ABSTRACT

Wet flue-gas desulfurization units in coal-fired power plants produce a large amount of sludge which must be disposed of, and which is currently landfilled in most cases. Increasing landfill costs are gradually forcing utilities to find other alternatives. In principle, this sludge can be used to make gypsum (CaSO$_4$·2H$_2$O) for products such as plaster-of-Paris and wallboard, but only if impurities such as unreacted limestone and soluble salts are removed, and the calcium sulfite (CaSO$_3$) is oxidized to calcium sulfate (CaSO$_4$). This project investigated methods for removing the impurities from the sludge so that high-quality, salable gypsum products can be made.

Two processes were studied, both separately and in combination: Water-only cycloning, and froth flotation. A large fraction (30-40%) of the impurities in the sludge are contained in the coarser, higher-density particles, which are readily removed using a water-only cyclone. Much of the remaining impurities are hydrophobic, and can be removed by froth flotation. A combined cyclone/froth flotation process has been found to be suitable for producing a high-purity product from scrubber sludge at low cost.
EXECUTIVE SUMMARY

The objective of this project is to purify the gypsum and calcium sulfite from power-plant flue-gas scrubber sludge to make high-quality, marketable products. This will eliminate the need for landfilling the sludge. The goal of the separation is to ensure that the gypsum is of consistently good quality for industrial use, by removing the unreacted limestone, soluble salts, and compounds which prevent the calcium sulfite from oxidizing to gypsum. Currently, scrubber sludge is unmarketable as gypsum due to its low purity and incomplete oxidation. The target of this project is to produce a gypsum product comparable in quality to the best-grade natural gypsum, which contains less than 2% limestone and negligible amounts of other impurities.

Wet flue-gas scrubbers remove sulfur oxides from flue gases by reacting a slurry of limestone in water with the sulfur oxides to produce relatively insoluble compounds, according to the following reactions:

\[ \text{CaCO}_3 + \text{SO}_2 + 1/2\text{H}_2\text{O} \rightarrow \text{Ca(SO}_3\text{)} \cdot 1/2\text{H}_2\text{O} + \text{CO}_2 \]
\[ \text{CaCO}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca(SO}_4\text{)} \cdot 2\text{H}_2\text{O} + \text{CO}_2 \]

The resulting scrubber sludge is composed of fine particulates of primarily calcium sulfite (\(\text{Ca(SO}_3\text{)} \cdot 1/2\text{H}_2\text{O}\)), limestone (\(\text{CaCO}_3\)), and gypsum (\(\text{Ca(SO}_4\text{)} \cdot 2\text{H}_2\text{O}\)). Other impurities include soot, silicates from the limestone, silicates from flyash, complex sulfur compounds, and steel chips and rust from the limestone grinding mill. The gypsum is the major marketable component, and can be used for the following purposes:

**Portland Cement:** Up to 5% of gypsum is added to control setting rate.

**Agricultural Soil Conditioner:** Gypsum aids in retaining organic nitrogen in the soil.

**Wallboard:** Single largest market, used in virtually all building construction for interior partitions.

**Plaster:** made by partially dehydrating gypsum to \(\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}\). Used for building products, dental plaster, orthopedic plaster, and related materials.

The potential market for scrubber sludge is large, with the annual U.S. gypsum consumption at approximately 25 million tons/year, while the annual U.S. scrubber sludge production is much less, at approximately 10 million tons/year. The gypsum market can therefore absorb the entire production of sludge in the U.S., provided that it is of high enough quality and low enough price.
Various impurities reduce the marketability of scrubber-sludge gypsum. Limestone, carbon, and complex sulfur compounds will interfere with the setting characteristics of gypsum plaster and cement, and must be removed. Iron and rust flakes produce an undesirable color in plaster, and should be minimized. Calcium sulfite must be oxidized completely to gypsum, as it interferes with calcination of gypsum.

This project investigated the use of hydrocyclones and froth flotation to separate the harmful impurities from scrubber sludge. These methods were studied because they are very versatile and low-cost. It was also found that there were no published methods for compositional analysis of scrubber sludge, and techniques for analyzing natural gypsum could not be applied because of the high concentration of calcium sulfite. A new, relatively simple, reproducible method for compositional analysis of scrubber sludge was therefore developed in this project.

