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EXECUTIVE SUMMARY

Objectives

This research was focused on evaluating hydrated cement sorbents in the U. C. pilot spray dryer. The main goal of this work was to determine the hydration conditions resulting in reactive hydrated cement sorbents. Hydration of cement was achieved by stirring or by grinding in a ball mill at either room temperature or elevated temperatures. Also, the effects of several additives were studied. Additives investigated include calcium chloride, natural diatomite, calcined diatomaceous earth, and fumed silica. The performance of these sorbents was compared with conventional slaked lime. Further, the specific surface area and pore volume of the dried SDA sorbents were measured and compared to reactivity. Bench-scale tests were performed to obtain a more detailed picture of the development of the aforementioned physical properties as a function of hydration time.

Conclusions

Over 95% SO₂ removal of a simulated high sulfur flue gas was achieved for hydrated cement sorbents produced under certain conditions and used in the pilot spray dryer at approach to saturation temperatures of ~11 ° C. Typically, hydrated cement sorbents more reactive than slaked lime were produced, but their reactivity was found to be a function of their preparation method. Grinding the material in a ball mill at room temperature with no additives resulted in the most reactive sorbents for the entire study.

Only the tests in which the cement sorbent was hydrated in a ball mill at a temperature of 70°C and with calcium chloride additive at room temperature resulted in cement sorbents that exhibited an increase in uptake over cement sorbents hydrated for the same amount of time at room temperature without additives. Although none of the elevated temperature or additive tests served to improve the reactivity of the enhanced cement sorbents beyond the maximum reactivity achieved by ball milling at room temperature without additives, all of them were at least as reactive as slaked lime. These results indicate that hydrated cement has the potential to be a very efficient and cost effective flue gas desulfurization sorbent in spray drying applications.

The baseline calcium hydroxide and cement results were used to estimate sorbent cost effectiveness based on the cost of the reagent. Calculations indicated a cost of about \$80/ton of SO₂ removed for quicklime, and a cost of \$70/ton SO₂ for the cement sorbents. This corresponds to a savings of \$10/ton of SO₂ removed, or 12.5 percent. As a further example, actual coal fired boiler operating data was used to calculate an annual savings in reagent cost of over \$600,000. Clearly, there is potential for significant cost savings in operating a spray drying system using hydrated cement in place of the conventional slaked lime.

Future Objectives

Since reactivity is most probably a complex function of physical and compositional parameters, future studies should include an investigation into the relationship between the composition of the hydration product and reactivity. If the work is involved in evaluating the use of this sorbent in dry FGD systems, such as duct

injection, the method of drying should be included as an important parameter to be studied.

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1.0 INTRODUCTION

Sulfur dioxide (SO_2) is a colorless gas with an irritating pungent odor, and is detectable by taste at levels of 0.3 to 1 ppm¹. Exposure to this pollutant at levels on the order of 1 ppm can lead to eye irritation and constriction of the airways in the respiratory tract. SO_2 is highly soluble in water, forming sulfuric acid upon absorption in the airway. Swelling of the airway and stimulated mucus secretion contributes to constriction. In addition to human health effects, gaseous SO_2 disrupts photosynthesis and can lead to plant damage or death. As a secondary result of this pollutant, acidic deposition can lead to the damage of materials such as paint, masonry, electrical contacts, and textiles. Acid deposition also results in the acidification of lakes and other surface waters, which poses a serious threat to aquatic animal and plant life.

High emissions of SO_2 to the atmosphere have long been associated with the burning of coal containing large amounts of sulfurous compounds, such as the coal mined in the northeastern and parts of the Midwestern portions of the United States. Therefore, many methods of flue gas desulfurization (FGD) have been investigated. Wet lime or limestone FGD units represent the majority of installed systems, treating about 65 percent of the coal combusted flue gas in the U.S. as of 1990². This is a proven technology and is currently cost-effective as compared to other techniques. Problems with wet systems include the production of large amounts of wet sludge that must be handled and disposed, and operational problems such as scaling and plugging. Other FGD methods include dry injection and spray drying absorption (SDA). Spray drying with lime is the only other

significant FGD technology, treating nearly 9 percent of the coal combusted flue gas in 1990.

Other methods of reducing SO₂ emissions from the combustion of flue gas include methods of cleaning the coal prior to combustion and switching from high-sulfur eastern coal to low sulfur western coal. However, coal switching can have a devastating effect on a local economy. In Ohio, for example, the coal industry accounts for more than \$950 million and employs nearly 6,200 people³. Coal combustion accounts for 90 percent of the electricity generated in Ohio, which has an estimated 200-year supply of coal based on current reserves and rate of use.

Spray drying absorption, or SDA, is a proven flue gas desulfurization (FGD) technology for the combustion of low sulfur coal (less than 2% by weight). The first full-scale utility spray drying unit was operational in 1980, and as of 1990 there were 17 full-scale SDA's treating over of 6000 MW of coal combusted flue gas in the U.S.⁴ These units have been primarily designed for low sulfur western subbituminous and lignite coal applications and have demonstrated the ability to achieve over 90 percent SO₂ removal efficiency. However, high removal efficiencies when treating flue gas from the combustion of medium to high sulfur coal (2% - 3.2% or greater) requires excessive reagent and leads to greater cost.^{5,6} The motivation for developing this technology for medium to high sulfur coal applications is that SDA has many benefits over conventional limestone wet scrubbing, including⁷:

- Dry and insoluble waste product
- Smaller space requirements resulting in an easier retrofit

- Use of mild steel in construction
- Average capital cost savings of 65 dollars per kw

A simple schematic of a spray drying chamber highlighting the important operating parameters is presented in Figure 1-1. The SDA process typically involves the

Figure 1-1. General SDA Schematic

atomization of a hydrated lime ($\text{Ca}(\text{OH})_2$) feed as it enters a drying chamber into which gas is drawn at around 300°F. SO_2 in the flue gas is absorbed into the liquid droplets and reacts with dissolved calcium ions to form calcium sulfite and calcium sulfate salts, which deposit on unreacted reagent. Drying of the atomized slurry is ensured by

operating the chamber so that the temperature of the exiting flue gas is above the dew point at an approach to saturation temperature, which is the difference between the outlet flue gas temperature and the dew point. Gas residence time in SDA's range from 10 to 15 seconds, after which the dried product is conveyed pneumatically from the spray drying chamber to a particulate collection device. Fabric filters are preferred over electrostatic precipitators for particulate collection because the dried product collected on the filter material also reacts with the flue gas and can account for up to 20 percent of the overall SO₂ removal efficiency⁸.

Additional important parameters associated with SDA include stoichiometric ratio, SO₂ removal efficiency, calcium utilization, and SO₂ uptake. Stoichiometric ratio is the molar ratio of calcium to sulfur at the entrance of the spray drying chamber, and removal efficiency is simply the ratio of SO₂ removed to that entering the chamber. calcium utilization is calculated as the removal efficiency divided by stoichiometric ratio. SO₂ uptake, expressed as mmol of SO₂ removed per gram of calcium, is calculated as calcium utilization divided by the molecular weight of calcium.

Limitations of SDA technology for high sulfur coal applications are associated with the formation of an inert product layer on unreacted sorbent. This process hinders the dissolution of calcium ions and decreases the utilization of the sorbent. Any additive that either increases the solubility of calcium in solution or reacts with hydrated lime to form products that are more reactive with SO₂ has the potential to increase the effectiveness of calcium-based SDA sorbents for treating high sulfur flue gas. Fly ash has been found to be one additive that, when hydrated with lime, has the potential to form

a product that is more reactive with SO_2 .

