrubber sludge from 5.6% by weight to below 2.0% by weight. The resulting clean calcium sulfite/sulfate material can be oxidized into a synthetic gypsum that can be used in several markets which include: wallboard manufacturing, plaster, portland cement, and as a soil conditioner.

Single stage water-only cycloning removed nearly 50% of the limestone by weight from the scrubber sludge and maintained a weight recovery of 76%. Froth flotation produced a calcium sulfite/sulfate that contained 4.30% limestone by weight with a 71% weight recovery. These methods were successful in removing some of the limestone impurity, but were not able to meet the specifications needed. However, the combination of water-only cycloning and froth flotation provided a clean, useful calcium sulfite/sulfate material with a limestone grade of 1.70% by weight and a total weight recovery of nearly 66%.

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CHAPTER 1

INTRODUCTION

A tremendous amount of wet flue-gas desulfurization scrubber sludge (estimated 20 million metric tons per year) is currently being landfilled at a huge cost to utility companies. Scrubber sludge is the solid precipitate by-product of desulfurization of flue-gas from power stations burning high sulfur coal. The amount of this sludge is expected to increase in the near future due to ever increasing governmental regulation concerning the amount of sulfur emissions. Scrubber sludge is a fine, grey colored powder that contains calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$), calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), limestone (CaCO_3), silicates, and iron oxides.

The cost for landfill space is at a premium in high population areas. The literature has reported that landfill cost can average \$17 per ton for bulky, stable, non-toxic waste (Baillod et al., 1990). Therefore scrubber sludge cannot be considered valueless, because of the cost associated with landfilling this material. Is this material only suitable for landfilling, or is there opportunity to develop new technology, which would make use for the mineral value of the material by conversion to synthetic gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)?

Natural gypsum is used in many different industries, such as wallboard manufacturing, plaster, portland cement, and agriculture soil conditioners. Currently, natural gypsum is mined and processed like other industrial minerals. This processing includes reducing to a desirable size distribution and removal of any impurities. Using scrubber sludge as a synthetic gypsum to replace natural gypsum already has the benefit that the synthetic material is already a powder, and so there is no need to reduce its particle size. However, potential users of gypsum are not eager to purchase this synthetic gypsum because it contains certain impurities, and is of uneven quality in its raw form. It is the goal of this study to determine a separation strategy which would produce a clean synthetic gypsum that could be used as a replacement for natural gypsum.

Background

The Clean Air Act Amendments (CAAA) of 1990 have limited the amount of sulfur oxides that can be produced by coal burning utility companies. This has caused utility companies to re-evaluate their operating strategy. There are three strategies for controlling the amount of sulfur oxide emissions. These include fuel switching, pre-combustion desulfurization, and post-combustion desulfurization. The passage of the CAAA has led to tremendous activity in the research and development of post-combustion desulfurization, especially flue-gas desulfurization (FGD). One hundred and eighty nine FGD processes have been identified in a report to the Electric Power Research Institute (EPRI), (Radian Corporation, 1984). However, most of these methods are still laboratory and pilot plant processes, and only a few have been commercialized. The most industrially used method is wet flue-gas desulfurization. There are several reasons for this: low operating cost, high reliability and high SO_2 removal.

Wet flue-gas desulfurization uses ground limestone or lime to convert sulfur oxide gases into a solid precipitate. Schematic of a wet flue-gas scrubber is given in Figure 1.1. Chemical reactions involved in desulfurization using limestone (CaCO_3) are given below:

Sulfur Dioxide Hydration:

Limestone Reactions:

Overall Reaction:

Figure 1.1: Schematic of wet flue-gas desulfurization scrubber.

Requirements of Gypsum Industry

There are many possible markets for a high quality synthetic gypsum. These include: prefabricated products (wallboard), plaster, additives in portland cement, and soil conditioners. The largest user of natural gypsum (~75% of the annual U.S. consumption) is the production of prefabricated products, predominately wallboard (Luckervich, 1993). The wallboard industry would therefore be the preferred market for this synthetic gypsum. However, before synthetic gypsum can be used as a replacement for natural gypsum the impurities in the synthetic gypsum must be reduced to levels that are similar to natural gypsum or lower.

The most abundant impurity in this scrubber sludge was unreacted limestone. Table 1.1 gives the chemical analysis of a scrubber sludge which was obtained for this study from a utility company burning high sulfur coal. The unreacted limestone is due to incomplete dissolution of the limestone during its reaction with sulfur oxides. There are several reasons for incomplete dissolution of the limestone: particle size distribution, fluctuation in sulfur oxide concentration due to inconsistencies in coal, purity of the limestone, and better sulfur oxide removal at higher scrubber pH (where limestone is less soluble). Other impurities in the scrubber sludge were iron chips produced during the grinding of the limestone.

Impure scrubber sludge can lead to several difficulties in wallboard manufacturing. These include: excess equipment wear, poor paper adhesion, and discoloration of the wallboard. However the biggest problem with impurities is they reduce the purity of the gypsum, which makes it difficult to control the hardening rate of the calcium sulfate/water paste. The acceptable weight percent of impurities for wallboard vary from manufacturer to manufacturer but most of them require a minimum of 95.0% by weight gypsum in their raw material (Ojanpera et al. 1993; Abbott, et al., 1993; Mayer, 1993; and Fellman et al, 1993). The maximum level of unreacted limestone present varies but 2.0% by weight or less is considered acceptable. Further reduction of the impurities could also open up additional markets for this synthetic gypsum.

Characterization of Test Material

The wet flue-gas desulfurization scrubber sludge obtained for this study was from a coal burning power station in Illinois. This 400 MW power station burned a high sulfur coal (3.48% Sulfur by weight) and used limestone as the absorbent. They produce approximately 170,000 tons (dry weight) of scrubber sludge per year. This material is pumped out the bottom of the scrubber at 13.5% solids by weight. The material is then de-watered and mixed with flyash, another by-product of coal combustion, and then landfilled. The chemical composition and physical properties of this scrubber sludge are given in Table 1.1. X-ray diffraction was also used to characterize the compounds in this scrubber sludge, producing the results given in Figure 1.2. Along with labeled compounds, peaks for quartz (SiO_2) and Dolomite ($\text{CaMg}(\text{CO}_3)_2$) were determined. Particle size distribution of the raw scrubber sludge and the limestone absorbent are given in Figure 1.3. These size distributions were determined by Microtrac (laser diffraction technique).

Figure 1.2: X-ray diffraction results of raw scrubber sample reached from the Central Illinois Light Company. The dominant phase is $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$, with the CaCO_3 being residual absorbent. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Quartz (SiO_2) and Dolomite ($\text{CaMg}(\text{CO}_3)_2$) were also detectable in trace amounts.

Table 1.1: Characteristics of the major components in a naturally-oxidized wet flue-gas scrubber sludge investigated in this study

Component	Percent Weight	Specific Gravity (g/cm^3)	Solubility in Water (g/L)
Calcium Sulfit ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$)	~77.0	2.52	0.04
Calcium Sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	~14.0	2.32	3.2
Calcium Carbonate (CaCO_3)	~5.6	2.71	0.013
Silicate	1.5-2.5	2.6-2.9	Insoluble
Iron Oxides	0.5-1.5	7.8	Insoluble

Size Distribution of Scrubber Sludge and Pre-Reacted Limestone

Figure 1.3: Size distribution of limestone before it was reacted with sulfur oxides, and the resulting scrubber sludge. Size distributions were determined by Microtrac (laser diffraction technique). The scrubber sludge was coarser than the original limestone, due to growth of calcium sulfite crystals in the scrubber.

Scanning Electron Microscopy Study

The objectives for this portion of the project was to use SEM as a tool for the general characterization of the components of a wet flue-gas scrubber sludge, and to examine the morphology of the particles to determine whether there were any factors which would be important in the removal of the unreacted limestone. This could provide valuable information for the flotation of unreacted limestone from calcium sulfite/sulfate. The use of Auger analysis for the detection of surface layers on the particles was also considered, because Auger analysis is ideally suited for determining the characteristics of thin surface layers which have different properties than the substrate. However, Auger analysis is not practical for this application, because the scrubber sludge is mostly composed of hydrated calcium salts, which will tend to decompose in a hard vacuum. Since Auger analysis requires a very hard vacuum (at least 10^{-7} torr, and preferably 10^{-9} torr), it is not practical to analyze scrubber sludge by this means. Either the water vapor released by the particles will spoil the vacuum and make analysis difficult or impossible, or the particles will disintegrate as they lose their water of crystallization, changing the properties of the particles before they are analyzed.

Samples were prepared for analysis using the following procedure. A layer of conductive carbon paint was put onto a bakelite slug, to make a sticky, conductive surface for the scrubber sludge particles to adhere to. A carbon coating was then made over the particles, using either an SPI carbon coater, or a Denton DV-502 carbon evaporator. This carbon coat was needed to prevent

electrical charge from building up on the non-conductive sludge particles. For the Denton DV-502 Evaporator, the thickness of the carbon coat was approximately 200-300 Angstroms, while the thickness of the carbon layer from the SPI Carbon Coater was unpredictable.

Two major types of particles were observed when investigating the raw scrubber sludge, see Figure 1.4 (Raw Feed). The flat, platy particles produced large Ca and S peaks when analyzed by Energy Dispersive X-Ray Spectrometer (EDS) analysis, and were determined to be calcium sulfite. These flat, platy particles also covered the majority of the specimen, which makes sense because calcium sulfite is the most abundant constituent in scrubber sludge. The other noticeable particles present were irregular, and blocky in shape. These particles produced large Ca and Mg peaks, and were determined to be unreacted limestone. The large difference in morphology of the two major components in the scrubber sludge made it easy to distinguish between calcium sulfite and unreacted limestone. No coating of calcium sulfite onto the limestone was immediately obvious in this specimen.

Figure 1.4: Backscattered electron image of a raw feed sample (Sample 1). The flat plates were determined to be calcium sulfite, and the irregular object in the middle was unreacted limestone. The difference in particle morphology made it very easy to find unreacted limestone particles.

Specimens made with a different type of carbon coat (Denton DV-502 Evaporator) are shown in Figure 1.5 and 1.6. The first observation that was made was the smoothness of the surfaces compared to the first specimen investigated. This was due to a better, more even carbon coat. An exhaustive investigation of both raw and cycloned scrubber sludge was done to find a limestone particle with a detectable calcium sulfite layer, but no such particle was ever found. It was therefore considered unlikely that formation of sulfite layers was a major interference during the

flotation of unreacted limestone. The scanning electron microscopy study did provide more information about scrubber sludge, especially the morphology of the particles. In particular the calcium sulfite was found to have a greatly different particle shape than the limestone. The calcium sulfite consisted of very thin plates, as shown in Figure 1.6, while the limestone was much more blocky and irregular in shape, see Figure 1.5.

Figure 1.5: Secondary electron image of raw feed with the carbon coating applied with the Denton evaporator. The carbon coating was much more uniform, and the artifact seen in the previous micrographs is absent.

Figure 1.6: Secondary electron image of the calcium sulfite plates. Note the thinness of the plates, showing that the morphology difference between the calcium sulfite and the irregular, blocky unreacted limestone is very pronounced.

Separation Strategy

The goal of this study was to reduce the amount of impurities (limestone) in the scrubber sludge, to produce a useful calcium sulfite/sulfate product. This clean product could then be oxidized into a high grade synthetic gypsum which could be used for wallboard and plaster manufacturing. The maximum allowable limit for limestone impurity was taken to be 2.0% by weight. Several different physical separation techniques were investigated. Physical separation techniques can be divided into four major categories: gravity (separation based on differences in specific gravity of particles), physico-chemical (separation based on the difference in surface properties of particles), magnetic (separation based on differences in magnetic susceptibility), and high tension (separation based on differences on electric conductivity of particles).

Magnetic and high tension separation were eliminated as possible methods for removal of limestone from calcium sulfite/sulfate for several reasons. The major impurity (limestone) to be reduced is not susceptible to a magnetic force, and the quantity of iron oxides was not sufficient for this separation to be worthwhile for removing only the iron. High tension separation would be possible, but separation efficiency would be low due to the small particle size of the material. The cost of de-watering and drying the sludge to a level that could be separated by the high tension process would also be high.

Gravity and physico-chemical techniques showed the best promise for separating limestone impurities based on the characterization of the material. Either one of these methods or a combination thereof (gravity and physico-chemical separation) could be used to provide a useful synthetic gypsum product. The first method that was investigated was separation based on difference in specific gravity of the impurities and the valuable product. This is covered in Chapters 2 and 3, “Processing of Wet Flue-Gas Desulfurization Sludge using Water-Only Cycloning” and “Mathematical Modeling of Cyclones”. Single stage water-only cycloning was explored in Chapter 2, whereas Chapter 3 reviewed cyclone modelling. Along with this review of cyclone modelling, actual cyclone data was used to determine the performance of an additional cyclone. The results of the model were then verified by experimental work.