A great deal of industrial support was provided which was useful in this project. This was provided by Central Illinois Light Co., who provided access to the CILCO Duck Creek power station, and provided scrubber sludge samples and technical expertise; Empire Coal Co., who supported development of a new type of flotation column at a cost of $250,000; Krebs Engineers, who provided the hydrocyclones used in this project; and Polysonics, Inc., who provided instrumentation for the hydrocyclones.

The flotation column used in this project was developed at MTU as a subcontract for the Empire Coal Co., Ohio. It has been extensively tested both in the laboratory and in the Empire Coal processing plant, with excellent results. Benefits of the column include: greater selectivity than other flotation machines; more compact than other column designs; operating costs comparable to conventional machines; and robust design, resistant to plugging and operating instabilities.

Two types of hydrocyclone were used in this study: a conventional cyclone which primarily separates particles based on their sizes, and a water-only cyclone which separates based on both size and density. The water-only cyclone produced a slightly superior separation of impurities from the sludge, and was also less prone to plugging than the conventional cyclone.

The 4" diameter water-only cyclone could remove up to 43% of the unreacted limestone from the sludge, while recovering 88% of the sludge as a cleaned product. The cyclone also removed essentially all of the particles coarser than 212 micrometers, which includes most of the rust flakes, grinding ball chips, gravel, and incompletely ground limestone.
The scrubber sludge was determined to contain hydrophobic (poorly wettable) particles which were rich in limestone, soot, and other impurities, while the calcium sulfite and gypsum were hydrophilic (easily wettable). The hydrophobic impurities can be removed by froth flotation, which is designed to separate particles based on wettability differences. Experiments were carried out using oleic acid and sodium silicate to enhance the separation by increasing the differences in hydrophobicity, and the highest flotation selectivity was at very low reagent dosages.

Column flotation is a recent development from conventional flotation, and is much more selective due to a number of design improvements. It was therefore used in conjunction with the water-only cyclone to produce a highly-cleaned product from the sludge. Using the two processes in series, the amount of unreacted limestone could be reduced from 5.6% to only 2.2%, which is comparable to good-quality natural gypsum.
OBJECTIVES

The overall objective of the project was to produce a consistently high-quality, marketable product from the sludge formed during wet flue-gas desulfurization. Specifically, this was accomplished by separating the gypsum and calcium sulfite from the unreacted limestone, soot, reduced sulfur compounds, grinding ball chips, fine gravel, sand, and similar impurities. This was done through the following tasks:

Task 1: Development of analytical procedures, and characterization of sludge samples;
Task 2: Separation by water-only cyclones, based on particle densities;
Task 3: Separation by froth flotation, based on surface chemistry; and
Task 4: Oxidation of calcium sulfite to either gypsum or calcium sulfate hemihydrate ("Plaster of Paris")

Tasks 1-3 have been completed, and Task 4 was scheduled for the second year of the project.

INTRODUCTION AND BACKGROUND

When coal-fired power plants burn high-sulfur coal, such as most Illinois coals, the combustion gases contain too much sulfur to pass EPA air-quality standards. The gases must therefore be scrubbed to remove the sulfur. The most common scrubbing method is wet flue-gas desulfurization, which reacts the gases with a slurry of finely-ground limestone in water. The sulfur oxides then precipitate as calcium sulfate ($\text{CaSO}_4$) and calcium sulfite ($\text{CaSO}_3$), and these solids are then collected, filtered to remove the water, and disposed of by landfiling. This sludge is a significant disposal problem, and so it would be desirable to convert it to a marketable product instead.

Ideally, the scrubber sludge will consist of gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$), which is useful for making plaster, gypsum wallboard, cement, and similar products. However, the sludge is not usable in its raw form, for two reasons. First, it contains impurities such as unreacted limestone and soot, which would prevent plaster made from the sludge from setting properly. Second, the dominant species in the sludge is calcium sulfite ($\text{CaSO}_3\cdot1/2\text{H}_2\text{O}$), which must be oxidized to gypsum before it can be used to make plaster. It is therefore necessary to remove the limestone and its associated impurities, and to completely oxidize the calcium sulfite to gypsum, before the sludge can be marketed.

This project is investigating two methods for purifying the scrubber sludge:
1. Separating the coarser limestone and other dense impurities from the gypsum using a water-only cyclone. This is a cyclone which is designed to have increased ability to
separate particles by density, and is very compact and
cheap to operate. It is mainly suitable for removing the
coarser particles, such as coarse unreacted limestone,
grinding ball chips, and gravel contained in the limestone
fed to the scrubber.