1.1 Fly Ash/Hydrated Lime Sorbents

Most full-scale spray drying units recycle a portion of their waste solids back to the feed slurry. Operating with waste recycle results in higher calcium utilization because this permits partially reacted sorbent to more fully react with the flue gas. Further, recycling fly ash together with spent solids results in better sorbent utilization than recycle of spray dryer waste alone⁹. This phenomenon promoted interest in using fly ash as an additive for calcium-based FGD sorbents. Fly ash has shown promise as a calcium-based sorbent additive in several studies on dry sorbent injection into a humidified gas stream¹⁰⁻¹⁴ and in a few bench-scale spray drying simulations^{15,16}. In a series of fly ash/hydrated lime sorbent studies conducted with the U.C. pilot spray dryer a significant increase in calcium utilization was experienced for specific fly ash/slaked lime hydration conditions¹⁷.

The increase in calcium utilization associated with the fly ash/hydrated lime sorbents has been linked to the formation of calcium silicate hydrate (C-S-H), which is a product of the pozzolanic reactions that occur due to the alumino-silica content of fly ash in the presence of calcium.^{11,16,18,19} One researcher determined the amount of C-S-H formation for different slurry preparation methods¹⁶. The results of that study indicate that the formation of the reactive product is very sensitive to hydration conditions and the type of fly ash used as different products were formed under similar hydration conditions. This complexity was also experienced in a pilot spray dryer study in which the effects of

various hydration procedures were researched²⁰.

These problems may be associated with variability in fly ash composition, even in fly ash from the same coal source. Also, fly ash contains a large amount of inert material which adds unreactive solids to the feed slurry. Consequently, it has been proposed that highly reactive sorbents containing C-S-H could be produced through an alternative means by hydrating type I Portland cement, which has a uniform composition²¹.

1.2 Research Objective

This research was focused on evaluating hydrated cement sorbents in the U. C. pilot spray dryer. This work follows on that of other Ohio Coal Development Office funded projects^{16, 21, 22} where substantial analytical and experimental efforts have shown that type 1 Portland cement could have superior SO₂ uptake properties. The main goal of this work was to determine the hydration conditions resulting in reactive hydrated cement sorbents. Hydration of cement was achieved by stirring or by grinding in a ball mill at either room temperature or elevated temperatures. Also, the effects of several additives were studied. Additives investigated include calcium chloride, natural diatomite, calcined diatomaceous earth, and fumed silica. The performance of these sorbents was compared with conventional slaked lime. Further, the specific surface area and pore volume of the dried SDA sorbents were measured and compared to reactivity. Bench-scale tests were performed to obtain a more detailed picture of the development of the aforementioned physical properties as a function of hydration time.

2.0 EXPERIMENTAL METHOD

A detailed description of the experimental methods and materials used is presented in this chapter. A summary of equipment utilized in completing this project is presented in Table 2-1.

2.1 Overview of the UC Pilot Spray Drying System

A flow diagram of the pilot plant is presented in Figure 2-1. The system can be grouped into three distinct sections: (1) the spray drying equipment connected by the thick solid lines in Figure 2-1; (2) the parameter measurement and data acquisition system connected by the dashed lines; and (3) the slurry preparation system connected by the thin solid lines.

2.1.1 Spray Drying Equipment

The spray drying chamber consists of a cylindrical section with a diameter of 0.91 meters (3 feet) and a conical constriction at the bottom. The overall height of the unit is 2.13 meters (7 feet) with the conical section comprising 1.22 meters (4 feet) of that length. Air enters the chamber at the top of the cylinder, and exits at the bottom of the conical section.

The maximum air flow capacity of the system is 425 standard cubic meters per hour (250 standard cubic feet per minute). Air flow rate was monitored using a differential pressure gauge which measured the pressure drop across an orifice. The

orifice meter was calibrated following EPA Methods 1 and 2²³.

The inlet heater has a 10 kw capacity and is capable of heating the ambient air drawn through it to 150°C. A kerosene blower was used to boost the inlet temperatures to 160°C. Simulated sulfur-laden flue gas was created by injecting SO₂ just upstream of the spray drying chamber. The SO₂ was generated by heating a gauged cylinder of anhydrous liquid SO₂. During a test, slight adjustments to the gauge were made to keep the concentration at the desired value.

A two-fluid atomizer (Spray Systems Company, #SUE28A) with external mixing was used to atomize the feed slurry as it was injected into the drying chamber. This type of atomizer works by shearing the liquid with a crosscurrent flow of compressed air (483 KPa, 20 mm o.d. line) after the slurry is forced through a central orifice. Slurry feed rates were measured by an electromagnetic flow meter and had typical values around 0.3 liters per minute, depending on the desired approach to saturation temperature. The flow meter was calibrated periodically using a stop watch and graduated cylinder to obtain a linear conversion algorithm.

The particulate control device located downstream of the spray drying chamber consists of a single compartment self-cleaning pulse-jet fabric filter with 42 individual bags providing a total surface area of about 9 square meters (nearly 100 square feet). The pressure drop across the fabric filter is measured by a differential pressure gage. The system's automated cleaning system was bypassed so that the bags could be cleaned at the operators discretion to maintain a constant pressure drop across the device for all tests.

2.1.2 Parameter Measurement and Data Acquisition System

SO₂ concentration and flue gas temperature were monitored continuously via non-dispersive infrared analyzers (Horiba, PIR 2000) and thermocouples, respectively. Ports for these devices are located at the inlet and outlet of the spray dryer, and at the outlet of the baghouse. The SO₂ analyzers were calibrated before each test using a certified calibration gas with a concentration of 2800 parts per million (ppm) SO₂. Gas flow through the monitors was kept constant between 1 and 2 L/min using rotometers (Brooks, 1355-01F1AAG) that were calibrated using a bubble meter. Background air was used as the zero gas. Data was collected on a remote personal computer and used for subsequent removal efficiency and SO₂ uptake calculations. Calculation procedures are outlined in detail in Appendix A.

Other parameters that were required for each test included the ambient air dry and wet bulb temperatures. These were obtained using a mercury thermometer. Wet bulb temperature was measured by encasing the bulb of the thermometer in a saturated sponge and placing it in a high velocity air stream at the entrance to an exhaust fan. These parameters were used to determine the saturation temperature of the simulated flue gas using an appropriate psychometric chart. The saturation temperature of the simulated flue gas was typically on the order of 40°C (100°F).

2.1.3 Slurry Preparation System

The slurry preparation system includes two 113.6 liter (30 gallon) HDPE tanks with one used for lime slaking and the other for the feed slurry. Liquids in each tank

were mixed with a 0.186 KW (1/4 hp) mixer. Liquids were transported to various stages of the system by a membrane pump. As a new improvement for the work performed in completing this thesis, a screw-type Moyno pump replaced the membrane pump for feeding the slurry to the spray drying chamber. The screw-type pump provides a steady flow as compared to the pulsing flow provided by the membrane pump.

Heated slurries agitated by stirring were prepared in a 75.7 liter (20 gallon) stainless steel kettle, which is outfitted with a steam jacket. The desired temperature of the slurry in the kettle was maintained by controlling steam flow using a steam solenoid actuated by a temperature controller. Slurry was agitated in the cooker with a pneumatic mixer.

