



Project Summary

Evaluation of FGD Dry Injection Sorbents and Additives: Volume 1. Development of High Reactivity Sorbents

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EPA's efforts to develop low cost, retrofit flue gas cleaning technology include the development of highly reactive sorbents. Recent work addressing lime enhancement by slurring with siliceous materials and testing in a laboratory packed-bed reactor is discussed in this report.

The solids generated from a furnace limestone injection process were reactivated by slurring at elevated temperatures. Compared with untreated solids, reactivity toward SO₂ was significantly enhanced by hydration. The SO₂ capture by solids increased with increasing time and temperature of hydration. The SO₂ capture was probably enhanced by the calcium aluminate silicate hydrates formed during the slurring process.

In addition to flyash, silica from alternative sources was reacted with lime. The dry sorbents produced by slurring several diatomaceous earths, or montmorillonitic clays, with lime were found to be highly reactive with SO₂. The most reactive sorbent was generated by slurring silica/lime at a weight ratio of 1 to 1. The morphology of the developed sorbents was characterized.

Several additives were tested to evaluate their potential to promote the lime/silica reaction rate and increase sorbent reactivity. Of those tested, NaOH, Na₂HPO₄ · 7H₂O, (NH₄)₂HPO₄, and H₃PO₄ were found

effective in enhancing the flyash/lime reaction. The maximum enhancement effect was obtained by using 4 to 8 mol % additives.

Pressure hydration of flyash and lime fostered the formation of a reactive sorbent much quicker, and used less flyash, than did atmospheric hydration. The reactivity of the sorbent in the packed bed reactor correlated well with B.E.T. surface area, increasing with increasing surface area. The optimum temperature range for the pressure hydration of flyash with lime was between 110 and 160°C.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Highly reactive sorbents are needed for the dry sorbent injection flue gas desulfurization (FGD) process. The dry sorbent injection concept is very attractive, especially for retrofitting existing power plants, because of its technical simplicity and low capital cost. However, due to limited space and the high velocity of flue gas, an extremely short gas/solid reaction time is available for SO₂ absorption. As a result, very low

utilization (less than 30%) was obtained by using a conventional sorbent such as lime. Better sorbent utilization could be achieved when the sodium based sorbents, such as nahcolite and trona, were used. Sodium salts generated from FGD processes possess much higher solubility in water (12.5 g of Na_2SO_3 per 100 g of cold water) than do calcium salts (0.0043 g of $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ per 100 g of cold water), and therefore may constitute the environmental hazard of leaching salts into ground water if the waste is disposed of in landfills.

Calcium silicate hydrates produced by pozzolanic reaction between silica and lime in water at elevated temperatures are very attractive calcium based sorbents for dry injection processes. When prepared in appropriate forms, these hydrates are very reactive with SO_2 and should result in good sorbent utilization. Previous study has shown that reactive calcium silicate hydrates can be produced by slurring flyash with lime at temperatures below 100°C (atmospheric hydration), but relatively high flyash/lime ratios (greater than 3) and long reaction times (longer than 8 h) are required. For commercial application this method might not be viable. A high flyash/lime ratio would increase flue gas duct loading and overload the particulate control device. The long reaction time would increase the reactor size and capital cost. Goals of this work included: evaluation of potential techniques of reducing the flyash/lime ratio as well as the reaction time, and applying the concept of using silica/lime sorbent to reactivate solids from furnace limestone injection processes to enhance overall SO_2 removal and promote waste utilization.

The major experimental apparatus used was a laboratory-scale packed bed reactor. The glass reactor (45 mm diameter, 150 mm long) was packed with powdered sorbent mixed with 70-mesh sand to prevent channeling. The reactivity of various sorbents was measured by the quantity of SO_2 absorbed under typical dry injection flue gas conditions. Reagent grade $\text{Ca}(\text{OH})_2$ was used as the baseline sorbent. Calcium silicate hydrates were prepared by pressure hydration or by slurring siliceous materials with lime in a stirred beaker immersed in a thermostated water bath. After mixing, the samples were vacuum filtered and dried before testing in the reactor. A stainless steel high pressure 300 mL vessel was used to prepare the calcium silicate hydrates at temperatures above 100°C (pressure hydration). The high pressure vessel was

heated electrically and its temperature controlled by a thermocouple. Sorbent reactivity was calculated in terms of SO_2 capture and lime conversion. SO_2 capture was defined as the amount of SO_2 absorbed per unit weight of sorbent (mmol SO_2/g). Lime conversion was the percent of lime in the sorbent which reacted with the absorbed SO_2 assuming that CaSO_3 was the product.