2. Separating the finer limestone, soot, and reduced sulfur
species from the gypsum and calcium sulfite using froth
flotation. The flotation process is somewhat more
expensive than the water-only cyclone, but is considerably
more versatile. This process is best suited for removing
very fine particles, and so is complementary with the
water-only cyclone which removes the coarser particles.
Work done in this project has shown that limestone and its
associated impurities in the sludge are naturally
hydrophobic, and so can be removed by froth flotation with
a minimum of chemical reagents.

EXPERIMENTAL PROCEDURES

Analytical Procedure:

X-ray diffraction showed that the sludge is mainly calcium
sulfite and limestone, with undetectable amounts of free
gypsum. However, chemical analysis showed that the calcium
sulfite crystals contain up to 15% calcium sulfate (gypsum)
in solid solution.

Existing standard methods for analysis of gypsum and
limestone mixtures could not deal with the presence of
calcium sulfite, and were completely useless for this sludge.
It was therefore necessary to develop a new procedure, which
was a modification of ASTM Method E 1131-86, Standard Test
Method for Compositional Analysis by Thermogravimetry. The
complete procedure is as follows:
1. Dry the sludge at 45°C to remove all of the free water,
leaving only chemically-bound water.
2. Disperse 1 gm sludge in 10 ml of 30% hydrogen peroxide,
agitate 4 hours 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).
3. 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).
4. 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).
5. Compare with standardized mixtures of gypsum and limestone
to determine composition. Standardized mixtures were
prepared from analytical-grade synthetic gypsum (99.5%
Ca(SO₄)\(\cdot\)2H₂O) and calcium carbonate (99.9% CaCO₃).
The quantity of insoluble material was determined using
standard ASTM analytical procedures. A typical composition is
given in Table 1.
Table 1: Approximate composition of scrubber sludge, determined by chemical analysis. The individual samples of sludge varied somewhat in composition, due to the scrubber operation not being perfectly uniform, and to gradual chemical reactions occurring in the sludge during transport and storage.

<table>
<thead>
<tr>
<th>Component</th>
<th>Approx. % Wt.</th>
<th>Solubility in water, g/liter</th>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite, CaCO₃</td>
<td>6</td>
<td>0.013</td>
<td>2.71</td>
</tr>
<tr>
<td>Calcium Sulfite, CaSO₃·1/2H₂O</td>
<td>77</td>
<td>0.04</td>
<td>2.52</td>
</tr>
<tr>
<td>Gypsum, CaSO₄·2H₂O</td>
<td>14</td>
<td>3.2</td>
<td>2.32</td>
</tr>
<tr>
<td>Iron, Fe (grinding mill chips)</td>
<td>1</td>
<td>Insoluble</td>
<td>7.8</td>
</tr>
<tr>
<td>Silicates</td>
<td>2</td>
<td>Insoluble</td>
<td>2.6-2.9</td>
</tr>
</tbody>
</table>

Hydrocyclone Test Procedure:

Two Krebs hydrocyclones were used: a water-only cyclone of the design shown in Figure 1; and a conventional cyclone with a 15° cone angle, adjustable spigot diameter, and a 9.5 inch body length, but otherwise the same dimensions. The cyclones were mounted on the test circuit shown in Figure 2, which allowed precise sample collection, variation of pump speed, and measurement of the feed slurry pressure and flowrate. The cyclone type, slurry percent solids, and pressure were varied to determine the best processing conditions. Each test used approximately 4 kilograms of raw sludge. The conditions used in the tests were as follows:

Feed was 5.6% limestone.
20.5% solids: Water-Only Cyclone
7-13 psi, 10 tests
12.6% solids: Water-Only Cyclone
15, 10, and 5 psi, 3 tests at each pressure
5.0% solids: Water-Only Cyclone
15, 10, and 5 psi, 3 tests at each pressure
Sizing cyclone, 1/2" spigot
15, 10, and 5 psi, 3 tests at each pressure
Sizing cyclone, 5/8" spigot
15, 10, and 5 psi, 3 tests at each pressure
Figure 1. Schematic of the Krebs water-only cyclone used in this project, showing all dimensions. The conventional sizing cyclone that was also used differed in having a constant cone angle of 15°, a body length of 9.5 inches, and a variable spigot diameter.