The second method of separation that was evaluated was based on the physico-chemical surfaces of the components in the scrubber sludge. Before this study was initiated, an understanding of the surface charge was necessary to determine which type of flotation reagents would preferentially adsorb onto the impurities and not the useful product. This work was covered in Chapter 4, “Zeta Potential Study of the Components of a Wet Flue-Gas Desulfurization Scrubber Sludge”. The separation work based on physico chemical properties was covered in Chapter 5, “Processing of a Wet Flue-Gas Desulfurization Scrubber Sludge using Froth Flotation.” The flotation of raw scrubber sludge was explored along with the combination of gravity separation and froth flotation. The final chapter covers the conclusions of removing the impurities from a naturally-oxidized wet flue-gas desulfurization scrubber sludge to produce a clean product that can be used as a replacement for natural gypsum.

CHAPTER 2

WET FLUE-GAS SCRUBBER SLUDGE PROCESSING WITH WATER ONLY CYCLONE

Abstract

A typical 400 MW power station burning coal containing 3.48% sulfur produces 170,000 tons of scrubber sludge per year. This scrubber sludge is a fine, grey-colored powder, which is landfilled. This sludge contains calcium sulfite/sulfate, unreacted limestone, silicates and iron oxides. These products slightly differ in densities. An experimental test rig consisting of a 50.8 mm water-only cyclone, was designed to separate the components of the scrubber sludge. Single stage water-only cycloning was capable of removing 48.2% of the unreacted limestone, while maintaining a 75.6% weight recovery of the useful product. This separation process is highly economical and provides coal burning utility companies with an alternative to landfilling their wet-flue gas desulfurization sludge.

Introduction

Background

The Clean Air Act Amendments (CAAA) of 1990 have limited the amount of sulfur oxides that can be produced by coal burning utility companies. This has caused utility companies to re-evaluate their operating strategy. There are three strategies for controlling the amount of sulfur oxide emissions. These include fuel switching, pre-combustion desulfurization, and post-combustion desulfurization. The passage of the CAAA has led to tremendous activity in the research and development of post-combustion desulfurization, especially flue-gas desulfurization (FGD). One hundred and eighty nine FGD processes have been identified in a report to the Electric Power Research Institute (EPRI), (Radian Corporation, 1984). However, most of these methods are still limited to laboratory and pilot plant activities. The most industrially used method is wet flue-gas desulfurization. Wet flue-gas desulfurization is widely used due to its low operating cost, high reliability and high SO₂ removal.

Wet flue-gas desulfurization uses ground limestone or lime to convert sulfur oxide gases into a solid precipitate. Chemical reactions for lime and limestone desulfurization are given below (Fellman and Cheremisinoff, 1993):

Overall Limestone Reaction:

Overall Lime Reaction

This solid precipitate is better known as scrubber sludge or gypsite. Scrubber sludge from wet flue-gas desulfurization typically contains calcium sulfite (CaSO₃•0.5H₂O), calcium sulfate (CaSO₄•2H₂O), calcium carbonate (CaCO₃) and various other impurities. Wet flue-gas desulfurization can be broken down into two groups: natural and forced oxidation. The only

difference between the two is that the calcium sulfite is completely oxidized into calcium sulfate in the forced-oxidation scrubbing process. The types of impurities remains the same in both types of scrubber sludge. The major disadvantage of this method is the enormous amount of scrubber sludge produced which needs to be landfilled. A typical 400 MW power station that burns a high sulfur coal produces 170,000 tons of wet flue-gas scrubber sludge per year. This sludge is not only costly for the utility company to landfill, but may present danger to the environment. If calcium sulfite is not fully oxidized it can lead to water pollution (Erwin, Wang, and Hudson, 1982). Therefore, the development of new technology which would reduce impurities, such as limestone, from a wet flue-gas desulfurization scrubber sludge to produce a high grade calcium sulfite/sulfate, which could be oxidized into a synthetic gypsum would benefit not only the utility companies but also the environment.

Requirements of Gypsum Industry

There are many possible markets for a high quality synthetic gypsum. These include: prefabricated products (wallboard), plaster, additives in portland cement, and soil conditioners. The largest user of natural gypsum (~75% of the annual U.S. consumption) is in the prefabricated products, predominately wallboard (Luckervich, 1993). The wallboard industry would therefore be the preferred market for this synthetic gypsum. However, before synthetic gypsum can be used as a replacement for natural gypsum the impurities in the synthetic gypsum must be reduced to levels that are similar to natural gypsum or lower.

The most abundant impurity in this scrubber sludge was unreacted limestone. Table 2.1 gives a typical analysis of a scrubber sludge obtained from a utility company burning a high sulfur coal. The unreacted limestone is due to incomplete dissolution of the limestone during its reaction with sulfur oxides. There are several reasons for incomplete dissolution of the limestone: particle size distribution, fluctuation in sulfur oxide concentration due to inconsistencies in coal, purity of the limestone, and better sulfur oxide removal at higher scrubber pH. Other impurities in the scrubber sludge were iron chips obtained from the grinding of the limestone.

Table 2.1: Characteristics of the major components in a naturally-oxidized wet flue-gas scrubber sludge investigated in this study

Component	Specific Gravity (g/cm ³)	Percent Weight	Solubility in Water (g/L)
Calcium Sulfite (CaSO ₃ •1/2H ₂ O)	2.52	~77.0	0.04
Calcium Sulfate (CaSO ₄ •2H ₂ O)	2.32	~14.0	3.2
Calcium Carbonate (CaCO ₃)	2.71	~5.6	0.013
Silicate	2.6-2.9	1.5-2.5	Insoluble
Iron Oxides	7.8	0.5-1.5	Insoluble

Impure scrubber sludge can lead to several difficulties in wallboard manufacturing. These include: excess equipment wear, poor paper adhesion, and discoloration of the wallboard. However the biggest problem with impurities is they reduce the purity of the gypsum which makes it difficult to control the hardening rate of the wallboard. The acceptable weight percent of impurities for wallboard vary from manufacturer to manufacturer but most of them require a minimum of 95.0% by weight gypsum in their raw material (Ojanpera et al. 1993, Abbott, et al., 1993 and Mayer, 1993). The maximum level of unreacted limestone present varies but 2.0% by weight or less is considered acceptable. Further reduction of the impurities could also open up additional markets for this synthetic gypsum.

The goal of this project was to reduce the unreacted limestone content from 5.6% by weight in a currently landfilled wet flue-gas desulfurization scrubber sludge to below 2.0% by weight for a useful product that can be oxidized into a synthetic gypsum product for the wallboard and plaster industries. Water-only cycloning was selected as the method for removing limestone impurity for several reasons. The first was that the scrubber sludge comes out of the scrubber as a wet product, therefore from an economical viewpoint the separation process should be a wet process. The second reason was water-only cycloning separates largely based on the particle density whereas conventional hydrocyclones separate primarily on the basis of particle size. As Table 2.1 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. The final reason was that cycloning is a very simple operation, and therefore low in both capital and operating cost.

Experimental

Material

The scrubber sludge investigated in this work was from a natural-oxidized scrubber. This was done for two reasons. First there is a larger percentage of natural-oxidized scrubbers compared to force-oxidized scrubbers. Second, the extra component in natural-oxidized scrubber sludge, calcium sulfite, was expected to hinder the separation process. Therefore if a clean product could be obtained from a natural-oxidized scrubber, a clean product could certainly be obtained from a forced-oxidized scrubber. This material contained 5.6+/-0.3% limestone by weight and the size distribution of this material is given in Figure 2.1.

Size Distribution of Scrubber Sludge and Pre-Reacted Limestone

Figure 2.1: Size distribution of limestone before it was reacted with sulfur oxides and size distribution of resulting scrubber sludge. Size distributions were determined by laser diffraction.

Equipment

Water-only cyclone tests were carried out on three 50.8 mm diameter cyclones. These cyclones were geometrically similar but had different vortex finders and spigot diameter ratios. Dimensions of the water-only cyclones are given in Figure 2.2. A schematic of the water-only cyclone test rig is given in Figure 2.3. The test rig was operated in closed circuit with a 1L4 CDQ progressing cavity pump and a feed sump (20 liter capacity). The pump was driven by a 2 HP variable speed motor. The cyclone overflow and underflow were discharged under free fall into the sump. This allowed for overflow and underflow samples to be collected simultaneously. A pressure gauge (diaphragm type) was also mounted at the feed inlet of the water-only cyclone.

Operating Conditions

During the cyclone operation the dense material reported to the underflow of the cyclone, whereas the less dense material (cleaner calcium sulfite/sulfate product) reported to the overflow. In order to achieve optimum operation the following parameters were investigated: vortex finder (overflow nozzle), spigot diameter (underflow nozzle), inlet feed pressure, and weight percent solids of the feed slurry. The selected ratios of vortex finders to spigot diameters were 2.2, 2.3, and 2.7; the selected inlet feed pressures were 5.0, 10.0, 20.0, 25.0, 35.0, and 45.0; and the selected weight percents were 3.0, 5.0, 10.0 and 20.0.

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 sample of approximately 950.0 grams of scrubber sludge was suspended in water at the desired percent solids by weight.
- 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 feed inlet pressure.
- Samples of the overflow and underflow were then taken simultaneously to determine percent solids and flowrate. Temperature and pH of the samples were also taken at this time. Samples were then filtered and placed in a drying oven. Samples were then re-weighed and prepared for chemical analysis.

Dimensions of Water-Only Cyclones in mm						
Feed Inlet Diameter D_i	Cyclone Diameter D_c	Vortex Finder D_v	Spigot Diameter D_s	V	H	α (deg.)
10	51	14	6	25	27	90
8	51	11	5	25	29	90
6	51	8	3	22	30	90

Figure 2.2: Schematic of 50.8 mm water-only cyclone with corresponding dimensions.

Figure 2.3: Schematic of 50.8 mm diameter hydrocyclone test rig. The rig consists of a progressive cavity pump connected to a two horsepower variable speed motor. The motor controller was wired for three phase power, and the whole test rig was made portable with the addition of wheels to the base plate. The sump was designed to hold up to 20 liters of slurry. The piping was made from 3/4 inch PVC pipe, and a pressure gauge which ranges from 0 to 60 psi was also attached.

Results and Discussion

Selection of Vortex Finder and Spigot Diameter Combination

The results of varying the vortex finder and spigot diameter are given in Table 2.2. The largest vortex finder (14 mm) and spigot diameter (6 mm) produced the best weight recovery of desired product. However, this water-only cyclone was unable to reduce the concentration of unreacted limestone to a level which was suitable. The middle-size water-only cyclone (vortex finder = 11 mm and spigot diameter = 5 mm) provided the cleanest 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 was no better than the medium sized cyclone and the weight recovery decreased at the same pressure. The water-only cyclone with a vortex of 11 mm and a spigot diameter of 5 mm provided the cleanest material of the vortex finders and spigot diameters that were investigated. However a clean product with a maximum of 2.0% by weight unreacted limestone was not achieved. Therefore further studies were performed to see the effect of inlet feed pressure and weight percent solids.

Table 2.2: Selection of vortex finder and spigot diameter combination on a 50.8 mm water-only cyclone for removing the more dense impurities (limestone) from the less dense useful product (calcium sulfite/sulfate) at 5.0% solids by weight. Feed material to the water-only cyclone contained 5.6 +/- 0.3% limestone.

Dimensions of Vortex Finder and Spigot Diameters (mm)	Percent Solids by Weight	Feed Pressure (psi)	Percentage of Limestone in Gypsum Product	Percent Weight Recovery of the Gypsum Product
Vortex Finder = 14 mm Spigot Diameter = 6 mm	5.0	5	4.03 +/- 0.07	93.8
	5.0	10	3.88 +/- 0.08	93.0
	5.0	20	3.71 +/- 0.11	92.6
Vortex Finder = 11 mm Spigot Diameter = 5 mm	5.0	5	3.45 +/- 0.10	84.1
	5.0	10	3.36 +/- 0.10	81.1
	5.0	20	3.21 +/- 0.11	78.2
Vortex Finder = 8 mm Spigot Diameter = 3 mm	5.0	20	3.31 +/- 0.06	71.0

Effect of Inlet Feed Pressure

As the pressure was increased the amount of kinetic energy of the particles was also increased. This should theoretically produce a better separation. Therefore several additional tests were performed at higher pressures. These tests used a vortex finder of 11 mm and a spigot diameter of 5 mm because of the results already obtained in the last section. The results of increased inlet feed pressure are given in Table 2.3. As was expected the overflow product became cleaner at higher pressures. This was accompanied by a loss in the weight recovery of useful product.

Table 2.3: Effect of increasing feed inlet pressure for determining the optimum operating condition for the 50.8 mm 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% limestone.

Dimension of Water-Only Cyclone	Percent Solids by Weight	Pressure (psi)	Percentage of Limestone in Gypsum Product	Percent Weight Recovery of the Gypsum Product
Vortex Finder = 11 mm Spigot Diameter = 5 mm	5.0	25	3.03 +/- 0.09	78.1
	5.0	35	3.00 +/- 0.11	76.5
	5.0	45	2.89 +/- 0.10	75.6

Effect of Weight Percent Solids

The final operating variable investigated was the effect of weight percent solids of the feed slurry, Table 2.4. The feed weight percent solids selected were 3.0%, 5.0%, 10.0% and 20.0%. The remaining cyclone parameters were set at their optimum conditions which were determined in previous sections. An improvement in weight recovery at higher percent solids was observed, but with no improvement in grade.