Reactivation of Boiler Limestone Injection Solids

The objective of this segment of work was to apply the pozzolanic reaction concept to Boiler Limestone Injection Solids (BLIS). Their potential for producing reactive sorbent to increase overall SO_2 capture and sorbent utilization was evaluated.

Due to the low sorbent utilization of boiler limestone injection processes, BLIS usually contains significant amounts of unreacted lime. Other ingredients include calcium sulfate, limestone, and flyash. Six samples of BLIS, produced in 1981 by boiler limestone experiments, were tested. The untreated BLIS showed virtually no SO_2 removal capability in the packed bed reactor. Hydrating the BLIS at elevated temperatures for a prolonged period of time was tested as a means of reactivating these solids.

For the BLIS samples hydrated at 65 and 90°C over 1 to 8 h intervals, the SO_2 capture increased with increased time of hydration, but leveled off at about 1.8 mmol SO_2/g . X-ray elemental analysis of hydrated samples showed Al, S, and Ca peaks, suggesting that ettringite or other synthetic calcium aluminate sulfate crystals were formed during hydration. X-ray powder diffraction analyses confirmed the existence of those crystals and further suggested that they were hydrated crystals with a high water content. A significant increase of solid surface area by hydration was measured by B.E.T. analyses. The initial value for untreated BLIS was $2.67 \text{ m}^2/\text{g}$. The surface area of hydrated BLIS reached as high as $50.86 \text{ m}^2/\text{g}$. The surface area increased with both hydration time and temperature. A good correlation was obtained between the developed surface area and the reactivity of the hydrated BLIS (see Figure 1).

Screening of Alternative Sources of Silica

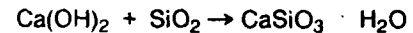
The objective of screening alternative silica sources was to evaluate the reactivity of various siliceous materials with lime. The siliceous materials

evaluated included cryptocrystalline forms of silica such as diatomaceous earths, tripolis, and pumices. Several grades of naturally occurring bentonitic clays and kaolins were also tested. Each sample of the siliceous materials tested was hydrated with lime at 90°C . The reactivity of the hydration product was evaluated in the bench-scale packed bed reactor.

The hydrates produced from the natural grade diatomaceous earths were more reactive than those from calcined earths. The calcination of diatomaceous earths used in commercial products, especially when sodium salts were used as an additive, caused by an 80% decrease of B.E.T. surface area. Sodium based additives used during calcination probably caused sintering at the high temperatures (above 900°C) in the kiln producing siliceous slag on the surface of diatomaceous earth similar to the glass layer on the surface of flyash particles.

The hydrates produced from naturally occurring bentonitic clays were also found to be more reactive than those from treated or "activated" clay. Hydrates from kaolins generally performed more poorly than bentonitic clays.

Parametric tests were conducted with the two most promising alternative siliceous materials—MN-53 (a diatomaceous earth) and Bentonite 149 (bentonitic clay). The most reactive hydrates were produced by reacting siliceous materials with lime at a silica/CaO ratio of about 1. Most likely the calcium silicate was formed during the hydration process according to the hypothetical reaction:



Assuming the relative reactivity toward SO_2 being in the order $\text{CaSiO}_3 \cdot \text{H}_2\text{O} > \text{Ca}(\text{OH})_2 > \text{SiO}_2$, only at equimolar condition can the greatest amount of the most reactive hydrates be produced. X-ray powder diffraction analysis confirmed that $\text{Ca}(\text{OH})_2$ and SiO_2 disappeared after hydration. The less unreacted $\text{Ca}(\text{OH})_2$ was, the more reactive were the hydrates.