The ball mill consisted of a drum roller (U.S. Stoneware) and a fabricated 113.6 liter (30 gallon) drum with a flanged lid. The drum was loaded with about 60 Kg (130 pounds) of 0.635 cm (1/4") diameter inert alumina oxide spheres. The rotational speed of the ball mill was kept between 40 and 50 revolutions per minute.

A steam-drum, shown schematically in Figure 2-2, was constructed for hydration at elevated temperature. The steam-drum is comprised of an inner drum which can slide into an outer drum. Both drums are fitted with flanged lids. The desired amounts of unhydrated components, the grinding media, and 15 gallons of water were introduced into the inner drum which was sealed. A gap between the two drums is maintained so that steam may pass through a shaft mounted to a flat bearing located in the center of the outer lid, pass around the inner drum, and exit through a similar bearing arrangement in the center of the bottom of the outer drum. The temperature of the slurry in the inner drum

was measured periodically using a thermocouple probe that can be inserted through a metal tube with a screw-on cap. The temperature port is welded to the lid of the inner drum and protrudes through a hole in the outer lid.

Calcium hydroxide slurry used in baseline testing was prepared by hydrating quicklime at a weight ratio of 4:1 water to CaO in the lime slaking tank. The quicklime (Dravo Lime Company 1/8" x 0 ") had a typical inert content of 15 weight percent with the balance CaO. The slurry was continuously recycled during hydration so that most of the grit could be removed in the cyclone. The hydration, which is highly exothermic, was continued until all solids were suspended in solution and the slurry returned to approximately room temperature. The slurry was then transported to the feed tank and diluted to a desirable solids content, typically between 10 and 15 percent, for baseline slaked lime tests. One baseline test was also performed where the quicklime was slaked, diluted, and subsequently transported to the ball mill for grinding at room temperature for three days prior to injection into the pilot spray dryer.

The initial cement-to-water ratio for all but one the hydrated cement tests was 10:1. Unlike the case for the baseline tests, no measures had to be taken during hydration to remove a grit component. Several methods of sorbent preparation were investigated. Hydrated cement sorbents were prepared by stirring in the feed tank at room temperature for a specific period of time, stirring at elevated temperatures in the cooker, and hydrating at room and elevated temperatures in the ball mill. Upon reaching the desired hydration time, hydrated cement slurries were immediately transferred to the feed tank for injection into the spray drying chamber.

2.1.4 Spray Dryer Operation

The focus of this work was on evaluating the effectiveness of cement sorbents prepared under varying hydration conditions. Therefore, the spray drying equipment had to be operated under the same conditions for all tests to maintain the sorbent preparation method as the only variable.

Inlet flue gas temperature was held at 160°C, and the inlet flue gas SO₂ concentration was kept between 2450 ppm to 2550 ppm to simulate high sulfur flue gas. The pressure drop across the baghouse was maintained at 2 mmHg (1.0 inches wg.). The flue gas volumetric flow rate was 320 standard cubic meters per hour (190 standard cubic feet per minute), corresponding to a gas residence time in the spray drying chamber of 9 seconds. The system was operated for a period of time sufficient to ensure steady-state conditions at approach to saturation temperatures of 16.7°C and 11.1°C (30 and 20°F). Each test provided one data point at each approach to saturation temperature.

2.2 Surface Area, Porosity and Calcium Content Determination

Pilot-scale samples were prepared for analysis by drying a small aliquot of slurry drawn from the feed tank in a desiccator at about 90°C under a slight vacuum (about -5" w.g.). The dried cake was then crushed to a fine powder and stored under nitrogen in sealed glass sample bottles.

The specific surface area and internal pore volume of the dried sorbents were measured using a single point Quantachrome Monosorb BET (MS-12) machine using nitrogen intrusion and a Quantachrome Autoscan (SP-10LV) high pressure (60 ksi)

mercury intrusion device, respectively. This data was used to investigate the development of surface area and internal pore volume as a function of sorbent preparation methods. The range of radii used for determining internal pore volume was between 5000 and 18 Å. The lower end of the range corresponds to the maximum pressure of the porosimeter, 60 ksi, and the upper end of the range was chosen to ensure that no interstitial volume would be included in the determination.

The calcium content of the dried sorbents was determined by following a wet-chemistry procedure outlined in ASTM C114. The method involved the removal of silicon, aluminum, titanium, phosphorus, and manganese from a 0.5 g sample of cement sorbent through a series of precipitations and filtrations. Calcium was then precipitated as an oxalate. After filtering, the oxalate was redissolved and titrated with a standardized solution of potassium permanganate (KMnO_4) to determine the calcium content as calcium oxide (CaO).

2.3 Bench-Scale Hydration of Cement Sorbents

The impetus for performing bench-scale tests was to develop a more complete picture of the time-dependent physical parameter development than could be achieved from the pilot-scale testing. Bench-scale tests were conducted using a small jar roller (U.S. Stoneware). Alumina oxide grinding spheres were placed in a 1 liter glass jar sealed with a stopper. The weight ratio of spheres-to-water, ratios of unhydrated components, as well as the rotational speed of the bench scale unit matched that of the pilot-scale ball mill. Samples were drawn periodically and dried in the desiccator under

the same conditions described above. The dried samples were then analyzed to determine surface area and pore volume development as a function of hydration time. Hydration at elevated temperatures was achieved using a low-power portable blower (Perfection MiniPro 1250). The effects of additives were also evaluated. The conditions for each bench-scale test were repeated once so that all of the bench-scale results represent two separate tests.

2.4 Properties of Quicklime, Cement, and Additives

Table 2-2 presents a typical analysis of the quicklime used for the baseline tests; and Table 2-3 presents the source, and measured surface area and intrusion volume of the raw materials used for the hydrated cement studies. Additives investigated included fumed silica, two forms of diatomaceous earth, and calcium chloride.

Silica fume is a by-product in the manufacture of ferro-silicon and silicon metal in an electric arc furnace. The condensed fume is spherical and highly reactive with an average diameter of $0.1\mu\text{m}^{24}$. Natural diatomaceous earth, or diatomite, consists of hydrated amorphous silica from the shells of microscopic aquatic algae. Infusorial earth is produced by calcining diatomite. Both fumed silica and diatomaceous earth provide sources of amorphous silica. The calcined product of diatomite may contain some crystalline silica as well as some metallic oxides. As shown in previous work, adding sources of amorphous silica should increase calcium utilization as compared to sorbents hydrated without the addition of amorphous silica^{16,22}. One researcher suggests that infusorial earth may not be as reactive as the natural diatomite because the calcining

process produces material containing crystalline silica²⁵.

Calcium chloride is a well-known accelerator for cement hydration. An addition of 2 percent calcium chloride by weight of cement is equivalent to an increase in hydration temperature of 12°C²⁶. Although the mechanism of acceleration is not well-known, the additive retards the hydration of tricalcium aluminate and increases the hydration rate of the silicates²⁴. Calcium chloride should also result in increased surface area and porosity of the cement paste. As an additional benefit, calcium chloride addition to hydrated lime slurries is known to improve calcium utilization in spray drying applications²⁷.