Table 2.4: Effect of feed percent solids for determining the optimum percent solids for the 50.8 mm water-only cyclone with a 11 mm vortex finder and a 5 mm spigot diameters. Feed material contained 5.6+/-0.3% limestone.

Dimension of Water-Only Cyclone	Feed Pressure (psi)	Percent Solids by Weight	Percentage of Limestone in Overflow	Percent Weight Recovery of the Overflow
Vortex Finder = 11 mm Spigot Diameter = 5 mm	45	3.0	3.00+/-0.10	69.3
	45	5.0	2.89+/-0.10	75.6
	45	10.0	3.26+/-0.04	79.8
	45	20.0	3.90+/-0.20	86.8

Conclusions

Single-stage water-only cycloning successfully removed nearly 50% of the unwanted limestone and maintained approximately 76% weight recovery. This material could be blended with natural gypsum to form a material that would be useful for wallboard manufacturing.

In general, increasing the feed inlet pressure tended to increase the removal of limestone from the overflow product, while increasing the percent solids tended to increase the overall weight yield of the overflow product. Similarly, larger-diameter spigots and vortex finders increased the yield, while smaller-diameter spigot diameters and vortex finders increased the limestone removal. The best combination of yield and limestone removal were achieved with the intermediate-size cyclone (vortex finder 11 mm, spigot 5 mm) operating at 5% feed solids and 45 psi inlet pressure.

It is suggested that a cleaner product could be obtained if a different process, such as froth flotation was used in series with single-stage water-only cycloning.

CHAPTER 3

MATHEMATICAL MODELLING OF CYCLONES

Abstract

The mathematical modelling work which has been reported in the literature for cyclones was briefly reviewed. Based on this, the results from the hydrocyclone separation tests were modelled to determine how closely the cyclone was approaching ideal performance, and to calculate whether a second stage of cycloning would be of any benefit. It was found that the cyclones were performing very well, and that there was such a small quantity of material bypassing the separation that there was little benefit to be gained from two-stage cycloning.

Introduction

Hydrocyclones are used to separate particles that are more massive from those that are less massive. If the mass difference is due simply to size, the hydrocyclone separates the particles by size, and is commonly used for controlling the product size in mineral grinding. If the mass difference is due to density, the hydrocyclone separates high-density particles from low-density particles, and is widely used in applications such as removing waste rock from coal. The basic principle of the cyclone is as shown in Figure 3.1:

Figure 3.1: As the water with suspended solids enters the cyclone, it swirls rapidly, causing the more massive particles to centrifuge to the cyclone wall. However, the spigot is not large enough to take all of the water, and so most of it leaves the cyclone through the vortex finder. The flow of water to the vortex finder is fast enough that the less-massive particles do not have time to centrifuge to the wall before they are carried out of the cyclone. The more-massive particles are gradually forced along the cone to the spigot, where they discharge along with a portion of the water as a spray.

Experimental work was carried out to separate limestone from scrubber sludge by cycloning, as described in Chapter 2. The cyclone was able to remove a large fraction of the limestone, but the cleaned product could not meet the target specification of less than 2.0% limestone by weight. There were two possible options for reaching the desired grade:

- Add a second stage of cycloning in series with the first stage, to increase the cycloning efficiency;
- Consider an alternative process for treating the cleaned product from the cyclone, such as magnetic separation, electrostatic or electrodynamic separation, or froth flotation.

To determine whether a second stage of cycloning could produce a material of the desired quality, it was decided to mathematically analyze the cyclone performance by development of efficiency curves. These results were then used to determine what level of performance could be expected from a second stage.

Hydrocyclone Models

Two types of mathematical models for cyclones have been described in the literature. These are:

- Phenomenological models, deriving the classification that occurs in a cyclone from basic principles, and
- Semi-Empirical models, based on largely empirical correlations of capacity, cut size, water split, and the partition curves.

Phenomenological Modelling

Many attempts to develop hydrocyclone models from first principles have been made (Barrientos and Concha, 1992; Devulapalli et al., 1993; Concha and Amendra, 1979; Rolden et al., 1993; Rajamani, 1986; Hsieh and Rajamani, 1988a). The basis for phenomenological modelling has largely been developed at the University of Utah (Hsieh and Rajamani, 1988a,b), and is the set of fluid dynamic equations that describe the multiple phase flow within the hydrocyclone. These equations have been used, along with experimental measurements made by Laser Doppler Velocimetry (LDV) to predict cyclone performance with considerable success. This procedure opens possibilities for the future improvement of cyclone design, since it can be used to evaluate every geometrical detail in the equipment. Nevertheless, Concha (1992) argues that the approach taken at the University of Utah is restricted to design applications, because the tremendous computer processing demands of the model make it too slow to be used in real-time simulations. Instead, Concha (1992) proposes a model of the cyclone based on calculation of the trajectory of particles that enter the cyclone, with the cyclone capacity calculated using empirical equations available in the literature.

Semi-Empirical Modelling

Semi-empirical models have been shown to be very effective for simulating hydrocyclone performance, and do not have the tremendous computer processing demands of the phenomenological models (Plitt, 1976; Lynch and Rao, 1977; Plitt and Kawatra, 1979). These methods are well-recognized, and have been discussed in standard texts in the mineral processing field (Wills, 1992).

Capacity and Water Flows. The capacity of a hydrocyclone is determined by the amount of water in the feed, the applied pressure, and the vortex finder diameter (Lynch, 1977; Lynch and Rao, 1977; Plitt, 1976), and these factors have been found to be related mathematically as follows:

$$Q = K(VF)^{1.0} P^{0.5} PW^{0.125}$$

where
 Q = Capacity, in gallons/minute
 VF = Vortex finder diameter, inches
 P = Pressure, psi
 PW = Percent water by weight in the feed
 K = Constant for the cyclone under consideration.

The quantity of water in the overflow of a cyclone is directly related to the quantity of water in the feed. The relationship between the two is given by the following equation:

$$WOF = 1.1 WF - 10Spig + K$$

where
 Spig = Spigot diameter
 WOF = Mass flowrate of water to the overflow
 WF = Mass flowrate of water in the feed
 K = Constant for the cyclone under consideration

Water Flow Ratio. In a hydrocyclone, the entering slurry is subjected to a centrifugal force, as given by the equation:

$$F = \frac{mv^2}{r}$$

where
 F = Centrifugal force acting on a particle
 m = Mass of particle
 v = Radial velocity of the particle
 r = Radius of the cyclone orbit

Therefore, if the particle mass (m) is small, the centrifugal force acting on the particle will also be small, and therefore the motion of fine particles is dominated by fluid drag forces and is carried along with the water to whichever product the water reports to. The bulk of the water reports to the overflow, which is the proper destination for the fine particles. However, a portion of the water discharges from the underflow, and carries with it a fraction of the fine particles which have bypassed the classification (Lynch, 1977; Plitt and Kawatra, 1979; Wills, 1992). It has been determined that the quantity of these unclassified particles can be readily calculated from the water flow ratio (R_f), which is the fraction of the total feed water which exits through the underflow, calculated as:

$$R_f = \frac{(WF - WOF)}{WF}$$

The particles discharged through the underflow of the cyclone therefore consist of two components:

- Unclassified particles, carried into the underflow by the water, and which have the size and density distribution of the original feed; and

- Particles which were concentrated into the underflow as a result of classification.

The value of R_f is an indicator of the imperfection of the process, and can be used to determine how much of a performance improvement could be produced by multiple stages of cycloning.

Efficiency (or Partition) Curves

The performance of a hydrocyclone can be conveniently analyzed by the use of efficiency curves. These curves represent the relationship between the size of a particle, and the probability that the particle will report to the underflow product. The probabilities are determined by measuring the mass flows and size distributions of both the overflow and underflow products, and calculating the weight fraction of each particle class which reported to the underflow (Lynch, 1977). These curves have the form shown in Figure 3.2. The steeper the central portion of the curve is, the sharper the classification, which indicates better cyclone performance.

Figure 3.2: Basic form of partition curves. Curve (A) represents a good, sharp separation, while (B) represents a poor separation. The bypass fraction, R_f , shows the fraction of the particles which bypass the classification.

Kelsall (1953) suggested that particles that are entrained in the water discharged through the underflow are not acted upon by the centrifugal forces. Therefore, if R_f is the fraction of feed fluid which reports to the underflow, then R_f is also the fraction of each particle size class which is carried into the underflow by entrainment, and therefore is not classified. It is therefore possible to mathematically compensate for the material bypassing the classification, and produce a

corrected efficiency curve, using the following correction:

$$E_c(I) = \frac{E_a(I) - R_f}{100 - R_f}$$

where $E_a(I)$ = Uncorrected partition coefficient, expressed as a percentage
 R_f = Bypass fraction, expressed as a percentage
 $E_c(I)$ = Corrected partition coefficient, expressed as a percentage

Once the corrected values of the partition coefficients for each particle size class have been calculated, the corrected curve can be plotted.

Cut Size (d_{50}) of a Hydrocyclone. The d_{50} size of a hydrocyclone is the particle size where a particle has an equal probability of reporting to either the overflow or the underflow (partition coefficient of 50%). If it is determined from a curve after correcting for the bypass fraction, then it is reported as the $d_{50(c)}$.

Reduced Efficiency Curve. Once the $d_{50(c)}$ size has been determined, it is possible to plot a normalized curve, with the corrected partition coefficients plotted against the normalized size, $d/d_{50(c)}$. This curve is termed the “reduced efficiency curve”, and is plotted as shown in Figure 3.3. For a given cyclone and feed percent solids, the reduced efficiency curve is constant regardless of fluctuations in feed pressure, slurry viscosity, and other parameters. The reduced efficiency curve can be expressed mathematically as:

$$E_c(I) = \frac{e^{\alpha x} - 1}{e^{\alpha x} + e^{\alpha} - 2}$$

where $E_c(I)$ = Corrected partition coefficient
 $x = d/d_{50(c)}$
 $\alpha =$ adjustable parameter

The value of α is an indicator of the sharpness of the separation, with increasingly large values indicating better classification. The classification is generally considered to be poor if $\alpha < 2$, and the classification is generally considered excellent if $\alpha > 4$.

Results and Discussion

The results of mathematical modelling of a series of ten cyclone tests are shown in Figures 3.4 through 3.13. The cyclone geometry was 14mm vortex finder and 6mm spigot for figures 3.4, 3.5, and 3.6, with the feed pressure increased for each test. Increasing feed pressure progressively increased the value of α while decreasing the value of R_f , showing that the cyclone performance was improved by increased feed pressure. Test number 13-M3 (Figure 3.6) showed the best efficiency of all of the tests, with an α of 7.04 and an R_f of only 5.4. However, this cyclone configuration resulted in a large d_{50c} size, which allowed a large amount of the limestone to remain in the cyclone overflow, and so this configuration was not fully suitable for this application.

Figure 3.3: Form of the reduced efficiency curve. For a given cyclone geometry and feed solids content, this curve will remain constant regardless of factors such as feed flowrate, inlet pressure, viscosity, etc.

Figure 3.4: Efficiency curves for test number 13-M1, test conditions were as follows: vortex finder = 14 mm, spigot diameter = 6 mm, inlet feed pressure = 5.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.5: Efficiency curves for test number 13-M2, test conditions were as follows: vortex finder = 14 mm, spigot diameter = 6 mm, inlet feed pressure = 10.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.6: Efficiency curves for test number 13-M3, test conditions were as follows: vortex finder = 14 mm, spigot diameter = 6 mm, inlet feed pressure = 20.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.7: Efficiency curves for test number 10-J1, test conditions were as follows: vortex finder = 8 mm, spigot diameter = 3 mm, inlet feed pressure = 20.0 psi, and feed percent solids of 5.0% by weight.

In a test with an 8mm vortex finder and a 3 mm spigot (Figure 3.7), the d_{50c} size was considerably finer than in the previous tests, which resulted in a poorer yield of clean product, due to diversion of a larger amount of material to the underflow. This test showed a high R_f value (21.47%) even though the inlet pressure was quite high, indicating that the performance for this cyclone configuration was not as good as with the larger openings.

The majority of the cyclone tests used an intermediate configuration of an 11 mm vortex finder, and a 5 mm spigot, which was found to give the best combination of good limestone removal and high product yield. These tests, shown in Figures 3.8 - 3.13, were conducted at steadily increasing inlet pressures, but the changes in the efficiency curves with pressure were not large. The major effect of the increasing pressure was to steadily decrease the d_{50c} size. It was also seen that R_f was largest at the lowest and the highest inlet pressures, with the best values of R_f being seen at 10 and 20 psi.

In the best cyclone tests, it was observed that the sharpness of separation was excellent, and that the bypass fraction (R_f) was less than 15%. This information can be used to evaluate whether the cyclone results can be improved by further cycloning. This involves using the model to determine the effect of d_{50} (cut size) and R_f (bypass fraction).