Froth Flotation Procedure:

The initial flotation tests used a standard Denver D-12 flotation machine, with a 1.2 liter flotation cell. Before testing, the sludge was dried at 45°C and divided into 50-gram flotation charges. The procedure used in flotation tests was as follows:
A. Suspend sludge in distilled water, at 4% solids by weight, add modifying reagent (if used), condition 5 minutes. Natural pH was 8.4.

B. Add collecting reagents (if used) and condition for 2 minutes.

C. Add frothing reagent (methyl isobutyl carbinol, or MIBC, 0.4 kg/metric ton sludge) and condition 15 seconds.

D. Start air injection, remove froth for 3 minutes, filter and dry products.

The collecting reagents tested were oleic acid and #2 fuel oil, which are widely used in carbonate flotation. The modifying reagent tested was sodium silicate, which is commonly used for improving the selectivity of carbonate and oxide flotation.

Combined Cyclone/Column Flotation Procedure:

Since water-only cycloning removes coarse impurities, while flotation removes fine impurities, a combined process was used to remove both the coarse and fine impurities.

A horizontally-baffled flotation column, as shown in Figure 3, was used for this process. This column was developed at Michigan Tech for making precise, highly efficient particle separations. The combined cyclone/column flotation circuit is shown in Figure 4.

The process conditions for column flotation were as follows:
Feed: 500 gms of cyclone overflow from the 20.5% solids water-only cyclone tests (13 psi)
Collector: None
Frother: DF 200 (a polypropylene glycol methyl ether), 0.03 g/liter in all water entering the column (0.36 kg/mt of solids)
Washwater flowrate: 1 liter/min
Total flotation time: 9 minutes
The DF 200 frother was used because it produces a more stable froth than does MIBC, which was necessary to achieve the 10" froth depth required for the column to work properly. Neither MIBC or DF 200 react strongly with particle surfaces, and so the relative particle hydrophobicities are roughly similar with both frothers.

Cyclone overflow from a high % solids test was used as the column feed because samples taken during the other cyclone tests were not large enough to supply the necessary 500 grams of feed. By operating the cyclone under more nearly optimum conditions, the quality of the final product will be further improved.
Figure 2. Hydrocyclone test circuit used for both types of hydrocyclone. The sampler collects simultaneous samples of both the overflow (clean product) and the underflow (reject product).
Figure 3. Schematic of the laboratory-scale MTU flotation column used in the combined cyclone/column flotation experiments. The column diameter is 3", and it is 6' tall. A larger, pilot-scale unit of the same design has also been constructed and tested, showing that this column design can be scaled up readily.
Figure 4. Basic flow diagram for combined cyclone/column flotation processing.

RESULTS AND DISCUSSION

Cyclone Results:

The cyclone results shown in Table 2 show that the best results are obtained at the highest operating pressure (15 psi) and the lowest solids concentration in the feed slurry (5% solids). The conventional cyclone results with a 1/2" diameter apex are not greatly inferior to the water-only cyclone, but the conventional cyclone was not able to process
slurries any more concentrated than 5% solids without plugging, and was very close to plugging with the 5% solids slurry at 15 psi. The water-only cyclone would therefore be preferred for mechanical reasons, even if the separation performance were somewhat inferior to that of the conventional cyclone.

Table 2: Comparison of water-only cycloning and conventional cycloning, over a range of operating pressures and slurry percent solids.

<table>
<thead>
<tr>
<th>Cyclone, and test conditions</th>
<th>Pressure (psi)</th>
<th>% Weight Recovery</th>
<th>% CaCO₃ in O'flow</th>
<th>% CaCO₃ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-Only Cyclone, 20.5% solids</td>
<td>7-13</td>
<td>90.9</td>
<td>5.1</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>93.0</td>
<td>3.8</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>92.7</td>
<td>4.0</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>92.7</td>
<td>4.2</td>
<td>26.0</td>
</tr>
<tr>
<td>Water-Only Cyclone, 12.6% solids</td>
<td>15</td>
<td>88.0</td>
<td>3.3</td>
<td>42.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>89.2</td>
<td>3.3</td>
<td>40.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>90.1</td>
<td>3.5</td>
<td>37.0</td>
</tr>
<tr>
<td>Conventional Cyclone, 0.5&quot; Spigot 5.0% solids</td>
<td>15</td>
<td>94.2</td>
<td>2.7</td>
<td>28.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>83.7</td>
<td>2.7</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>81.4</td>
<td>3.0</td>
<td>50.4</td>
</tr>
<tr>
<td>Conventional Cyclone, 0.625&quot; Spigot 5.0% solids</td>
<td>15</td>
<td>58.9</td>
<td>3.0</td>
<td>63.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>62.2</td>
<td>3.0</td>
<td>61.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>64.9</td>
<td>2.9</td>
<td>60.2</td>
</tr>
</tbody>
</table>