Table 2-1. Equipment Summary

Equipment	Manufacturer
Spray Drying Chamber	In-House
Baghouse	American Air Filter
Inlet Heating Elements	Watlow Co.
Exhaust Fan	American Manufacturing Company
Nozzle	Spraying Systems Company
Electromagnetic Flow Meter	Fisher-Porter
SO ₂ Analyzers	Horiba
Data Acquisition System	Strawberry Tree, Inc.
Drum Roller	U.S. Stoneware
Steam Drum	In-House
Cooker	In-House
HDPE Tanks	Nalgene
Membrane Pump	Aro Corporation
Screw-Type Pump	Moyno
Jar Roller	U.S. Stoneware
Surface Area Analyzer	Quantachrome
Porosimeter	Quantachrome

Table 2-2. Typical Quicklime Analysis (Dravo Lime - Black River, KY Plant)

Mineral	% Ignition
Calcium Oxide	90.0 (85.0 as available CaO)
Magnesium Oxide	2.5
Silicon Dioxide	2.8
Ferric Oxide	0.5
Aluminum Oxide	1.0
Sulfur	0.05
Phosphorus	0.004
Carbon Dioxide	2.1
Water	0.4

Table 2-3. Raw Materials

Material	Source	Surface Area (m²/g)	Intrusion Volume 0.5 to 0.0018 μm (cc/g)
Type I Portland Cement	Quikrete	1.4	0.10
Dihydrous Calcium Chloride	Fisher Scientific	0.6	0.09
Infusorial Earth	Fisher Scientific	0.9	0.18
Natural Diatomite	Celite Corp.	19.0	1.67
Fumed Silica (SiO ₂ gel powder)	Johnson-Mathey	380	0.89

Figure 2-1. U. C. Pilot Spray Dryer Flow Diagram

1" = 6"

Figure 2-2. Steam Drum

3.0 RESULTS AND DISCUSSION

Table 3-1 provides a summary of the hydration parameters for the complete matrix of pilot-scale testing performed for this study. As shown in the table, all of the cement tests except one were performed with the initial water-to-cement weight ratio of 10:1. Although that parameter was held constant for all but one test, several other parameters were varied to look at the effect of hydration time, hydration temperature, and method of mixing on the resulting reactivity of the sorbent. Unless otherwise expressed, the results presented in this section are for data obtained at an approach to saturation temperature of 11 °C (20 °F). The complete data set, including data obtained at approach to saturation temperatures of 16.7 °C is presented in Appendix C.

The location of the SO₂ sample line at the exit of the spray drying chamber resulted in frequent plugging problems. Consequently, there is limited data for removal efficiency across the spray drying chamber alone and the data presented here represents the integrated desulfurization across both the drying chamber and the baghouse. Since the spray drying system was operated under the same conditions for all tests, overall removal efficiency and uptake can be used to compare the effectiveness of different sorbents.

3.1 Slaked Lime Tests

Extensive spray dryer testing was performed to determine the removal efficiency and SO₂ uptake of the pilot-scale system operating with the typical reagent, hydrated

calcium hydroxide. Results of these baseline slaked lime tests have been presented in Figures 3-1 and 3-2. For these tests quicklime was slaked, diluted, and then injected into the spray drying system. The theoretical removal line in Figure 3-1 was generated assuming that one mole of calcium can react to remove one mole of SO_2 . Each point on Figures 3-1 and 3-2 corresponds to a separate pilot test for each approach to saturation temperature.

These results indicate a maximum removal efficiency of nearly 70 percent for stoichiometric ratios between 1.6 and 1.8 at an approach to saturation temperature of 16.7°C . The removal efficiency at a stoichiometric ratio of 0.8 is 56 percent, corresponding to an uptake of about 16 mmol SO_2 per gram of calcium. The limited data obtained at an approach to saturation of 11.1°C indicate that the efficiency of the slaked lime slurry did not improve by decreasing the approach to saturation temperature from 16.7°C to 11.1°C . The curve in Figure 3-1 is simply a second degree polynomial fit and the line in Figure 3-2 represents a straight line regression of the data for an approach to saturation of 16.7°C . These lines are added here for clarity and are not intended to represent the trend of the data beyond the experimental range of stoichiometric ratios. They appear in subsequent graphs as a representation of the baseline case for comparison with results from the hydrated cement tests.

3.1.1 Surface Area and Intrusion Volume Results for the Calcium Hydroxide Sorbents

The results of surface area and intrusion volume measurements of dried calcium hydroxide slurries are presented in Table 3-2. The average surface area of the baseline

reagent was on the order of 30 m²/g, and the average intrusion volume between 18 and 5000 Å was 1 cc/g.

3.1.2 Effect of Ball Milling Ca(OH)₂ Slurry

Slaked lime was ball milled for 3 days prior to spray dryer testing to determine the effect of grinding on the reactivity of the resulting lime sorbent. The removal efficiency and uptake results are presented in Figures 3-1 and 3-2. Grinding the material did appear to have a slight benefit. At 16.7°C approach to saturation the removal efficiency was about 64 percent, corresponding to an uptake of 20 mmol SO₂/g Ca. Unlike the other baseline data, decreasing the approach to saturation to 11°C did seem to provide additional benefit in that the removal efficiency increased by approximately 1/3 to 80 percent. These results may be related to the fact that surface area and intrusion volume also slightly increased to values of 35.5 m²/g and 1.18 cc/g, respectively. The surface area and pore volume results for all of the baseline work is summarized in Table 3-2.

3.2 Identification of the Most Effective Mixing Method for Cement Hydration

Initially, a series of tests were performed to compare the effects of milling and stirring during hydration of cement. As in the study referred to above^{16,22,28}, milling resulted in a more reactive sorbent. Figure 3-3 illustrates this result. All slurries were prepared at a 10:1 water-to-cement weight ratio and each point represents overall uptake for a separate spray dryer test. As shown, stirring the cement slurry for 17 hours at room temperature produced an unreactive sorbent with an SO₂ uptake well below the baseline results. Stirring the cement slurry for 24 hours at an elevated temperature of 60°C,

followed by milling in the ball mill at room temperature for 18 hours produced a cement sorbent as reactive as the baseline. Milling the cement slurry for 3 days prior to testing, however, produced a sorbent that was more reactive than the baseline. Based on these results in conjunction with the results referenced above, milling was utilized as the method of mixing for the remainder of this work.

3.3 Room Temperature Hydration of Type I Cement

Table 3-3 presents the results of a series of tests to determine the optimum time of hydration for ball milling cement slurry at room temperature. This data is represented graphically in Figure 3-4. These results indicate that the optimum hydration time was 3 days, which corresponds to the results referenced above^{16,22,28}. Note that the baseline uptake (the dashed line in Figure 3-4) was conservatively placed at 20 mmol/g which represents the uptake of the slaked lime that was milled 3 days prior to testing.

The average maximum uptake at an approach to saturation of 11 °C was just under 32 mmol/g, with values above 25 mmol/g for hydration times between 2 and 4 days. Figures 3-5 and 3-6 show the average and point values along with the range of one standard deviation for the data. The relative standard deviation values shown in Table 3-3 are simply the ratio of standard deviation to the mean, and serve as another indication of the spread of the data. The standard deviation for all values is within 10 percent of the mean except for the value corresponding to material that had been hydrated for 3 days and run at 11.1 °C approach to saturation. That data had a relative standard deviation of 13.6 percent. The large spread in that case is related to the fact that, for one of the tests run under those conditions, no increase in uptake was experienced as the approach to

saturation was decreased. This result is shown in Figure 3-4.