First, since the separation was very sharp (large alpha), there was very little material near the d_{50}

Figure 3.8: Efficiency curves for test number 2-B1, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5 mm, inlet feed pressure = 5.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.9: Efficiency curves for test number 2-B2, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5 mm, inlet feed pressure = 10.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.10: Efficiency curves for test number 2-B3, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5 mm, inlet feed pressure = 20.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.11: Efficiency curves for test number 1-A1-1, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5mm, inlet feed pressure = 25.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.12: Efficiency curves for test number 1-A1-2, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5 mm, inlet feed pressure = 35.0 psi, and feed percent solids of 5.0% by weight.

Figure 3.13: Efficiency curves for test number 1-A1-3, test conditions were as follows: vortex finder = 11 mm, spigot diameter = 5 mm, inlet feed pressure = 45.0 psi, and feed percent solids of 5.0% by weight.

size. Since only the particles near the d_{50} size are likely to be misplaced into the wrong product during classification, there is little room for improvement in this area.

Second, the material which was subjected to centrifugal force and hence to the separation was always between 77 and 95 percent for all test conditions. Therefore, if a cyclone is operated so that R_f , i.e. material not subjected to classification is small, a second stage cyclone will not produce a cleaner product than produced in the first stage of cycloning. In the following sections this was experimentally verified.

Two-Stage Cycloning

A conventional hydrocyclone with a vortex finder of 8 mm and a spigot diameter of 3.2 mm was selected as the second cyclone, and was used together with the water-only cyclone in the configuration shown in Figure 3.14.

Figure 3.14: Configuration of two-stage cycloning circuit.

This configuration was selected for several reasons:

- Screen analyses had indicated that the very fine particles were slightly richer in limestone than were the intermediate-size particles, and so removal of the fines had the potential to reduce the limestone content of the sludge
- Further reduction of limestone by density separation would be inefficient due to the small particle size of the remaining limestone, and so a cyclone was used for the second stage that was optimized for size separation rather than density separation;
- The removal of very fine material is preferred by the wallboard manufacturers, and the conventional cycloning was more efficient for removing fines than a water-only cyclone would be;
- Using the second-stage hydrocyclone underflow as the final product would result in a largely dewatered product, which would save in dewatering cost.

The results of the second stage of cycloning are given in Table 3.5. The second stage of cycloning could not reduce the amount of limestone in the useful product, and only resulted in a loss of weight recovery of the useful product. The only benefit of the second stage of cycloning was an

increase in percent solids of the useful product, which would help reduce the de-watering cost of this material.

Table 3.1. Results for two tests of the second-stage cyclone in a two stage cycloning process. The conventional hydrocyclone had a diameter of 50.8 mm with a vortex of 8 mm and a spigot diameter of 3.2 mm. The feed material for the second-stage cyclone was the overflow from water-only cycloning, and contained approximately 3.06% limestone

Cyclone Product		Feed Pressure (psi)	Percent Limestone in Product	Weight Recovery of Cyclone Product	Total Weight Recovery of Two Stage Cycloning
Test 1	Overflow	35	3.10+/-0.06	18.8	38.6
	Underflow (Useful Product)	35	3.03+/-0.05	81.2	61.4
Test 2	Overflow	45	3.07+/-0.04	16.7	37.0
	Underflow (Useful Product)	45	3.09+/-0.06	83.3	63.0

Conclusions

Mathematical modelling of the cyclone performance showed that the cyclone was performing well, and produced a sharp separation in most cases ($\alpha > 4$). It was also found that the value for R_f for the best test was only 5.4%, with typical values near 15%, showing that only a small fraction of the feed was bypassing the classification. Since reprocessing the cyclone product with a second cyclone would only have the effect of classifying the material that escaped classification on the first stage, there is little benefit to be gained by multi-stage cycloning.

Experiments with a second stage of cycloning confirmed that there was negligible benefit to be gained by multi-stage cycloning compared to single-stage cycloning. There was no significant difference in the unreacted limestone contents of the two products from the second-stage cyclone, showing that no additional separation had occurred. Any improvements on the separation by the first-stage cyclone would therefore have to be accomplished by other means, such as froth flotation.

CHAPTER 4

ZETA POTENTIAL MEASUREMENTS OF THE COMPONENTS OF WET FLUE-GAS SCRUBBER SLUDGE

Abstract

Power plants that utilize conventional wet flue-gas desulfurization methods produce enormous amounts of flue-gas scrubber sludge. A typical 400 MW power station that burns a high sulfur coal produces 170,000 tons of wet flue-gas scrubber sludge per year. This scrubber sludge is currently landfilled at an enormous cost to utility companies. This material could be used as a raw material for industries that use gypsum, such as the wallboard and plaster industries. However, before it can be used as feedstock for these industries, some of the impurities such as unreacted limestone and silicates must be removed from the scrubber sludge. Froth flotation has tremendous potential for separating these impurities from scrubber sludge. In order to select an optimum flotation process, it is necessary to characterize the surface properties of the major components in the scrubber sludge, which consist of calcium sulfite, calcium sulfate, calcium carbonate (limestone), and silica. In this study zeta potential measurements were used to determine the surface charge of the components in scrubber sludge, with the goal of optimizing a froth flotation process to produce a marketable gypsum product for the wallboard and plaster industries.

Introduction

Recent concern for the well-being of the environment has led to legislations, such as the Clean Air Act and the Pollution Prevention Act, which prevent sulfur oxide pollutants from being released into the atmosphere. This is of great concern for the utility industries which produced 15.6×10^6 tons of SO_x in 1985. This corresponds to 69.6% of all SO_x emissions produced in the United States (Pahl, Zimmerman, and Ryan, 1990). Many methods of desulfurization exist in the utility industry. One industrially proven method is wet flue-gas desulfurization. This method has become commonplace in the utility industry because of its low operating cost, high reliability and high SO_2 removal. Wet flue-gas desulfurization uses ground limestone or lime to convert sulfur oxides into a solid precipitate scrubber sludge which must be landfilled. This wet flue-gas desulfurization scrubber sludge typically contains calcium sulfite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium carbonate (CaCO_3) and various other impurities. The problem with wet flue-gas desulfurization is the huge amount of scrubber sludge produced. A typical 400 MW power station that burns a high sulfur coal produces 170,000 tons of wet flue-gas scrubber sludge per year. This sludge is not only costly for the utility company to landfill, but may present danger to the environment. If calcium sulfite is not fully oxidized it can lead to water pollution (Erwin, Wang, and Hudson, 1982). Therefore, the development of new technology which would purify wet flue-gas desulfurization scrubber sludge to a useful raw material would benefit not only the utility companies but also the environment.

The goal 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 for over 70 years (Roe, 1983). Before froth flotation work could begin, it was necessary to perform zeta potential measurements under various conditions to select the best reagents and their optimum dosage level. The significance of the Zeta potential, and the Electrical Double Layer model in general, is discussed in the following section (Crozier, 1992; Wills, 1992; Weiss, 1985; Fuerstenau and Raghavan, 1976).

The Electrical Double Layer

Factors Producing the Double Layer.

A particulate surface will have bonds that were broken when the surface was formed (“unsatisfied bonds”), as in the silica surface, see Figure 4.1. When a surface is immersed in water, the unsatisfied bonds on this surface quickly adsorb particular ions from solution. Different solids will adsorb different ions, but most oxides will adsorb H^+ and OH^- , while slightly-soluble salts will typically adsorb the ions that they are composed of. Depending on the conditions in the solution, the numbers of positive and negative ions adsorbed will usually not be balanced, and so these potential determining ions will produce a surface charge on the particle. The potential-determining ions are physically attached to the surface, as shown in Figure 4.1.

The electrical double layer (Figure 4.2) consists of two layers of ions from solution, which neutralize the surface charge. The Stern layer consists of hydrated ions which concentrate directly on the surface of the particles, and is one layer of ions thick. The diffuse layer is much thicker, and is a layer of water that is enriched in ions with a charge opposite to the surface charge. Between the Stern layer and the Diffuse layer, is the shear plane. When the particle moves relative to the fluid, this plane is the boundary between the fluid that moves along with the particle, and the fluid that moves along with the bulk fluid. When the Zeta potential is measured, it is a measure of the potential at the shear plane.

Methods for Altering the Electrical Double Layer

A. Potential-Determining Ions. By changing the relative concentrations of the potential-determining anions and cations in solution, both the sign and magnitude of the surface charge can be changed, as shown in Figure 4.3. For example, in quartz, where H^+ and OH^- are the potential-determining ions, the surface charge can be controlled by changing the pH, with the surface positively charged when pH is less than 3, and negatively charged when pH is greater than 3. In general, the surface charge can only be changed by the potential-determining ions, and other types of ions only change the Zeta potential.

B. Neutral Ions. Monovalent ions that are not potential-determining (such as Na^+ and Cl^- for silica surfaces) cannot affect the surface charge, but they can affect the rate at which the charge is neutralized in the bulk solution. Adding such neutral ions will increase the concentration of ions in both the Stern and diffuse layers. This causes the charge to be neutralized over a shorter distance, and the double layer is then said to be compressed, as illustrated in Figure 4.4. This reduces the magnitude of the Zeta potential, but cannot change its sign.

C. Specifically Adsorbed Ions. Some ions, (such as Ca^{+2}) when in contact with particular types of particles (such as silica), are specifically adsorbed onto the particle surface. They form a

Figure 4.1: Schematic of a silica surface, showing the unsatisfied bonds that were formed when the silica was broken to make the surface. These bonds provide surface charge, and also act as sites for adsorption of ions from solution.

chemical bond with the surface, so that they can attach to the surface regardless of the electrostatic charge. When these ions have charges of +2 or +3, this can cause an excess of charge to build up that has the opposite sign of the surface charge, as shown in Figure 4.5. The same effect can occur with surfaces with a positive charge, and multivalent anions in solution. Specifically adsorbed ions can therefore not only reduce the magnitude of the Zeta potential, but also change its sign. Adsorption of these ions on the surface is sometimes not reversible, and so they may be difficult to remove again once they have attached to the surface. It is important to

Figure 4.2: Structure of the electrical double layer.

remember that an ion that is specifically adsorbed on one type of surface will not necessarily specifically adsorb onto other types of surface.

D. Physically Adsorbed Ions. Molecules that consist of a nonpolar portion and an ionic portion, such as dodecylammonium chloride ($\text{C}_{12}\text{H}_{25}\text{NH}_3\text{Cl}$) are surface-active, which means that they tend to segregate on interfaces where they will have a lower energy than in the bulk solution. This is a result of hydrophobic bonding of the nonpolar portion of the molecule. After one layer of ionized molecules has associated with the surface by electrostatic attraction, additional molecules can then bond hydrophobically, producing an excess charge on the surface, as shown in Figure 4.6. Physically adsorbed ions can therefore also result in a change in both the magnitude and the sign of the Zeta potential. Their adsorption is generally reversible, and so they can be readily removed from the surface.

Figure 4.3: Effect of changing concentrations of potential-determining ions on the surface charge and zeta potential (charge at the shear plane).

Figure 4.4: Compression of the double layer by a neutral electrolyte

Figure 4.5: Reversal of the zeta potential by specifically-adsorbed ions

Figure 4.6: Reversal of zeta potential by physically-adsorbed ions.

E. Chemisorption. Chemisorption is superficially similar to physical adsorption, except that the energy of the molecule-surface bond is higher (typically greater than 10-15 Kilocalories/mole), and the bonding is not reversible. In chemisorption, a covalent bond is formed with the surface rather than the simple ionic bond of physical adsorption. This reaction is much more material-specific, and so chemisorption can be used to selectively alter the double layer for particular particles while having a minimal effect on other particle types.

Detailed Structure of the Stern Layer

The structure of the electrical double layer is actually more complex than that described so far, but the preceding description is sufficiently useful for most purposes. A more detailed model of the Stern Layer is as shown in Figure 4.7.:

Figure 4.7: Structure of the Stern plane.

The Inner Helmholtz Plane is the center of the oriented water molecules, specifically adsorbed ions, and other ions that are directly bonded to the surface. The Outer Helmholtz Plane is the center of the physically adsorbed counterions, which are solvated by water and ride on the ions and molecules of the inner Helmholtz plane. The shear plane is the boundary between the ions and molecules that are attached to the surface, and those which are still part of the bulk solution.

The shear plane is located outside of the outer Helmholtz plane, but it is uncertain just how thick the layer is between the shear plane and the surface.

Experimental

Zeta potential measurements were performed on calcium sulfite and calcium carbonate, both of which were obtained as reagent-grade powders. Calcium carbonate was investigated because it is the largest impurity by weight in the flue-gas scrubber sludge. Calcium sulfite was also investigated because it makes up approximately 80% of flue-gas scrubber sludge material and can be oxidized to gypsum, which is the useful product for the wallboard and plaster industry. Reagent-grade powders were selected because they were free of contaminants that would tend to obscure the results. Each powder was tested at several different collector concentrations.

Measurement Procedure:

Calcium sulfite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium carbonate (CaCO_3) were purchased from Pfaltz and Bauer Chemicals as reagent-grade powders. The silica was obtained from the U.S. Silica Company (Table 4.1). Suspensions were prepared by mixing distilled water and collector to give the desired concentration, then adding 0.1 grams of one of the powders to 140 ml of each solution. The suspensions were allowed to stand for 2 hours to equilibrate completely. The pH and zeta potentials for each solution were then measured. All the pH measurements were between 6.8 and 7.6, which corresponds to the natural pH of the scrubber sludge. All zeta potential measurements for this study were made using a microelectrophoresis zeta meter. Zeta potential measurements were repeated by filling the zeta-meter cell with a suspension, measuring the zeta potential twice, draining the cell, refilling with the same suspension, and measuring the zeta potential two more times, for a total of four measurements.