The overflow and underflow products for comparable tests with the conventional and water-only cyclones were divided into size fractions by wet-screening, and each size fraction was chemically analyzed to determine how the performance of each type of cyclone varied with size. The results are given in Table 3, and show that while the conventional cyclone removed a much larger percentage of the coarser particles than did the water-only cyclone, both types of cyclone removed about the
same proportion of the limestone. The water-only cyclone is therefore producing a more selective separation of the limestone. The graphs shown in Figures 5 and 6 show this more clearly.

Table 3: Weight and Limestone Removals for individual size fractions, at 10 psi feed pressure and 5% solids, for both the water-only cyclone and the conventional sizing cyclone (0.5" spigot)

<table>
<thead>
<tr>
<th>Particle Size (micrometers)</th>
<th>% of weight of material in a given size fraction to underflow</th>
<th>% of CaCO₃ in size fraction to underflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water-only cyclone</td>
<td>Sizing Cyclone</td>
</tr>
<tr>
<td>+104</td>
<td>49.98</td>
<td>97.21</td>
</tr>
<tr>
<td>104x74</td>
<td>12.34</td>
<td>40.49</td>
</tr>
<tr>
<td>74x52</td>
<td>3.78</td>
<td>14.01</td>
</tr>
<tr>
<td>52x37</td>
<td>5.64</td>
<td>4.40</td>
</tr>
<tr>
<td>37x25</td>
<td>4.89</td>
<td>3.58</td>
</tr>
<tr>
<td>-25</td>
<td>3.29</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Flotation Results:

The results of an initial multi-stage flotation experiment are given in Figure 7. This test was carried out to determine three things: 1. how much of the limestone can be removed using no reagents other than a frother, with only its own native hydrophobicity to carry it into the froth; 2. how much of the limestone-poor material reaching the froth was truly hydrophobic; and 3. could collectors such as oleic acid, either alone or in combination with oils such as #2 fuel oil, significantly increase the removal of limestone and other impurities by flotation.

Figure 7 shows that flotation without a collecting reagent could remove a significant amount of the limestone and associated impurities in a single stage of flotation, but that the froth contained a considerable amount of gypsum and calcium sulfite (the quantity of both compounds was combined, and they are reported together, as gypsum). By refloating the froth, it was shown that much of the gypsum in the first-stage
Figure 5. Separation results using the conventional cyclone with a 1/2" spigot diameter. The "partition coefficient" is the percentage of material in each size fraction that is removed in the reject (underflow) stream. These curves show that at each size, the particles rich in limestone are more likely to report to the reject than the other particles are. The area between the limestone and the total weight curves is a measure of the selectivity of the separation.

Froth was not truly hydrophobic, and had only floated by entrainment in the water carried into the froth.

Adding oleic acid to the sinks product from the first stage and refloating resulted in the removal of most of the remaining limestone, leaving a product that contained only 2.8% limestone. However, this also resulted in the flotation of much of the gypsum, so the final yield of clean product was only 27.7% of the starting weight.

Since using oleic acid did greatly improve the limestone removal, further tests were carried out to attempt to optimize the oleic acid addition so that good limestone removal could be achieved with a high yield of gypsum in the sink product. This was done by reducing the quantity of oleic
Figure 6. Separation results using the water-only cyclone to process a 5% solids scrubber-slag slurry. The separation between the partition curves for limestone and total weight is larger than for the conventional cyclone under the same conditions, showing that the water-only cyclone is a more selective separator in this application.

acid added in each test, and by using sodium silicate to modify the gypsum and calcium sulfite surfaces so that they would not be as likely to be made hydrophobic by the oleic acid.

The results of the flotation tests are given in Table 4, and show that sodium silicate, added alone, is a general depressant of all flotation. Addition of oleic acid produces some flotation in the presence of sodium silicate, but the selectivity is not noticeably greater than when the sludge is floated with no collectors and modifiers at all. Reducing the oleic acid dosage to very low levels is the most effective strategy, both because this gives the best separation, and because this will be the lowest-cost option in an industrial operation.
Figure 7. Multistage Flotation Results
Table 4: Single Stage Flotation Experiments. In these experiments, oleic acid was added as a 1% solution in #2 fuel oil, which made possible very low oleic acid dosages.