Removal efficiency for the most effective cement sorbent is shown in Figure 3-7. The best sorbent yielded a maximum overall removal efficiency of 0.88 at an approach to saturation of 11 °C and a stoichiometric ratio of 0.82; and an overall removal efficiency of 0.79 at an approach to saturation of 16.7 °C and a stoichiometric ratio of 0.75. In comparison, the removal efficiency achieved for the calcium hydroxide slurry was 0.55 at a stoichiometric ratio of 0.75 and approach to saturation of 16.7 °C. That corresponds to nearly a 50 percent increase in removal efficiency for hydrated cement sorbent over the conventional hydrated lime sorbent. These results compare quite favorably with the baseline and indicate that hydrated cement has the potential to be a more effective FGD agent for spray dryer applications than slaked lime.

3.3.1 Surface Area and Intrusion Volume Results for the Pilot-Scale Cement Sorbents

Figures 3-8 and 3-9 show the results of surface area and porosimetry analysis performed on dried samples of sorbents fed to the spray dryer. The surface area increased considerably from a value of around 1 m²/g for the cement clinker to values from 60 to 80 m²/g after 2 days of hydration. These values are over twice that for baseline Ca(OH)₂ slurry, as shown in Table 3-2. Therefore, larger surface area for the cement sorbent over slaked lime corresponds to an increase in effectiveness. (Note that surface area and porosity for time zero shown on the figures corresponds to a dried aliquot of cement slurry that had been stirred prior to injection into the spray dryer and not to unhydrated cement clinker.)

Evaluation of this data is difficult in that large variations in surface area for the same hydration conditions were observed. For example, material hydrated 3 days resulted in surface areas varying from around 60 m²/g to nearly 140 m²/g. One reason for this variation might be attributed to the presence of micropores, which can account for large amounts of internal surface area. Some of these tiny pores might be either destroyed or closed as the sample is dried, or the presence of micropores may be more pronounced in one representative sample than another. Because micropores can account for large amounts of surface area, one might expect a large difference in surface area between samples of slightly differing amounts of available micropores. Further, one might also expect this phenomenon to have a more pronounced effect on surface area as compared to intrusion volume due to the nature of the measurement method. Measuring surface area by nitrogen absorption has an order of magnitude lower limit for minimum accessible pore size than measurement of internal volume by mercury intrusion.

Figure 3-9 shows that internal pore volume is rapidly created and destroyed during the course of hydration. Maximum values for intrusion volume were between 1.4 and 1.6 cc/g, which correspond to values that are 40 to 60 percent larger than those for baseline sorbent, as shown in Table 3-2. Therefore, an increase in internal pore volume corresponds to an increase in sorbent effectiveness. The pore volume peaked at a hydration time of around 2 to 3 days, which corresponds roughly with time of hydration required for high sorbent utilization as shown in Figure 3-4. This phenomenon is discussed in more detail in section 3.3.3.

3.3.1.1 Comparison of Bench- and Pilot-Scale Results

Figures 3-10 and 3-11 show the surface area and porosimetry results of bench-scale ball milling at room temperature. The surface area results approached values on the order of $80 \text{ m}^2/\text{g}$, which is similar to results for the pilot-scale material. The shape and magnitude of the pore volume curve is very similar to the intrusion volume curve for the pilot-scale sorbents with peak values slightly higher, between 1.6 and 1.8 cc/g. Although the bench-scale results show the same general parameter development as for the pilot-scale results, this data also exhibits wide variation and is difficult to interpret.

3.3.2 Characterization of the Composition of the Cement Sorbents

Three samples of the material that was hydrated three days in the ball mill at room temperature were sent to Dr. Malcolm E. Kenney, Hurlbut Professor of Chemistry at Case Western Reserve University, for analysis. Two of the samples were of dried cement sorbent that had been hydrated 3 days in the ball mill at room temperature for two separate SDA tests. These two samples were of dried cement slurry that was collected before injection into the spray dryer. A third sample was of dry spent sorbent that had been hydrated for 3 days in the ball mill and collected from the fabric filters in the baghouse. The analysis, described previously, involved infrared spectroscopy and powder X-ray diffractometry as well as uptake determination in a sand bed reactor^{16,22,28}. The results of the analysis are reprinted in Table 3-4²⁹.

Based on previous results^{16,22,28}, the composition of the unreacted cement sorbents is consistent with that of a good cement sorbent. The composition of the spent cement sorbent is also consistent with what would be expected of a spent sorbent. In addition, the uptake values for the two unreacted sorbents are at the upper end of the range of a

well-made sorbent. These results compare favorably with the pilot-scale results presented above which indicate that hydrated cement prepared in this fashion results in effective SDA performance as compared to conventional slaked lime sorbent.

3.3.3 Relationship Between Reactivity and Physical Parameters

One goal of this study was to obtain some idea of how surface area and intrusion volume relate to reactivity. Qualitatively, it appears that pore volume may have a more dominant relationship with reactivity than surface area. It has been shown (Figure 3-9) that pore volume increases rapidly to some peak value and then decreases as hydration time increases, while surface area also increases rapidly in the initial stages of hydration and then increases at a slower rate as hydration proceeds. Similar to the relationship between pore volume and hydration time, SO_2 uptake increases to a peak value and then decreases as hydration time is increased. As stated previously, the peak intrusion volume occurred at a hydration time of 2 to 3 days, roughly corresponding with the hydration time required to produce the most reactive cement sorbent. In contrast, surface area slightly increases beyond the optimum hydration time as SO_2 uptake decreases.

To investigate this relationship further, uptake values for the complete set of tests in which cement was hydrated at room temperature in the ball mill was plotted as a function of both intrusion volume and surface area. These results are presented in Figures 3-12 and 3-13. Best fit lines were drawn through the data and the resulting coefficient of determination values (r^2) are shown to represent the relative degree of correlation between uptake and the particular physical parameter. The r^2 values for the correlation with intrusion volume, while not very high in either case, are higher than that for surface area.

No correlation was found to exist between uptake and surface area, as the r^2 values for both approach to saturation values are less than 0.5. This supports the idea that uptake may be more related to pore volume development than surface area.

3.3.4 Hydration at a Water-to-Cement Ratio of 8:1

One pilot-scale test was performed in which cement sorbent was hydrated in the ball mill at an initial ratio of 8:1 water-to-cement. The intent of this experiment was to run a spray dryer test at a higher stoichiometric ratio and compare the overall removal efficiency with values for cement sorbent hydrated in the ball mill at an initial water-to-cement ratio of 10:1. The results of the test are presented in Figure 3-14. At 16.7°C approach to saturation the removal efficiency was about 80 percent, which was not an improvement over tests run at lower stoichiometric ratios. However, 95 percent removal efficiency was achieved at 11.1°C approach to saturation, which is a significant improvement over results from tests run at lower stoichiometric ratios. An improvement in the utilization of the sorbent, however, was not witnessed in that the corresponding SO_2 uptake at 11.1°C was only about 17.7 mmol SO_2 /g Ca. The surface area and intrusion volume for this sorbent measured at 82.2 m^2/g and 1.71 cc/g, respectively. These values are similar to values for the cement sorbents hydrated for three days at an initial weight ratio of 10:1.