Table 4.1: Description of the reagent grade powders used for zeta potential studies

Type of Powder	Chemical Supplier	Particle Size, 80% Passing Size
Calcium Sulfite	Pfaltz & Bauer	82 microns
Calcium Sulfate	Pfaltz & Bauer	84 microns
Calcium Carbonate	Pfaltz & Bauer	20 microns
Silica	U.S. Silica Co.	47 microns

Types of Collectors

For this study, anionic, non-ionic and cationic collectors were selected to determine which type of collector would be best suited for scrubber sludge purification (Table 4.2). These collectors were selected because they had been reported to aid calcium carbonate flotation in some application, either in the literature or by industrial contacts. Since scrubber-sludge processing is a completely different application than anything that had been tried before, it was not possible to narrow the selection any further before beginning tests. Collector concentrations tested were at 0.0, 0.01, 0.02, 0.05, and 0.10 grams per liter

Table 4.2: Characteristics of collectors selected for the study

Collector Name	Chemical Structure	Collector Charge
Aero 845	Tetrasodium N-(1,2-dicarboxyethyl -N-octadecyl sulfosuccinamate)	Anionic
Oleic Acid	Fatty Acid	Anionic
S 701	1-(Ethylthio) Octana Poly(oxy(methyl-1,2-ethanediyl)), α -hydro- ω -hydroxy-	Non-Ionic
Ether Primary Amine	1-Propanamine, 3-(C ₈₋₁₀ -alkoxy)	Cationic
Aero 870	Ethoxylated Octadecylamine-Octadecylguanidine Complex	Cationic

Results and Discussion

When analyzing the zeta potential data with the various collectors, two characteristics were investigated. The first was to determine the degree of adsorption of the collector on the particles. This was done by analyzing the slope of the zeta potential curve. In order for the adsorption of a collector to be detected, an increase or decrease in the slope of the zeta potential curve must occur. The steeper the slope of the zeta potential curve, the greater the adsorption of the collector on the particle. The second area of interest was the point at which a plateau occurred on the zeta potential curve. This point indicates the maximum amount of collector that could be adsorbed by the particle surface. The relative positions of the horizontal plateaus for a given collector is a measure of the affinity of the collector for a particular particle. Therefore, the distance between the horizontal plateaus of the zeta potential curves for calcium carbonate and calcium sulfite should be great if a superior separation is to be achieved.

Effect of Anionic Collectors

Anionic collectors are those that have a negatively-charged polar group. These types of collectors did not have a pronounced effect on the zeta potentials of calcium carbonate and calcium sulfite (Figures 4.8 and 4.9). This was due to the negative surface charge of the calcium carbonate and calcium sulfite in distilled water ($\zeta = -24.1$ mV and $\zeta = -10.0$ mV respectively where ζ is the zeta potential of the particle), which repelled the collector from the particle surface. Because of similar charges (negative) on the particle surfaces and the collector, any adsorption of the collector on the surface of the calcium sulfite and calcium carbonate was by replacement of existing anions, and so little alteration in charge occurred. There was no chemical adsorption of either of these collectors, which would have been seen as an increasingly negative zeta potential at an increasing collector concentration. This was evident because the zeta potential varied only slightly with collector concentration for anionic collectors.

Zeta Potentials in Aero 845 Solutions

Figure 4.8. Aero 845 is an anionic collector produced by Cytec Industries Inc. (Bountiful, UT). The negative charge of the particles and the collector lead to a condition of repulsion. Therefore, the collector does not readily adsorb on the particles. This is evident by the near zero slope of the zeta potential curves.

Zeta Potentials in Oleic Acid Solutions

Figure 4.9. Oleic Acid is an anionic collector. Once again the negative charge of the particles and the collector lead to a condition of repulsion.

Effect of Non-Ionic Collectors

A non-ionic collector was also investigated in this study to determine its potential for separating calcium carbonate from calcium sulfite. This collector had no effect on the surface charge of the calcium carbonate and the calcium sulfite (Figure 4.10). This was expected because when a non-charged collector adsorbs on to the surface of a particle, a change in the surface charge of the particle does not occur. This is evident by the near zero slope of the zeta potential curves for calcium carbonate and calcium sulfite.

Figure 4.10. S 701 is a non-charged collector produced by Mineral Reagents International (Midland, MI). As would be expected this collector had no effect on the surface charge of the calcium carbonate or the calcium sulfite. This is evident because the curves are parallel to each other and the slopes of the zeta potential curves do not change.

Effect of Cationic Collectors

Cationic collectors are those whose polar group has a positive charge. These types of collectors had a much more pronounced effect on the zeta potential of calcium carbonate and calcium sulfite (Figures 4.11 and 4.12). This effect would be expected due to the attractive forces between the positive charge of the collector and the negative surface of the particles. Even though both calcium carbonate and calcium sulfite have negative surface charges and would be attracted to the positive charge of the collector, a separation can still be made if the collector has a stronger affinity for one of the particles. This would show up as a large difference in the horizontal plateaus of the zeta potential curves of the particles studied. Aero 870, a Cytec collector, was a much better collector for the separation of calcium carbonate than Ether Amine because Aero 870 adsorbed on the calcium carbonate at a very low concentration. This can be seen by comparing

the steepness of the slope of the zeta potential curve for the Aero 870 to the slope of Ether Amine. Aero 870 also shows a higher affinity for calcium carbonate than for calcium sulfite as is indicated by the higher horizontal zeta potential plateau, $\zeta = 60.0$ mV, compared to $\zeta = 23.0$ mV for calcium sulfite. The higher affinity of Aero 870 for calcium carbonate would indicate that the separation of calcium carbonate from calcium sulfite by froth flotation was possible using this reagent as a collector.

Figure 4.11. Ether Amine is a cationic collector. Parallelism of zeta potential curves can be seen until a concentration of 0.05 g/L is reached. After this point the slope of the calcium carbonate curve is steeper than the slope of calcium sulfite curve. The steeper slope indicates that calcium carbonate is preferred over calcium sulfite above this concentration. Ether Amine has the potential of providing a good separation but at a much higher concentration than with the Aero

Zeta Potentials in Aero 870 Solutions

Figure 4.12. Aero 870 is a cationic collector produced by Cytec Industries Inc. (Bountiful, UT), which of the collectors studied shows the best potential for aiding a separation between calcium carbonate and calcium sulfite. The steepness of the slope of the zeta potential curve at low concentrations indicates the collector is adsorbing to the surface. The higher zeta potential plateau for calcium carbonate over the calcium sulfite indicates that the collector has a higher affinity for calcium carbonate than for calcium sulfite.

Effect of Cationic Collector on Silica

Cationic collectors have a better potential for removing calcium carbonate from calcium sulfite than anionic or non-ionic collectors. However, there are other materials that are in flue-gas desulfurization scrubber sludge that must be separated, such as silica. Therefore zeta potential curves were also determined for silica. Due to the superior nature of Aero 870, the zeta potential curve for silica was determined with this collector (Figure 4.13). The silica zeta potential curve falls between the zeta potential curves for calcium carbonate and calcium sulfite. This indicates that the collector has a stronger affinity for the calcium carbonate than for silica. The collector also has a higher affinity for silica than for calcium sulfite. Therefore this collector has the potential to remove the majority of the impurities, calcium carbonate and silica, from wet flue-gas desulfurization scrubber sludge.

Zeta Potentials in Aero 870 Solutions

Figure 4.13. The zeta potential curve for silica lies between the calcium carbonate and calcium sulfite curves, indicating that both calcium carbonate and silica are preferred over calcium sulfite by the collector. Therefore, Aero 870 can possibly be used to separate calcium carbonate and silica (which are the impurities) from calcium sulfite.

Conclusions

The difference in affinity for calcium carbonate compared to calcium sulfite was greater for cationic collectors than for anionic collectors. This was evident by the large increase in the slopes of the zeta potential curves for cationic collectors, and the resulting magnitude difference in the plateaus of the zeta potential curves between calcium carbonate and calcium sulfite.

As expected, a non-ionic collector had no effect on the surface charge of the particle. Therefore this would not be a good collector for a selective separation between calcium carbonate and calcium sulfite.

Of the collectors tested, the collector that is likely to provide the best separation between calcium sulfite and the impurities (calcium carbonate and silica) is Aero 870 cationic collector produced by Cytec Industries Inc. Its rapid adsorption by calcium carbonate and silica at low concentrations, and its preferential adsorption by these particles compared to calcium sulfite, indicates that it is a selective collector for this application.

Even though Aero 870 has the characteristics of a good collector for the separation of calcium carbonate from a flue-gas desulfurization scrubber sludge, further laboratory flotation test work must be done to confirm this.

CHAPTER 5

WET FLUE-GAS SCRUBBER SLUDGE PROCESSING WITH FROTH FLOTATION

Abstract

An estimated 20 million metric tons per year of wet flue-gas desulfurization scrubber sludge is currently being landfilled. This sludge is a fine, grey colored powder which typically contains calcium sulfite/sulfate, unreacted limestone, silicates, and iron oxides. The differences in physico-chemical surface properties of these particles make it possible to separate these components. The reduction of limestone impurities in raw scrubber sludge feed, and scrubber sludge that was first processed with a water-only cyclone, using froth flotation were investigated.

Previous to this project, no attempt had ever been made to float limestone from a calcium sulfite matrix. There were therefore no prior studies which could recommend appropriate collectors for this work, and so it was necessary to determine suitable reagents from basic principles, by considering the properties of the individual reagents and measuring the zeta potentials of the particles surfaces. The zeta potential results described previously showed that Ethoxylated Octadecylamine-Octadecylguanidine Complex (Cytec Aero 870) would be the best collector for flotation of limestone from calcium sulfite, and was therefore selected for use in these experiments.

The combination of separation by water-only cycloning and froth flotation produced a clean calcium sulfite/sulfate product that could be used as a synthetic gypsum. This separation process provides coal burning utility companies with an alternative to landfilling their wet flue-gas desulfurization sludge.

Introduction

Background

The Clean Air Act Amendments (CAAA) of 1990 have limited the amount of sulfur oxides that can be produced by coal burning utility companies. This has caused utility companies to re-evaluate their operating strategy. There are three strategies for controlling the amount of sulfur oxide emissions. These include fuel switching, pre-combustion desulfurization, and post-combustion desulfurization. This study is focused on post-combustion. The passage of the CAAA has led to tremendous activity in the research and development of post-combustion desulfurization, especially flue-gas desulfurization (FGD). One hundred and eighty nine FGD processes have been identified in a report to the Electric Power Research Institute (EPRI), (Radian Corporation, 1984). However, most of these methods are still limited to laboratory and pilot plant activities. The most industrially used method is wet flue-gas desulfurization. Wet flue-gas desulfurization is widely used due to its low operating cost, high reliability and high SO₂ removal.

Wet flue-gas desulfurization uses ground limestone or lime to convert sulfur oxide gases into a solid precipitate (Goldstein, 1990). Chemical reactions for lime and limestone desulfurization are given below (Fellman and Cheremisinoff, 1993):

Overall Reaction with Limestone:

Overall Reaction with Lime:

This solid precipitate is better known as scrubber sludge or gypsite. Scrubber sludge from wet flue-gas desulfurization typically contains calcium sulfite ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$), calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium carbonate (CaCO_3) and various other impurities. Wet-flue gas desulfurization can be divided into two groups: natural and forced oxidation. The only difference between the two is that the calcium sulfite is completely oxidized into calcium sulfate in the forced-oxidation scrubbing process. The types of impurities remain the same in both types of scrubber sludge. The major disadvantage of wet flue-gas desulfurization is the enormous amount of scrubber sludge produced which needs to be landfilled. A typical 400 MW power station that burns a high sulfur coal produces 170,000 tons of wet flue-gas scrubber sludge per year. This sludge is not only costly for the utility company to landfill, but may present danger to the environment. If calcium sulfite is not fully oxidized it can lead to water pollution (Erwin, Wang, and Hudson, 1982). Therefore, the development of new technology which would reduce impurities, such as limestone, from a wet flue-gas desulfurization scrubber sludge to produce a high grade calcium sulfite/sulfate, which could be oxidized into a synthetic gypsum would benefit not only the utility companies but also the environment.

The study described here was funded by the DOE's Basic Coal Research Program, which exists for the purpose of developing innovative new technologies in novel applications, and not simply for routine data gathering or modeling/optimization of well-known processes. The purpose of the work was to produce a marketable-grade product using techniques that had never been applied to scrubber sludge before, and so the first goal was to determine whether the desired separation could be made at all. If an acceptable-grade product could not be made, then there would be no point in optimizing or mathematically modeling the process. The study therefore concentrated on demonstrating the overall feasibility of the concept, rather than on process optimization or development of models.