<table>
<thead>
<tr>
<th>Product</th>
<th>Sodium Silicate Kg/mt</th>
<th>Oleic Acid Kg/mt</th>
<th>% Weight</th>
<th>% Gypsum</th>
<th>% CaCO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Froth</td>
<td>8.0</td>
<td>0.0</td>
<td>0.0</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
<td>100.0</td>
<td>93.9</td>
</tr>
<tr>
<td>Froth</td>
<td>8.0</td>
<td>0.2</td>
<td>9.2</td>
<td>85.1</td>
<td>9.4</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
<td>90.8</td>
<td>94.6</td>
</tr>
<tr>
<td>Froth</td>
<td>0.8</td>
<td>0.2</td>
<td>65.4</td>
<td>94.0</td>
<td>5.7</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
<td>34.6</td>
<td>95.4</td>
</tr>
<tr>
<td>Froth</td>
<td>0.0</td>
<td>0.1</td>
<td>85.9</td>
<td>93.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
<td>14.1</td>
<td>92.0</td>
</tr>
<tr>
<td>Froth</td>
<td>0.0</td>
<td>0.02</td>
<td>30.4</td>
<td>90.4</td>
<td>8.2</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
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<td>69.6</td>
<td>95.0</td>
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<tr>
<td>Froth</td>
<td>0.0</td>
<td>0.002</td>
<td>29.2</td>
<td>90.1</td>
<td>9.1</td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
<td>70.8</td>
<td>95.7</td>
</tr>
</tbody>
</table>

Combined Water-Only Cyclone/Column Flotation Results:

The results of re-floating the clean product from the water-only cyclone with the MTU flotation column are given in Table 5. These results show that the highly-selective flotation column does an excellent job of removing the limestone which remains after cyclone treatment, producing a lower limestone content than could be achieved with either the cyclone or conventional flotation alone. At 2.2% limestone, the final column product is of comparable purity to high-grade natural limestone. Further improvements in both yield and product quality will be achievable by optimizing both the cyclone and column operating conditions.
Table 5: Combined Water-Only Cyclone/Column Flotation Results, floating with frother only (no collector or modifiers)

<table>
<thead>
<tr>
<th>Product</th>
<th>% Wt</th>
<th>%CaCO₃</th>
<th>Cumulative %CaCO₃ Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed to Process</td>
<td>100.0</td>
<td>5.6</td>
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</tr>
<tr>
<td>Cyclone Overflow</td>
<td>90.9</td>
<td>5.1</td>
<td>17.2</td>
</tr>
<tr>
<td>2 minute froth</td>
<td>3.59</td>
<td>14.2</td>
<td>26.3</td>
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<tr>
<td>3 minute froth</td>
<td>6.81</td>
<td>17.6</td>
<td>47.7</td>
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<tr>
<td>5 minute froth</td>
<td>6.29</td>
<td>12.2</td>
<td>61.4</td>
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<tr>
<td>9 minute froth</td>
<td>1.58</td>
<td>8.9</td>
<td>63.9</td>
</tr>
<tr>
<td>holdup</td>
<td>12.95</td>
<td>5.7</td>
<td>77.1</td>
</tr>
<tr>
<td>Sink product</td>
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<td>2.2</td>
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Conclusions

Froth flotation, with frother alone or with small amounts of oleic acid as collector, is capable of removing the bulk of the fine limestone from scrubber sludge, as well as other hydrophobic impurities such as soot.

Water-Only cycloning removes approximately 30% of the limestone from scrubber sludge, while recovering approximately 90% of the weight to the clean product.

The conventional cyclone is inferior to the water-only cyclone for this application, due both to choking problems with a small spigot, and to its lesser ability to separate the limestone impurity from the sludge.

Cycloning and froth flotation are highly complimentary processes, with the cyclone removing the coarser impurities while the flotation removes the finer impurities. Using a combination of water-only cycloning and column flotation, a product containing only 2.2% limestone at 59.7% weight recovery could be produced, as compared to best results of 3.3% limestone at 88% recovery for the cyclone alone, and 2.8% limestone at 27.7% recovery for flotation alone.