3.4 Cement Sorbents Hydrated at an Elevated Temperature and With Several Additives

Pilot-scale results for tests in which cement was hydrated at an elevated

temperature in the steam drum and at room temperature with several additives are presented in Table 3-5. All of the data in the table corresponds to an 11.1°C approach to saturation. The uptake results for this data are compared to uptake results for cement sorbents hydrated for the same time period in the ball mill at room temperature, as shown in Table 3-3 and Figure 3-4. In general, these results are somewhat disappointing. Although some of the hydration conditions led to cement sorbents that were more reactive for the same time of hydration, in all cases no improvement over the most effective hydrated cement sorbents prepared at room temperature with no additives was achieved. However, in all cases these sorbents performed at least as well as the conventional Ca(OH)_2 sorbent.

3.4.1 Cement Sorbents Hydrated at an Elevated Temperature in the Steam Drum

Cement was hydrated in the steam drum (Figure 3-2) at an elevated temperature of about 70°C (160°F). SDA results at an approach to saturation temperature of 11.1°C for hydration times of 3, 9, and 18 hours are presented in Table 3-5. The main objective of these tests was to produce a reactive sorbent in a shorter hydration time. No data for cement sorbents hydrated at room temperature in the ball mill without additives was obtained at these hydration times. However, approximate uptake values based on a linear trend of the data between 0 and 2 days of hydration, as shown in Figure 3-4, were compared with the cement sorbents hydrated at elevated an temperature. This comparison indicates a significant improvement over the cement sorbents hydrated for the same amount of time at room temperature in that uptake values were 70 - 75 percent higher for the material hydrated at 70°C. However, cement sorbents as reactive as the

most reactive sorbent prepared at room temperature were not produced. In comparison with the slaked lime results, the uptake results for these cement sorbents correspond to a 5 percent increase at 3 hours hydration, and a 28 percent increase at 18 hours hydration over the 20 mmol SO₂/g Ca results achieved with slaked lime.

3.4.1.1 Surface Area and Intrusion Volume Results for the Pilot- and Bench-Scale Cement Sorbents

The surface area and intrusion volume results are presented in Figures 3-15 and 3-16. In comparing these results with those in Figures 3-8 and 3-9, surface area appeared to develop more quickly than for the material hydrated at room temperature. Surface area increased to values on the order of 80 m²/g even after 3 hours of hydration. Material hydrated at room temperature did not reach surface areas that high until a hydration time of 2 to 3 days. These larger surface area values do correspond with greater uptake as compared to cement sorbent prepared at room temperature in the ball mill for the same hydration time. The large surface areas, however, do not correspond to uptake values as high as the most reactive sorbent prepared at room temperature. Intrusion volume also appeared to develop more quickly, reaching a value of 1.4 cc/g after 18 hours. As shown in Figure 3-9, the intrusion volume for the material hydrated at room temperature for 18 hours was about 1.0 cc/g. As apparent in Figure 3-16, the intrusion volume curve appears to be increasing to some peak value which may occur at a hydration time greater than 18 hours. Although the data indicates that the hydration time may have to be increased beyond 18 hours to produce a more reactive sorbent, the hydration time was not extended further in this study due to operational constraints. The steam drum was designed in such

a way that the pressure in the inner drum had to be released every 30 to 45 minutes, resulting in the fact that the drum could not be left unattended.

Bench-scale surface area and intrusion volume results for cement hydrated in the jar roller at about 60°C (140°F) are summarized in Figures 3-17 and 3-18. Unlike the pilot-scale material hydrated at 70°C, high surface area values of about 80 m²/g did not develop any quicker than for the material hydrated at room temperature as shown in Figure 3-10. Intrusion volume also did not develop more rapidly than bench scale cement sorbent hydrated at room temperature as shown in Figure 3-11. Similar to the cement hydrated at room temperature, the material milled at an elevated temperature reached a peak value of about 1.6 cc/g at about 2 days. The result that parameter development was not accelerated may have been due in part to the fact that the bench-scale slurry could only be heated to 60°C, while pilot-scale material was hydrated in the steam drum at about 70°C. The higher hydration temperature achieved in the steam drum may have increased the rate of development of the physical parameters as compared to both room and 60°C hydration temperatures.

3.4.2 Dihydrous Calcium Chloride Additive

Calcium chloride was added in hopes of accelerating hydration, thereby decreasing the time required to produce reactive sorbents. As shown in Table 3-5, the uptake value achieved after a hydration of only 24 hours was approximately 40 percent higher than that for the hydrated cement with no additives. However, a higher uptake value was not achieved by increasing the time of hydration to 2 days. Cement sorbent as reactive as the most reactive cement sorbent with no additives was not produced. The

results are somewhat promising in that a cement sorbent hydrated for 1 day with CaCl_2 achieved an uptake that was within 12 percent of the most reactive sorbent prepared without additives, which was hydrated for 3 days. Further, these results indicate a 40-45 percent improvement as compared to a slaked lime uptake of 20 mmol $\text{SO}_2/\text{g Ca}$.

3.4.2.1 Surface Area and Intrusion Volume Results for the Pilot- and Bench-Scale Cement Sorbents

The surface area and intrusion volume results of the two pilot-scale tests are presented in Figure 3-19. The surface area values are around $80 \text{ m}^2/\text{g}$, which is typical of the cement sorbents hydrated without additives. The intrusion volume has a value of about 1.2 cc/g for the two day hydration and appears to be increasing from 1 to 2 days of hydration, indicating that a longer hydration time may result in a larger intrusion volume and potentially a more reactive cement sorbent. However, increasing the hydration beyond 2 days defeats the purpose of adding this material. Also, the uptake values increased less than 5 percent upon increasing the hydration time from 1 to 2 days.

The surface area and intrusion volume results of the bench-scale tests are presented in Figures 3-20 and 3-21. Similar to the pilot-scale results, the surface area curve reached $80 \text{ m}^2/\text{g}$ after about 1 day of hydration. That surface area was reached earlier than the tests performed at room temperature with no additives. A maximum intrusion value of about 1.6 cc/g was reached at around 2 days, which is similar to the time required to reach the peak value for the tests performed with no additives at room temperature. It appears from these results that this additive increases the rate of surface area development, but has little affect on intrusion volume development when added in

these amounts.

3.4.3 Infusorial Earth Additive

As shown in Table 3-5, cement sorbent prepared at room temperature in the ball mill with infusorial earth additive resulted in sorbents that performed 6 and 22 percent below the material without additives for 3 and 4 days of hydration, respectively. (Note that a spray dryer test was conducted for the cement sorbent hydrated two days with calcined infusorial earth as an additive, but had to be aborted due to SDA operational problems.) These results indicate that a cement sorbent less reactive than the cement sorbents without additives was produced. In addition, this cement sorbent corresponds to a 7 to 50 percent increase over the slaked lime uptake of 20 mmol $\text{SO}_2/\text{g Ca}$.

3.4.3.1 Surface Area and Intrusion Volume Results for the Pilot- and Bench-Scale Cement Sorbents

Surface area and intrusion volume values for the pilot-scale material are presented in Figure 3-22. Surface area analysis yielded values around 80 m^2/g , typical of the cement sorbents with no additives. The intrusion volume curve is quite different, increasing from a value near 1.3 cc/g at 2 days to a value of nearly 2 cc/g at 4 days. The higher intrusion volumes as compared to the other cement sorbents did not correspond to higher uptake values, however.

The results of surface area and intrusion volume determination for the bench-scale tests are presented in Figures 3-23 and 3-24. The surface area curve is similar to previous curves, approaching values between 60 and 80 m^2/g after a hydration of about 2 days.