Effects of Additives on Sorbent Reactivity

The objective of this segment was to evaluate the effectiveness of additives enhancing reactivity of hydrates produced by flyash/lime slurring. The additives tested included sodium hydroxide, sodium phosphate, amn

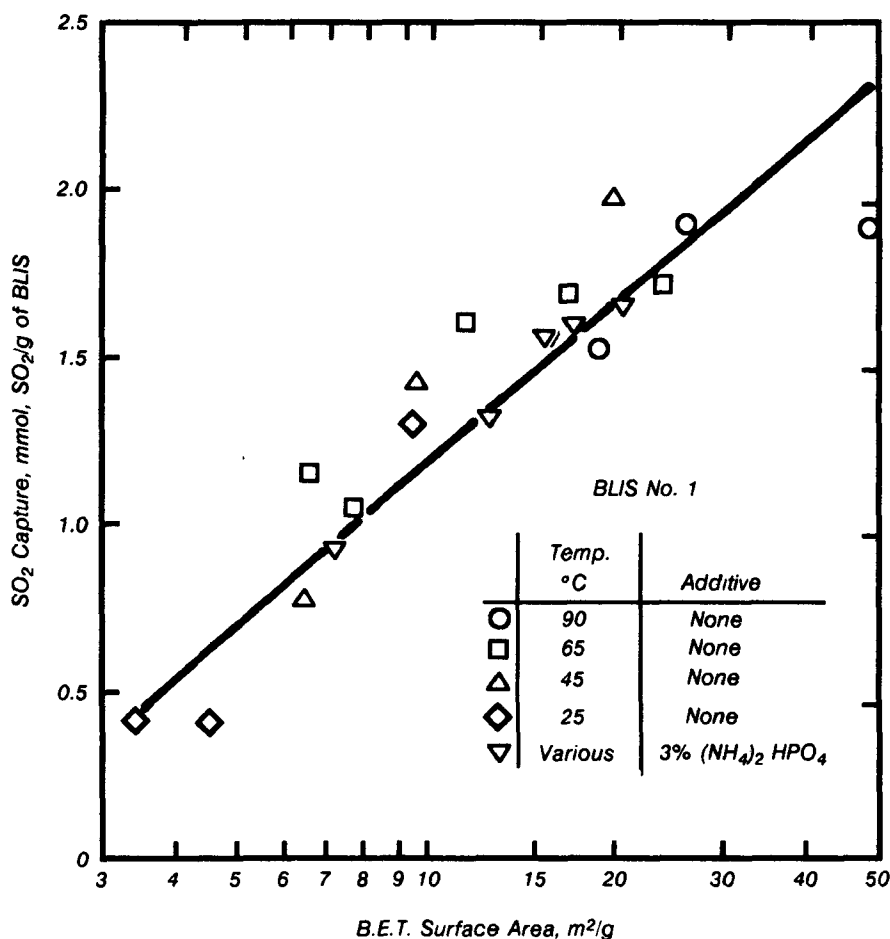


Figure 1. Correlation between the surface area developed during hydration and SO₂ capture by BLIS No. 1 in the sand bed.

nium phosphate, and phosphoric acid. Sodium hydroxide has the potential of enhancing the reaction rate between flyash and lime by increasing the solubility of silica. Phosphates could promote the flyash/lime reaction by increasing the flyash dissolution rate resulting from their ability to attack the glassy layer on flyash particle surfaces.

Sodium hydroxide tests were performed at a flyash/Ca(OH)₂ ratio of 2.3 to 1. The enhancement effect was reflected by an increase of lime conversion from 35 to 50% when comparing the reactivity of hydrates prepared with and without NaOH addition. The maximum enhancement effect was obtained with a dose of 4 mol % of NaOH additive (based on Na/Ca ratios). The higher the NaOH concentration in the flyash/lime slurry, the more pronounced the enhancement effect (Figure 2).