Requirements of Gypsum Industry

There are many possible markets for a high quality synthetic gypsum. These include: prefabrication products (wallboard), plaster, additives in portland cement, and soil conditioners. The largest user of natural gypsum (~75% of the annual U.S. consumption) is in the prefabricated products, predominately wallboard (Luckervich, 1993). The wallboard industry would therefore be the preferred market for this synthetic gypsum. However, before synthetic gypsum can be used as a replacement for natural gypsum the impurities in the synthetic gypsum must be reduced to levels that are similar to natural gypsum or lower.

The most abundant impurity in this scrubber sludge was unreacted limestone. Table 5.1 gives a chemical analysis of the scrubber sludge used in this study, which was obtained from a utility company burning a high sulfur coal. The unreacted limestone is due to incomplete dissolution of the limestone during its reaction with sulfur oxides. There are several reasons for incomplete dissolution of the limestone: size distribution of limestone particles, fluctuation in sulfur oxide

concentration due to inconsistencies in coal, purity of the limestone, and better sulfur oxide removal at higher scrubber pH (where the limestone is less soluble). Other impurities in the scrubber sludge were iron chips produced during grinding of the limestone, and silicate minerals which had been present in the limestone.

Table 5.1: Characteristics of the major components in a naturally-oxidized wet flue-gas scrubber sludge investigated in this study.

Component	Specific Gravity (g/cm ³)	Percent Weight	Solubility in Water (g/L)
Calcium Sulfite (CaSO ₃ •1/2H ₂ O)	2.52	~77.0	0.04
Calcium Sulfate (CaSO ₄ •2H ₂ O)	2.32	~14.0	3.2
Calcium Carbonate (CaCO ₃)	2.71	~5.6	0.013
Silicate	2.6-2.9	1.5-2.5	Insoluble
Iron Oxides	7.8	0.5-1.5	Insoluble

Impure scrubber sludge can lead to several difficulties in wallboard manufacturing. These include: excess equipment wear, poor paper adhesion, and discoloration of the wallboard. However, the biggest problem with impurities in the scrubber sludge is that they reduce the purity of the synthetic gypsum, which alters the hardening rate of the gypsum paste after the wallboard is formed. The acceptable weight percent of impurities for wallboard vary from manufacturer to manufacturer but most of them require a minimum of 95.0% by weight gypsum in their raw material (Ojanpera et al. 1993, Abbott, et al., 1993 and Mayer, 1993). The maximum level of unreacted limestone present varies but 2.0% by weight or less is considered acceptable. Further reduction of the impurities could also open up additional markets for this synthetic gypsum.

The goal of this project was to reduce the unreacted limestone from 5.6% by weight in a currently landfilled wet flue-gas desulfurization scrubber sludge to below 2.0% by weight for a useful calcium sulfite/sulfate product that can be oxidized into a synthetic gypsum product for wallboard and plaster manufacturing. Previous work, see Chapter 2, demonstrated that water-only cyclone could remove nearly 50% of the limestone. However this was not clean enough for industrial use, so an additional purification technique was needed. Froth flotation was selected as the next purification step for several reasons. Flotation is a wet process, therefore material directly out of the scrubber or from the water-only cyclone would not have to be de-watered before processing. The size distribution of the material was within range of the size limits of froth flotation. The final reason was froth flotation is a proven technology which has been commercially successful.

A reverse flotation was selected as the best flotation option for providing a clean sulfite/sulfate material. Reverse flotation is the flotation of the impurities (limestone) instead of the valuable

product (calcium sulfite/sulfate). The main reason for floating the impurities over the useful product was that the impurities represent such a small portion of the total weight, therefore reducing the amount of flotation reagents needed and also the cost of separation. Froth flotation had never been attempted with any material similar to this scrubber sludge, and so there was no data available for selecting suitable flotation reagents or conditions. It was necessary to characterize the material, and determine how it would react with a wide range of reagents, before it was possible to choose effective reagents for froth flotation studies.

Experimental

Materials

The scrubber sludge investigated in this work was from a natural-oxidized scrubber. This was done for two reasons:

1. There are a larger number of natural-oxidized scrubbers in use than force-oxidized scrubbers, and so studies of sludge from natural-oxidized scrubbers are of greater industrial interest.
2. The extra component in natural-oxidized scrubber sludge, calcium sulfite, was expected to hinder the separation process. Therefore if a clean product could be obtained from a natural-oxidized scrubber under adverse conditions, a clean product could certainly be obtained from a forced-oxidized scrubber.

Two different types of feed material were investigated to determine which could be treated to produce an acceptable-quality product (less than 2.0% limestone by weight).

1. The first material investigated was raw scrubber sludge from the plant. The size distribution of this material can be seen in Figure 5.1. The limestone grade was 5.6 +/- 0.30% by weight.
2. The second material investigated was the overflow product from water-only cycloning of the raw scrubber sludge. Cycloning removed the coarse particles, and markedly reduced the quantity of limestone remaining in the feed. The size distribution of this material can be seen in Figure 5.2. The limestone grade of this material was 2.89 +/- 0.10%, with a weight recovery of 75.6% by weight from the cyclone.

Size Distribution of Scrubber Sludge and Pre-Reacted Limestone

Figure 5.1: Size distribution of limestone before it was reacted with sulfur oxides and the resulting scrubber sludge. Size distributions were determined by microtrac size analysis (which uses laser diffraction).

Size Distribution of Products from the Water-Only Cyclone

Figure 5.2: The size distribution of the products of water-only cycloning. These size distributions were determined by microtrac size analysis (which uses laser diffraction). The overflow material was further processed with froth flotation to remove the remaining limestone impurities.

Froth Flotation Test Procedure

Flotation experiments were carried out in a laboratory-scale Denver machine, which simulates the performance of the conventional flotation equipment that is used on an industrial scale. The procedure for conventional froth flotation experiments was as follows:

- The laboratory scale Denver flotation machine and 2.5 liter working volume cell were thoroughly washed out with water and dried.
- 2.5 liters of scrubber sludge-saturated water (to minimize dissolution) was added to the flotation cell.
- A 115 gram sample was then added to the cell as the impeller was running. The suspension was allowed to condition for 2 minutes. The impeller speed was set at 1250 rpm.
- The appropriate amount of collector was added and the suspension was conditioned for another 2 minutes. Collector concentration was added as kilograms of collector per metric ton of feed material, Kg/mt.
- Frother was then added and conditioning continued for 15 seconds.
- The air valve was opened to start flotation by allowing air bubbles to enter the pulp. The material was hand scrapped into a tared pan until the test was finished, 5 minutes for these experiments.
- The floated material was then weighed, and a sample of the slurry was taken for pH and temperature measurements.
- The flotation products were then filtered, dried at 40°C, and prepared for chemical analysis.
- Each test condition was then repeated in order to calculate an average and a standard deviation.

Flotation Reagents

Previous to this project, no attempt had ever been made to float limestone from a calcium sulfite matrix. Previous work had either floated limestone or calcite from silicate or phosphate minerals, or simply used it as a model compound for unselective bulk flotation (Bermudez et al, 1996; Elgillani and Abouzeid, 1993; Cases et al, 1986; Fuerstenau and Palmer, 1976; Mayer, 1993; Ozcan and Bulut, 1993; Shao and Guo, 1989; Smith and Akhtar, 1976; Wills, 1992; Elgillani and Abouzeid, 1993; Hogg, 1989; Hanna and Somasundaran, 1976; Woods and Richardson, 1986). Because there were no prior studies which could recommend appropriate collectors for this work, it was necessary to determine suitable reagents from basic principles, by considering the properties of the individual reagents and measuring the zeta potentials of the particles surfaces. There are many potential collecting reagents, with the important classes of reagent summarized in Figure 5.3 (Crozier, 1992; Wills, 1992; Fuerstenau and Herrera-Urbina, 1989). These reagent types vary widely in their characteristics, their selectivity towards particular classes of minerals, and their sensitivity to variations in factors such as pH and ionic strength.

Figure 5.3: Summary of the available collector types (Wills, 1992)

In particular, the ionic collectors are sensitive to the surface charge that develops on the surfaces of particles in aqueous suspension. A detailed zeta potential study was carried out (as described in a previous chapter) to determine the sign of the surface charges on the important particles that make up scrubber sludge, and this was used to choose which type of collector was best suited for this separation. A wide range of collectors was investigated, including cationic, non-ionic, and anionic collectors.

The zeta potential study provided a fundamental understanding of the surface charge of the components in the scrubber sludge (Shoop and Kawatra, 1996), and determined that all of the particle types had negatively-charged surfaces at the relevant pH values, with limestone being most strongly negative. Given this information, the properties of the various types of collector were considered and reviewed to determine which would be most suitable:

Nonionic Collectors: These collectors include non-polar oils, such as kerosene and fuel oil. They are used to make naturally hydrophobic particles become more hydrophobic, and are widely used in coal flotation, and as extenders for other types of collectors. Since the unreacted limestone in the scrubber sludge was not naturally hydrophobic, this type of collector was not suitable

if used alone, but may have some value in combination with other collectors.

Carboxylic Collectors (anionic): Carboxylic acid collectors, such as oleic acid, form negatively-charged collector ions when dissolved in water, and so they will be attracted to positively-charged surfaces. These collectors are also known to specifically adsorb onto calcium salt particles, regardless of their surface charges, as they make a weak chemical bond with the calcium ions. Carboxylic collectors are therefore regularly used to float calcium minerals away from other minerals which do not contain calcium. However, in this study, both the limestone (calcium carbonate) and the calcium sulfite are calcium salts, and so a reagent that bonds to the calcium will not be effective. Also, since both calcium sulfite and calcium carbonate were found to have negative surface charges in the Zeta potential studies, there would be no tendency for the carboxylic collectors to attach selectively based on the particle surface charges.

Sulfate and Sulfonate Collectors (anionic): Unlike the carboxylic collectors, the sulfate and sulfonate collectors do not have a specific affinity for calcium ions. Since they are also negatively charged, they will have no electrostatic attraction to the scrubber sludge particles, and so they will not be useful collectors in this application.

Xanthates and Dithiophosphates (anionic): These collectors are primarily used for flotation of sulfide minerals, where they chemically react with the sulfur atoms to form a strongly-bonded hydrophobic layer. They are very effective for sulfide minerals, but they do not work for more oxidized sulfur compounds (such as sulfates or sulfites) because the sulfur atoms are not in the correct oxidation state to form a bond with them.

Cationic Collectors: These collectors are based around nitrogen atoms (mainly amine and guanidine derivatives) because these molecules will form positively-charged ions in aqueous solution. Since they are positively-charged, cationic collectors will be electrostatically attracted to negatively-charged mineral surfaces, and so are the best choice for flotation of minerals with negative zeta potentials. Since limestone and silica were more negatively charged than the calcium sulfite at the natural pH for the scrubber sludge, cationic collectors were expected to be selective for limestone and silica, with less tendency to adsorb onto calcium sulfite. The zeta potential results showed that Ethoxylated Octadecylamine-Octadecylguanidine Complex (Cytec Aero 870) was more strongly adsorbed onto the limestone surface than any other available reagent, including other cationic reagents. It was adsorbed onto the limestone at a considerably higher level than would be expected if it were simply neutralizing the surface charge, showing that it had a specific affinity for the limestone surface. Its adsorption by the calcium sulfite was considerably less, and it showed a larger difference between its adsorption by the limestone and by the calcium sulfite than any other reagent. Based on this, it was predicted to be the most suitable collector for separating the limestone impurity from the calcium sulfite in the scrubber sludge, and so was selected for use in the flotation studies.

A polypropylene glycol methyl ether (Dow Froth 200) with a molecular weight of approximately 200 was selected as the frother for all experiments. This frother was used because it was a biodegradable reagent that would break down after the material has been removed from the flotation cell. This would help eliminate any further environmental problems while processing this material. The dosage of frother was determined by the minimum amount needed to form a

stable froth. A complete list of the test conditions for froth flotation experiments is given in Table 5.2.

Table 5.2: List of experimental conditions for froth flotation experiments

Type of Feed Material	Dosage of Frother (Dow Froth 200) Kg/mt	Dosage of Cationic Collector (Aero 870) Kg/mt
Raw Scrubber Sludge with a Limestone Concentration of 5.6 +/- 0.3% by weight.	0.20	0.050
		0.100
		0.200
		0.300
Scrubber Sludge that had been Pre-Treated with Water-Only Cyclone. Limestone Concentrations was 2.9+/- 0.10.	0.10	0.050
		0.100
		0.200
		0.300

Results and Discussion

Effect of Floating Raw scrubber Sludge, with No Pre-Treatment

The results of floating raw scrubber sludge are given in Figure 5.3-5.4. The pH in these tests varied from 7.40 to 7.65 and the pulp temperature varied from 20.2 °C to 21.2 °C. Limestone particles were floated, reducing the limestone content of the remaining valuable material, shown by Figure 5.4. The reduction of limestone in the calcium sulfite/sulfate increased as collector dosage was increased. The cleanest product (lowest limestone grade was 4.30% +/- 0.09 limestone by weight) was obtained at a collector dosage of 0.3 Kg/mt. This reduction in limestone grade with increasing dosage was expected because the collector was progressively covering more of the available limestone surface, rendering it more easily floatable and increasing its removal from the scrubber sludge. However, further increases in collector dosage caused the collector to interfere with the properties of the frother. This was observed as a breaking down of the froth layer and the formation of large coalesced bubbles.