Unlike the pilot-scale results for this additive, the intrusion volume curve is also similar to previous curves exhibiting a maximum value around 1.8 cc/g between 2 and 3 days.

3.4.4 Natural Diatomite Additive

Although natural diatomite was expected to perform better than the calcined infusorial earth as an amorphous silica additive, this additive performed no better than the calcined additive. As shown in Table 3-5, uptake values for this sorbent were 21 to 28 percent lower than what was achieved for the cement sorbents without additives. However, these cement sorbents performed 5 to 19 percent better than the slaked lime uptake of 20 mmol SO₂/g Ca.

3.4.4.1 Surface Area and Intrusion Volume Results for the Pilot- and Bench-Scale Cement Sorbents

Surface area and intrusion volume results are presented in Figures 3-25. Surface area was greater than what was achieved for the cement sorbent without additives. The material with diatomite additive had surface areas between 100 and 120 m²/g. The intrusion volume results for this additive also increased with hydration time, jumping from around 1.5 cc/g at 3 days to about 2.2 cc/g at 4 days. However, higher surface area and intrusion volume values as compared to other cement sorbents did not correspond to higher reactivity.

Bench-scale results are presented in Figures 3-26 and 3-27. Similar to pilot-scale results, surface areas on the order of 100 m²/g were exhibited. These values are also higher than for the bench-scale cement sorbents without additives. As shown on the

pilot-scale, the intrusion volume curve appeared to increase over the hydration time investigated to a value of about 2.5 cc/g, occurring at about 6 days.

3.4.5 Fumed Silica

Due the expense of fumed silica (\$100 per Kg), only enough material was purchased to perform two SDA tests. No bench-scale testing was performed. Although fumed silica proved to be a good additive for cement sorbents in another study^{16,22,28}, these results indicate that SDA performance was not improved by adding this material. As shown in Table 3-5, cement sorbent with this additive yielded uptake values 15 and 36 percent lower than what was achieved for the cement sorbent without additives. These results also indicate a 2 to 28 percent increase over the performance of $\text{Ca}(\text{OH})_2$ with an uptake of 20 mmol $\text{SO}_2/\text{g Ca}$.

3.4.5.1 Surface Area and Intrusion Volume Results for the Pilot-Scale Cement Sorbents

Surface area and intrusion volume results are presented in Figure 3-28. Like natural diatomite, this additive resulted in surface areas in excess of 100 m^2/g . Pore volume was slightly higher than other results, with a value of over 1.8 cc/g after three days of hydration in the ball mill. Large surface areas and pore volume did not correspond to an increase in sorbent effectiveness.

3.5 Cost and Operational Considerations

The baseline and cement results can be used to estimate sorbent cost effectiveness

based on the cost of the reagent. Calculations result in a cost of about \$80/ton of SO_2 removed for quicklime, and a cost of \$70/ton SO_2 for the cement sorbents. This corresponds to a savings of \$10/ton of SO_2 removed, or 12.5 percent. As a further example, actual coal fired boiler operating data from a recent article³⁰ can be used to calculate an annual savings in reagent cost of over \$600,000. Clearly, there is potential for significant cost savings in operating a spray drying system using hydrated cement in place of the conventional slaked lime.

Reagent cost used in this analysis was \$50 per ton of quicklime³¹ and \$65 per ton of cement¹¹. The calculation for cement was based on 63% CaO and an uptake of 32 mmol SO_2 /g Ca, and the calculation for quicklime was based on 85% CaO and an uptake of 16 mmol SO_2 /g Ca. The yearly cost savings was calculated from operating data from an actual 300 MW facility emitting 13,700 lb/hr SO_2 before controls. A removal efficiency of 90 percent was assumed.

The use of the cement sorbents resulted in an improvement in the operation of the spray dryer associated with the problem of plugging of the atomizer. Nozzle plugging was a problem in operating the system with slaked lime due to the portion of inert "grit" (up to 10%) in quicklime. Because of this problem, the solids content of the slaked lime slurries had to be limited to an upper value of about 15 percent. Since cement slurry essentially has no inert material and is comprised of small particles at the water-to-solids ratio for this study, one would not expect plugging to be much of a problem when using this reagent. An additional benefit was that the pretreatment step of passing the slurry through a cyclone or screen to remove larger particles was not necessary in preparing the hydrated cement sorbent. Plugging was not experienced for any of the cement sorbent

hydrated less than 5 days. Plugging was experienced for two tests where the cement was hydrated 6 and 10 days. This was probably due to a noticeable increase in viscosity of the material that was hydrated past 5 days.

A problem associated with hydrated cement sorbents is that some preparation methods, such as hydration time, are more critical as compared to slaked lime preparation. It was shown that specific hydration conditions corresponded to more or less reactive material. For example, reactivity appeared to increase with hydration time to a peak value, and decrease thereafter. This result would indicate that, unlike slaked lime sorbents, the hydrated cement material could not be stored for a long period of time before use.

Table 3-1. Test Matrix

Reagent(s)	Weight Ratio (Water:Reagents)	Method of Mixing	Hydration Time	Hydration Temp.
Ca(OH) ₂	~9:1	Stirred	~1 Hour	~25°C (Room Temp.)
Ca(OH) ₂	~9:1	Milled	3 Days	~25°C
Cement	10:1	Stirred	17 Hours	~25°C
Cement	10:1	Milled	18 Hours	~25°C
Cement	10:1	Stirred	24 Hours	60°C
Cement	10:1	Stirred & Milled	24 Hours & 18 Hours	60°C & ~25°C
Cement	10:1	Milled	0.75, 2, 3, 4, & 5 Days	~25°C
Cement	8:1	Milled	3 Days	~25°C
Cement	10:1	Milled	3, 6, 9, 12 & 18 Hours	70°C
Cement : CaCl ₂	10:1:0.02	Milled	1 & 2 Days	~25°C
Cement : Infusorial Earth	10:1: 0.2	Milled	2, 3, & 4 Days	~25°C
Cement : Diatomite	10:1: 0.2	Milled	2, 3, & 4 Days	~25°C
Cement : Fumed Silica	10:1:0.1	Milled	2 & 3 Days	~25°C

Table 3-2. Physical Parameters of Dried Baseline Slurry

Mill Time	Surface Area (m ² /g)	Intrusion Volume 0.5 μm - 0.0018 μm (cc/g)
Not Milled	31.3	1.00
3 Days	35.5	1.18

Table 3-3. Summary of the Effect of Mill Time on Cement Sorbents Hydrated at Room Temperature

Appr. to Sat. (°C)	Mill Time (days)	Average Overall Uptake (mmol SO ₂ /g Ca)	Number of Data Points	Sample Standard Deviation	Relative Standard Deviation (%)
11.1	0	11.3	1	----	----
	2	30.0	2	0.515	1.72
	3	31.9	3	4.34	13.6
	4	27.3	2	0.981	3.59
	5	21.7	1	----	----
16.7	0	9.27	1	----	----
	2	22.1	2	1.30	5.88
	3	26.9	3	1.11	4.13
	4	23.5	2	1.62	6.89
	5	20.6	1	----	----

Table 3-4. Composition and Uptake of Sorbents Sent to Case Western Reserve University (ref 29).

	CSH^{a,b} (%)	CH (%)	AFm (%)	cem (%)	sulf (%)	un (%)	SO₂ Uptake (mmol/g)
Unreacted Sorbent-1	50	20	25	5			8.4
Unreacted Sorbent-2	50	20	20	10			7.6
Spent Sorbent	20	10		10	40	20	

^a CSH, CaO-SiO₂-H₂O; CH, Ca(OH)₂; AFm, [Ca₂(Al,Fe)(OH)₆]₂(SO₄, CO₃, 2OH)•6H₂O or related amorphous phase; cem, mainly unreacted dicalcium silicate; sulf, CaSO₃•0.5H₂O; un, unidentified.

^bAmount inferred from data obtained and literature data.

Table 3-5. Spray Dryer Tests at an Elevated Temperature and with Additive-Enhanced Cement Sorbents^a

Additive/ Hyd. Temp.	Additive:Cement Weight Ratio	Mill Time (days)	Stoichiometric Ratio	Removal Efficiency	Overall Uptake (mmol SO ₂ / g Ca)	%Increase (%Deficit) ^b
None/ 70°C	N/A	0.125	0.88	0.74	21.0	70 ^c
		0.375	0.77	0.71	24.3	75 ^c
		0.75	0.73	0.74	25.6	70 ^c
Calcium Chloride/ 25°C	0.02:1	1	0.696	0.779	28.0	40 ^c
		2	0.713	0.828	29.0	(3)
Infusorial Earth/ 25°C	0.2:1	3	0.724	0.867	29.9	(6)
		4	0.966	0.825	21.3	(22)
Diatomite/ 25°C	0.2:1	2	0.791	0.751	23.7	(21)
		3	0.893	0.824	23.1	(28)
		4	1.07	0.892	20.9	(23)
Fumed Silica/ 25°C	0.1:1	2	0.788	0.802	25.5	(15)
		3	1.08	0.872	20.3	(36)

^aAll data for spray dryer tests performed at 11.1°C approach to saturation.

^bComparison with pilot-scale uptake at the same hydration time for cement sorbent hydrated at room temperature without additives

^cApproximation based on trend of data as shown in Figure 4

Figure 3-1. Baseline Ca(OH)₂ Removal Efficiency

Figure 3-2. Baseline Ca(OH)₂ Overall Uptake

Figure 3-3. Effect of Mixing Method on Effectiveness of Hydrated Cement Sorbent

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Figure 3-19. Surface Area and Intrusion Volume of Pilot-Scale Cement Sorbent with CaCl₂ Additive

Figure 3-20. Surface Area and Intrusion Volume of Pilot-Scale Cement Sorbent with Infusorial Earth Additive

Figure 3-21. Intrusion Volume of Bench-Scale Cement Sorbents with CaCl_2 Additive

Figure 3-22. Surface Area of Bench-Scale Cement Sorbents with Infusorial Earth Additive

Figure 3-23. Surface Area of Bench-Scale Cement Sorbents with Infusorial Earth Additive

Figure 3-24. Surface Area and Intrusion Volume of Pilot-Scale Cement Sorbent with Diatomite Additive

Figure 3-25. Intrusion Volume of Bench-Scale Cement Sorbents with Infusorial Earth Additive

Figure 3-26. Surface Area of Bench-Scale Cement Sorbents with Diatomite Additive

Figure 3-27. Intrusion Volume of Bench-Scale Cement Sorbents with Diatomite Additive

Figure 3-28. Surface Area and Intrusion Volume of Pilot-Scale Cement Sorbent with Fumed Silica Additive

4.0 CONCLUSIONS

This research was engaged in evaluating hydrated type I Portland cement as a new SDA sorbent. The performance of hydrated cement sorbents in the U.C. pilot spray dryer was compared to the performance of the conventional SDA sorbent, a slurry of calcium hydroxide. Several cement sorbent preparation parameters were varied, including hydration time, temperature, and method of mixing. Also, the effect of several additives on the reactivity of the resulting enhanced hydrated cement reagent were studied. Samples of hydrated cement were analyzed for surface area and internal pore volume development as a function of time, and these physical parameters were compared to sorbent effectiveness. In addition, bench scale tests were performed to provide a more detailed picture of physical parameter development than could be derived from the pilot-scale work alone.

Hydrated cement sorbents more reactive than slaked lime were produced, but only under certain preparation methods. Ball milling proved to be the preferential method of mixing over stirring. The reactivity of sorbents prepared in this fashion at room temperature without additives appeared to increase to a peak value at 3 days of hydration, and decrease for hydration times longer than 3 days. Hydration of cement sorbent in the ball mill at room temperature without additives with an initial water-to-solids content of 8:1 resulted in an increase in removal efficiency, but a decrease in overall uptake.

Hydration at an elevated temperature and with dihydrous calcium chloride resulted in cement sorbents that provided an increase in uptake over cement sorbents

hydrated for the same amount of time at room temperature without additives. Hydration of cement with infusorial earth, diatomite, and fumed silica did not result in an improvement over hydrated cement at room temperature. Further, none of these methods served to improve the reactivity of the cement sorbents beyond the maximum uptake achieved by ball milling at room temperature without additives. However, in all cases the sorbents hydrated at an elevated temperature and with additives resulted in sorbents that performed better than the best results obtained with slaked lime.

Surface area and internal pore volume development for the pilot-scale material prepared in the ball mill at room temperature without additives were compared with overall uptake for these sorbents. Reactivity for these cement sorbents appeared to correlate more closely with pore volume than surface area. Internal pore volume increased to a peak value at roughly the same time of hydration required for the most reactive sorbent. Surface area increased rapidly to assume a somewhat constant value, which did not correspond with the aforementioned decrease in reactivity for longer hydration times. This result is important in that many studies are concentrated on determining the relationship between reactivity and surface area without looking at other physical parameters.

Interpretation of the measured physical parameters was difficult in that a wide variation in the results was experienced for data at the same hydration time under the same hydration conditions. This was probably associated with the important role of water in the structure of cement, and the fact that surface area and internal pore volume was lost when the material was dried for analysis. Drying the samples for analysis may

have resulted in the destruction or inaccessibility of some of the micropores, which account for large amounts of surface and volume.

An analysis was performed in which the cost effectiveness of the hydrated cement sorbents hydrated in the ball mill at room temperature with no additives was compared with that for slaked lime. This analysis indicated that cement sorbent uptake values that were twice what was achieved for slaked lime corresponded to a 12.5 percent savings in reagent cost. For the parameters used in this cost analysis, uptake of the cement sorbent would have to be at least 75 percent greater than slaked lime to realize a reagent cost savings.

Although the pilot-scale results are promising in that an improvement in sorbent effectiveness over slaked lime was observed, use of this material may be limited in SDA applications. It was found that the material was more reactive for intermediate hydration times when prepared under certain conditions. Further, spray dryer operational problems associated with an increase in the viscosity of the material for longer hydration times was experienced. Unlike slaked lime, cement sorbents cannot be stored in slurry form for a long period and used on an as-needed basis. As the material is stored the hydration reaction would proceed, resulting in unwanted physical properties such as a decrease in internal pore volume and an increase in viscosity.

In summary, the results of this study indicate that hydrated cement can be an effective desulfurization agent in SDA applications. Since reactivity is most probably a complex function of physical and compositional parameters, future studies should include an investigation into the relationship between the composition of the hydration product

and reactivity. If the work is involved in evaluating the use of this sorbent in dry FGD systems, such as duct injection, the method of drying should be included as an important parameter to be studied.

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