Figure 5.5 compares the effect of weight recovery versus collector dosage. The weight recovery of useful product continued to decrease as collector dosage was increased. This was also expected because of the collector adsorbing to a large quantity of negative surface sites. The weight recovery for the lowest grade (4.30% +/- 0.09 limestone) material was 71.9% +/- 2.4. The theoretical best results for floating raw scrubber sludge would be a grade of 0.0% limestone (a grade of below 2.0% limestone for industrial use) in the useful product and a weight recovery of 94.4% solids by weight of the useful product. The best results obtained from this investigation was a grade of 4.30% +/-0.09 limestone in the useful product with a weight recovery of 71.9% +/- 2.4. Further increases in collector dosage were not expected to improve these results, because

Figure 5.4 shows that at the higher dosages, the limestone content of the product was levelling off, indicating that further increases of collector would not improve the grade further.

Limestone Grade in Calcium Sulfitite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 5.4: Variation of limestone grade in the valuable product (calcium sulfitite/sulfate) as a function of increasing collector dosage (Aero 870) for raw scrubber sludge feed. Limestone impurity was decreased at higher collector dosages. These results confirm the prediction from the zeta potential results that Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) would be an effective collector for removing unreacted limestone from scrubber sludge.

Weight Recovery of Calcium Sulfit/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 5.5: Weight recovery of valuable product (calcium sulfit/sulfate) compared with collector dosage for raw scrubber sludge feed. The continued decrease in weight recovery at higher collector dosage was expected due the collector adsorbing to a larger quantity of unwanted limestone particles and also to highly charged calcium sulfit/sulfate particles.

While the flotation of the raw scrubber sludge removed a portion of the limestone, it did not approach the desired level of less than 2.0% limestone by weight. There were two hypotheses for why the flotation of the raw scrubber sludge did not reduce the limestone content further:

- Large particle size of some of the impurities, and particularly of the most limestone-rich particles, which would make them difficult to recover by froth flotation. Wet-screening of the sludge (Table 5.3) showed that approximately 50% of the limestone is coarser than 45 microns, which is approximately the limit of particle size for cationic flotation (Colombo, 1986). Since it is well known that sufficiently coarse particles are more difficult to float than fine particles, this effect is considered to be a very likely cause of the poor limestone removals by flotation of the raw feed.

Table 5.3: Wet Screen Analysis of Raw Scrubber Sludge

Size Fraction (microns)	% Weight Recovery of Raw Sludge	% Weight Passing of Raw Sludge	% Weight Recovery of Limestone	% Weight Passing of Limestone
+ 106	2.6	-	3.7	-
-106 + 75	10.5	97.4	13.0	96.3
-75 + 53	13.5	86.9	16.7	83.3
-53 + 45	14.6	73.4	14.8	66.6
-45 + 38	10.1	58.8	9.3	51.8
-38 + 25	11.3	48.7	7.4	42.5
-25	37.4	37.4	35.1	35.1

- Lack of liberated surfaces on the calcium carbonate (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. Since the limestone was being converted to calcium sulfite in the flue-gas scrubber, it is considered likely that the limestone particles became coated with a surface layer of calcium sulfite (Gage and Rochelle, 1992). If present, this surface layer would cause the limestone particles to respond to flotation as if they were calcium sulfite particles, which would make them more difficult to remove. However, this possibility was disproved by an extensive surface characterization study (see chapter 1). This microscopy study was unable to find one unreacted limestone particle that had a surface coating.

Effect of Floating Scrubber Sludge After Cyclone Pre-Treatment

Water-only cycloning was determined in a previous part of this research to be beneficial for removing limestone impurities. The primary benefit was that it could reduce the raw scrubber sludge from a limestone grade of 5.6% to 2.9% by weight in the overflow product of the cyclone. If the overflow was then used as a flotation feed, the amount of limestone which flotation would have to remove to meet specifications could be reduced markedly. Water-only cyclones separate based on the difference in specific gravity of the particle, and to some degree by the difference in size of the particles. They therefore remove the largest, highest specific gravity particles from the scrubber sludge. Since the cyclone could reduce the limestone content of the sludge to only half of the level seen in the raw feed, this indicates that much of the unreacted limestone was part of the coarse, higher density fraction, which would be poorly removed by flotation in any case.

The results of floating scrubber sludge that had been previously treated with water-only cyclone are given in Figures 5.6 and 5.7. The pH in these test varied from 7.00 to 7.37, and the pulp temperature varied from 20.5 °C to 20.9 °C. Successful results were obtained as the collector

dosage was increased. The maximum reduction in limestone impurity (to approximately 1.70% limestone by weight in the valuable calcium sulfite/sulfate product) occurred at a collector dosage of 0.20Kg/mt. This now provided a method for producing a clean calcium sulfite/sulfate product, which met the specification of <2.0% limestone and could be used for the production of wallboard.

Figure 5.7 shows the effect of weight recovery verses collector dosage. As the collector dosage was increased, a decrease in weight recovery of useful product was observed. This was similar to the effect seen in the flotation of raw scrubber sludge. However, at a collector dosage of 0.30 Kg/mt, an increase in weight recovery was observed. This was due to the high collector concentration reacting with the frother (Leja, 1989) which was observed to cause the bubbles in the froth to coalesce and coarsen. The reduced bubble surface area of the froth resulted in more material falling out of the froth back into the flotation cell, and so the weight recovery was reduced. This effect limits the practical dosage of collector to less than 0.30 Kg/mt.

Limestone Grade in Calcium Sulfite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 5.6: Limestone content remaining in the valuable product (calcium sulfite/sulfate) as a function collector dosage, for scrubber sludge that had been previously treated with a water-only cyclone before flotation. Limestone impurity decreased as collector dosage increased until a minimum limestone grade (~1.70% limestone by weight) was achieved at a collector dosage of 0.20 Kg/mt. The combined separation strategy of water-only cycloning and froth flotation provided a calcium sulfite/sulfate that was clean enough to be use as a synthetic gypsum.

Weight Recovery of Calcium Sulfite/Sulfate Product vs. Collector Dosage (Aero 870)

Figure 5.7: Weight recovery of valuable product (calcium sulfite/sulfate) as a function of collector dosage, for scrubber sludge that had been processed through a water-only cyclone prior to froth flotation. Weight recovery decreased as collector dosage was increased until a maximum weight recovery (~87.0% by weight) was reached at a collector dosage of 0.20 Kg/mt.

Conclusions

Flotation of limestone from calcium sulfite had never been attempted previous to this study, and so there was no prior literature which could be used to clearly recommend a particular flotation reagent for this application. It was therefore necessary to study the surface charge of the particles present in scrubber sludge, and conduct Zeta potential studies to determine which reagents would interact usefully with the particle surfaces. The Zeta potential studies, which were described in a previous chapter, had predicted that of the numerous collectors considered, the cationic collector Aero 870 (Ethoxylated Octadecylamine Octadecylguanidine Complex) would be the most effective reagent for removing unreacted limestone from scrubber sludge by froth flotation. The flotation studies which were conducted confirmed that this reagent was an effective collector for removing limestone from calcium sulfite scrubber sludge.

In flotation tests with raw, untreated scrubber sludge, it was not possible to produce a product which would meet the desired specification of less than 2.0% limestone by weight. This is believed to be mainly due to the large amount of limestone present in the coarsest fraction of the

sludge, as determined by screen analyses. The coarse particles are more difficult to remove by froth flotation than the fine particles, and so flotation of the raw feed is unable to reduce the limestone content to much less than 4.3%.

Since both the calcium carbonate and calcium sulfite have negative surface charges, they both have an affinity for the cationic collector, although the collector adsorbs more strongly onto the calcium carbonate. It is therefore important not to add excessive collector, because once the calcium carbonate is completely coated with collector, the reagent which remains will be adsorbed by the calcium sulfite and the selectivity will be reduced.

A clean calcium sulfite/sulfate product could be produced by froth flotation when raw scrubber sludge was processed in a water-only cyclone prior to flotation. The pre-treatment with the cyclone removed the unfloatable coarse particles, and in the process reduced the limestone content of the sludge from 5.6% to only 2.9%. When the cycloned sludge was used as flotation feed, the overall grade of the clean product produced by flotation was approximately 1.70% limestone by weight, with a total weight recovery for the combined cyclone/flotation process being nearly 66.0%

CHAPTER 6

CONCLUSIONS

Single-stage water-only cycloning successfully removed nearly 50% of the unwanted limestone and maintained approximately 76% weight recovery. This does not meet the specifications for industrial gypsum, but it could be blended with natural gypsum to form a material that would be useful for wallboard manufacturing.

Mathematical modeling of the cyclone performance showed that the cyclone was performing well, and produced a sharp separation in most cases, with values of alpha near 4. It was also found that the value for R_f varied between 5.4 and 23.1% for all test conditions, showing that only a small fraction of the feed was bypassing the classification. Since reprocessing the cyclone product with a second cyclone would only have the effect of classifying the material that escaped classification on the first stage, there would be little benefit to be gained by multi-stage cycloning.

Two-stage cycloning reduced the weight recovery of the useful product by 16.7% without any further reduction in the amount of limestone in the useful product as predicted by mathematical modeling. Two-stage cycloning did increase the percent solids by weight of the useful product, which would be beneficial in de-watering cost, but due to the decrease in weight recovery of the useful product two stage-cycloning would not be recommended. Instead, cycloning followed by a different process (froth flotation) was investigated.

Froth flotation of a material similar to scrubber sludge has never been attempted before, and so it was necessary to determine the most suitable flotation reagents from first principles. The major need was to find a collector that was selective for calcium carbonate relative to calcium sulfite. Zeta potential studies showed that the difference in affinity for calcium carbonate compared to calcium sulfite was greater for cationic collectors than for anionic collectors. This was evident by the large increase in the slopes of the zeta potential curves for cationic collectors, and the resulting magnitude difference in the plateaus of the zeta potential curves between calcium carbonate and calcium sulfite.

As expected, a non-ionic collector had no effect on the surface charge of the particle, and did not have any obvious affinity for either type of particle examined. Therefore this would not be a good collector for a selective separation of calcium carbonate from calcium sulfite.

Of the collectors tested, the collector that is likely to provide the best separation between calcium sulfite and the impurities (calcium carbonate and silica) is Ethoxylated Octadecylamine Octadecylguanidine Complex (Aero 870) a cationic collector produced by Cytec Industries Inc. Its rapid adsorption by calcium carbonate and silica at low concentrations, and its preferential adsorption by these particles compared to calcium sulfite, indicates that it is a selective collector for this application.

In flotation tests with raw, untreated scrubber sludge, it was not possible to produce a product which would meet the desired specification of less than 2.0% limestone by weight. This is believed to be mainly due to the large amount of limestone present in the coarsest fraction of the

sludge, as determined by screen analyses. The coarse particles are more difficult to remove by froth flotation than the fine particles, and so flotation of the raw feed is unable to reduce the limestone content to much less than 4.3%.

Since both the calcium carbonate and calcium sulfite have negative surface charges, they both have an affinity for the Aero 870 cationic collector, although the collector adsorbs more strongly onto the calcium carbonate. It is therefore important not to add excessive collector, because once the calcium carbonate is completely coated with collector, the reagent which remains will be adsorbed by the calcium sulfite and the selectivity will be reduced.

A clean calcium sulfite/sulfate product could be produced by froth flotation when raw scrubber sludge was processed in a water-only cyclone prior to flotation. The pre-treatment with the cyclone removed the unfloatable coarse particles, and in the process reduced the limestone content of the sludge from 5.6% to only 2.9%. When the cycloned sludge was used as flotation feed, the overall grade of the clean product produced by flotation was approximately 1.70% limestone by weight, with a total weight recovery for the combined cyclone/flotation process being nearly 66.0%.

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**APPENDIX I: PROCEDURE USED TO DETERMINE CHEMICAL COMPOSITION
OF WET FLUE-GAS DESULFURIZATION SCRUBBER SLUDGE**

The procedure used to determine the major components in a wet flue-gas desulfurization scrubber sludge was based on the modification of ASTM Method E 1131-86, Standard Test Method for Compositional Analysis by Thermogravimetry. Modification of this method was necessary because it could not deal with the presence of calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$). Therefore, the calcium sulfite hemihydrate had to be completely oxidized into calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) before the procedure could be used. The complete procedure is as follows.

- Dry the scrubber sludge at 45°C to remove all of the free water, leaving only chemically-bound water.
- Disperse 1 gram sludge in 10 milliliters of 30% hydrogen peroxide, agitate 4 to oxidize the sulfite to sulfate, and dry at 45°C . Measure weight gain from oxidation to calculate initial sulfite content (pure calcium sulfite will increase in weight by 33.3% upon oxidation to gypsum).
- Heat to 250°C for 2 hours, measure weight loss from dehydration of gypsum (gypsum will lose 20.6% of its weight upon calcination to anhydrous calcium sulfate).
- Heat to 950°C for 2 hours, measure weight loss from calcination of limestone (limestone will lose 44.0% of its weight upon calcination to lime).
- Compare with standardized mixtures of gypsum and limestone to determine composition. Standardized mixtures were prepared from analytical-grade synthetic gypsum (99.5% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium carbonate (99.9% CaCO_3).

APPENDIX II: WATER-ONLY CYCLONE TESTS

Water-Only Cyclone Test Number: 13-M-1 Date: 7-18-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 5.0 psi

Vortex Finder (mm): 14 mm

Spigot Diameter (mm): 6 mm

pH of the Slurry: 7.67

Temperature of the Slurry: 20.0°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	11,097.5	497.0	4.5	93.8
Underflow	269.2	32.9	12.2	6.2

Limestone Grade in the Overflow: 4.30 +/- 0.07

Limestone Grade in the Underflow: 22.88 +/-0.20

Water-Only Cyclone Test Number: 13-M-2 Date: 7-18-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 10.0 psi

Vortex Finder (mm): 14 mm

Spigot Diameter (mm): 6 mm

pH of the Slurry: 7.91

Temperature of the Slurry: 20.0°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	12,745.7	587.4	4.6	92.6
Underflow	305.0	47.1	15.4	7.4

Limestone Grade in the Overflow: 3.83 +/-0.08

Limestone Grade in the Underflow: 27.45 +/-0.20

Water-Only Cyclone Test Number: 13-M-3 Date: 7-18-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 20.0 psi

Vortex Finder (mm): 14 mm

Spigot Diameter (mm): 6 mm

pH of the Slurry: 7.53

Temperature of the Slurry: 20.8°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	13,672.9	625.5	4.6	93.0
Underflow	218.3	47.2	21.6	7.0

Limestone Grade in the Overflow: 3.71 +/- 0.11

Limestone Grade in the Underflow: 29.93 +/-0.40

Water-Only Cyclone Test Number: 2-B-1 Date: 7-19-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 5.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.75

Temperature of the Slurry: 21.0°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	11,685.5	475.5	4.1	84.1
Underflow	777.4	89.6	11.5	15.9

Limestone Grade in the Overflow: 3.45 +/- 0.10

Limestone Grade in the Underflow: 14.54 +/-0.25

Water-Only Cyclone Test Number: 2-B-2 Date: 7-19-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 10.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.67

Temperature of the Slurry: 20.7°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	12,440.3	516.4	4.2	81.1
Underflow	775.9	120.2	15.5	18.9

Limestone Grade in the Overflow: 3.36 +/- 0.10

Limestone Grade in the Underflow: 14.32 +/-0.23

Water-Only Cyclone Test Number: 2-B-3 Date: 7-19-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 20.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.58

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	13,059.3	522.3	4.0	78.2
Underflow	805.7	145.5	18.1	21.8

Limestone Grade in the Overflow: 3.21 +/- 0.11

Limestone Grade in the Underflow: 13.69 +/-0.06

Water-Only Cyclone Test Number: 10-J-1 Date: 8-11-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 20.0 psi

Vortex Finder (mm): 8 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 8.06

Temperature of the Slurry: 22.8°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	11,612.8	414.6	3.6	71.0
Underflow	849.2	169.2	19.9	29.0

Limestone Grade in the Overflow: 3.31 +/- 0.11

Limestone Grade in the Underflow: 10.68 +/-0.19

Water-Only Cyclone Test Number: 1-A-1-1 Date: 9-5-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 25.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.60

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	4,112.0	161.8	3.9	78.1
Underflow	215.8	45.5	21.1	21.9

Limestone Grade in the Overflow: 3.03 +/- 0.09

Limestone Grade in the Underflow: 13.56 +/-0.34

Water-Only Cyclone Test Number: 1-A-1-2 Date: 9-5-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 35.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.71

Temperature of the Slurry: 20.8°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	3,955.2	149.2	3.8	76.5
Underflow	209.8	45.9	21.9	23.5

Limestone Grade in the Overflow: 3.00 +/- 0.11

Limestone Grade in the Underflow: 13.29 +/-0.11

Water-Only Cyclone Test Number: 1-A-1-3 Date: 9-5-95

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 45.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 7.58

Temperature of the Slurry: 21.0°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	4,016.4	149.2	3.7	75.6
Underflow	217.2	48.1	22.1	24.4

Limestone Grade in the Overflow: 2.89 +/- 0.10

Limestone Grade in the Underflow: 13.12 +/-0.21

Water-Only Cyclone Test Number: 7-G-2 Date: 2-19-96

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 10.0% by weight

Inlet Feed Pressure (psi): 45.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 8.54

Temperature of the Slurry: 20.8°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	4,126.1	326.4	7.9	79.8
Underflow	277.3	82.6	29.8	20.2

Limestone Grade in the Overflow: 3.26 +/- 0.04

Limestone Grade in the Underflow: 13.89 +/-0.06

Water-Only Cyclone Test Number: 7-G-3 Date: 2-14-96

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 20.0% by weight

Inlet Feed Pressure (psi): 45.0 psi

Vortex Finder (mm): 11 mm

Spigot Diameter (mm): 5 mm

pH of the Slurry: 8.91

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	4102.9	710.7	17.3	86.8
Underflow	310.6	108.5	34.9	13.2

Limestone Grade in the Overflow: 3.90 +/- 0.20

Limestone Grade in the Underflow: 13.22 +/-0.16

Hydrocyclone Test Number: 4-D-1-3-A

Date: 4-10-96

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 35.0 psi

Vortex Finder (mm): 8 mm

Spigot Diameter (mm): 3.2 mm

pH of the Slurry: 7.90

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	3902.1	37.8	1.0	18.8
Underflow	508.1	163.0	32.1	81.2

Limestone Grade in the Overflow: 3.10 +/- 0.06

Limestone Grade in the Underflow: 3.03 +/-0.05

Hydrocyclone Test Number: 4-D-1-3-B

Date: 4-10-96

Test Parameters for a 50.8mm Diameter Water-only Cyclone

Weight% Solids of Feed Slurry: 5.0% by weight

Inlet Feed Pressure (psi): 45.0 psi

Vortex Finder (mm): 8 mm

Spigot Diameter (mm): 3.2 mm

pH of the Slurry: 7.98

Temperature of the Slurry: 20.4°C

Physical Characteristics of the Products from the Water-Only Cyclone

Flotation Products	Wet Weight (grams)	Dry Weight (grams)	Percent Solids by Weight	Weight Recovery
Overflow	4451.2	38.2	0.9	16.7
Underflow	594.8	190.3	32.0	83.3

Limestone Grade in the Overflow: 3.07 +/- 0.04

Limestone Grade in the Underflow: 3.09 +/-0.06

APPENDIX III: FROTH FLOTATION TESTS

Froth Flotation Test Number: 4-D-2-7

Date: 4-2-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.05 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.5°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	23.9	21.0
Tails*	88.3	79.0

Limestone Grade in the Concentrate: 6.98 +/- 0.06

Limestone Grade in the Tails*: 4.64 +/-0.10

Froth Flotation Test Number: 4-D-2-14

Date: 4-2-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.05 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 22.0°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	26.3	23.3
Tails*	86.5	76.7

Limestone Grade in the Concentrate: 7.19 +/- 0.08

Limestone Grade in the Tails*: 4.47 +/- 0.06

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-2-18

Date: 4-2-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.05 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.8°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	27.9	25.1
Tails*	83.4	74.9

Limestone Grade in the Concentrate: 6.74 +/- 0.05

Limestone Grade in the Tails*: 4.59 +/- 0.03

Froth Flotation Test Number: 4-D-2-5

Date: 3-26-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.1 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 21.2°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	33.2	29.0
Tails*	79.9	71.0

Limestone Grade in the Concentrate: 6.55 +/- 0.01

Limestone Grade in the Tails*: 4.60 +/- 0.08

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-2-15

Date: 3-26-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.1 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 21.8°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	27.1	24.0
Tails*	85.6	76.0

Limestone Grade in the Concentrate: 7.48 +/- 0.03

Limestone Grade in the Tails*: 4.66 +/- 0.09

Froth Flotation Test Number: 4-D-2-19

Date: 4-3-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.1 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.4°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	31.1	27.9
Tails*	80.3	72.1

Limestone Grade in the Concentrate: 6.98 +/- 0.08

Limestone Grade in the Tails*: 4.48 +/- 0.09

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-2-6

Date: 3-26-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.2 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	29.2	26.0
Tails*	83.8	74.0

Limestone Grade in the Concentrate: 7.43 +/- 0.14

Limestone Grade in the Tails*: 4.47 +/-0.08

Froth Flotation Test Number: 4-D-2-20

Date: 4-3-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.2 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.4°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	30.8	27.8
Tails*	80.1	72.2

Limestone Grade in the Concentrate: 7.00 +/- 0.11

Limestone Grade in the Tails*: 4.38 +/- 0.15

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-2-9

Date: 4-9-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.3 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.2°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	20.9	18.5
Tails*	92.3	81.5

Limestone Grade in the Concentrate: 8.68 +/- 0.04

Limestone Grade in the Tails*: 4.40 +/-0.08

Froth Flotation Test Number: 4-D-2-17

Date: 4-3-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.3 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.6°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	33.4	30.0
Tails*	78.1	70.0

Limestone Grade in the Concentrate: 6.89 +/- 0.05

Limestone Grade in the Tails*: 4.25 +/- 0.07

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-2-21

Date: 4-3-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.3 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 19.7°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	28.3	25.4
Tails*	83.0	74.6

Limestone Grade in the Concentrate: 7.41 +/- 0.03

Limestone Grade in the Tails*: 4.24 +/- 0.07

Froth Flotation Test Number: 4-D-2-23

Date: 6-21-96

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Raw Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.3 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.2 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.3°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	32.5	29.0
Tails*	79.6	71.0

Limestone Grade in the Concentrate: 7.21 +/- 0.15

Limestone Grade in the Tails*: 4.20 +/- 0.03

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 8-H-3

Date: 10-31-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.05 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.5°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	10.9	9.5
Tails*	103.6	90.5

Limestone Grade in the Concentrate: 10.20 +/- 0.08

Limestone Grade in the Tails*: 2.05 +/-0.08

Froth Flotation Test Number: 8-H-16

Date: 10-31-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.05 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.5°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	12.7	10.6
Tails*	102.8	89.4

Limestone Grade in the Concentrate: 10.33 +/- 0.09

Limestone Grade in the Tails*: 2.13 +/- 0.10

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 8-H-5

Date: 11-1-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.10 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.7°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	9.6	8.4
Tails*	105.0	91.6

Limestone Grade in the Concentrate: 13.47 +/- 0.04

Limestone Grade in the Tails*: 1.89 +/-0.02

Froth Flotation Test Number: 8-H-12

Date: 11-1-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.10 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.10Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 21.0°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	16.4	13.7
Tails*	103.0	86.3

Limestone Grade in the Concentrate: 11.24 +/- 0.06

Limestone Grade in the Tails*: 1.69 +/- 0.12

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 8-H-13

Date: 11-1-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.10 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.4°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	17.5	14.6
Tails*	102.2	85.4

Limestone Grade in the Concentrate: 10.75 +/- 0.06

Limestone Grade in the Tails*: 1.69 +/- 0.06

Froth Flotation Test Number: 8-H-7

Date: 11-6-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.20 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.6°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	12.9	11.3
Tails*	101.6	88.7

Limestone Grade in the Concentrate: 12.91 +/- 0.04

Limestone Grade in the Tails*: 1.78 +/-0.06

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 8-H-14

Date: 11-6-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.20 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 21.0°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	18.6	15.6
Tails*	100.5	84.4

Limestone Grade in the Concentrate: 10.47 +/- 0.09

Limestone Grade in the Tails*: 1.51 +/- 0.05

Froth Flotation Test Number: 8-H-15

Date: 11-6-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.20 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.6°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	15.0	12.6
Tails*	104.3	87.4

Limestone Grade in the Concentrate: 11.59 +/- 0.05

Limestone Grade in the Tails*: 1.84 +/- 0.02

* This is a reverse flotation, therefore the tails are the useful product.

Froth Flotation Test Number: 4-D-5-1

Date: 11-6-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.30 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 20.8°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	12.5	10.8
Tails*	103.0	89.2

Limestone Grade in the Concentrate: 10.76 +/- 0.08

Limestone Grade in the Tails*: 2.06 +/- 0.05

Froth Flotation Test Number: 4-D-5-2

Date: 11-6-95

Working Volume of Flotation Cell: 2.5 liters

Impeller Speed (rpm): 1250

Type of Feed Material: Cyclone Overflow Scrubber Sludge

Type and Dosage of Collector: Aero 870 @ 0.30 Kg/mt

Type and Dosage of Frother: Dow Froth 200 @ 0.1 Kg/mt

Flotation Time: 5 minutes

Temperature of the Slurry: 21.1°C

Physical Characteristics of the Products from Froth Flotation

Flotation Products	Dry Weight (grams)	Weight Recovery
Concentrate	14.0	12.1
Tails*	101.3	87.9

Limestone Grade in the Concentrate: 11.35 +/- 0.15

Limestone Grade in the Tails*: 1.92 +/- 0.10

* This is a reverse flotation, therefore the tails are the useful product.