Three phosphates, Na₂HPO₄ · 7H₂O, (NH₄)₂HPO₄, and H₃PO₄ were tested. All data showed that the maximum enhancement occurred when a dose of 4 to 8 mol % phosphate (based on PO₄/Ca ratios) was used to slurry the flyash with lime. When CaO instead of Ca(OH)₂ was slurried with flyash, the amount of phosphate needed to reach the same degree of reactivity was 50 and 70%, respectively, when (NH₄)₂HPO₄ and Na₂HPO₄ · 7H₂O were used. For example, a maximum lime conversion of 50% was reached when 4 and 8 mol % of (NH₄)₂HPO₄ respectively, were added during the slurrying of flyash with CaO and Ca(OH)₂. The result may stem from the dispersing properties of phosphates, present during the hydration of CaO, which create finer particles in the product compared to those obtained using Ca(OH)₂.

Pressure Hydration Evaluation

Pressure hydration was evaluated as a way to produce calcium silicate hydrates for dry SO₂ control. The focus was on the pressure hydration of flyash or diatomaceous earth with Ca(OH)₂, aimed at reducing the time of hydration and the weight ratio of siliceous materials to lime.

Pressure hydration is used commercially to hydrate dolomitic lime (CaO + MgO), as MgO usually is difficult to hydrate completely within a reasonable period of time under atmospheric conditions. Pressure hydration allows the use of high temperatures (above 100°C) and high pressure (above 1 atm) to accelerate the reaction rate. For the silica/lime reaction, the high temperature of pressure hydration increases the silica solubility and enhances the pozzolanic reaction rate.

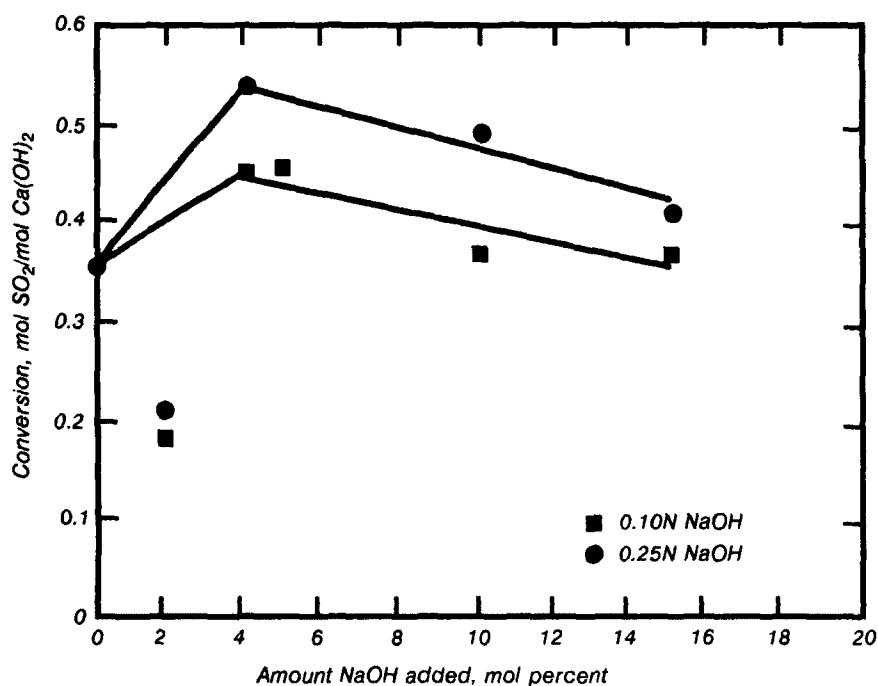


Figure 2. The effect of NaOH addition during slurring on the reactivity of dry sorbent in the sand-bed reactor (preparation conditions: slurring at 90°C for 8 h; sand-bed reactor conditions: 60% relative humidity, 64.4°C temperature, and 500 ppm SO₂ concentration).

Comparing atmospheric hydrates with pressure hydrates, the data clearly showed that a significant decrease of time of hydration is possible when the hydration temperature is increased. For example, atmospheric hydration at 90°C for 8 h was required to enhance the conversion of Ca(OH)₂ up to 35%, when the weight ratio of flyash to Ca(OH)₂ was 2.3 to 1. The same conversion was achieved for the same reactants and weight ratio after they had been pressure hydrated at 150°C for 1 h (Figure 3). Pressure hydration could also reduce the flyash/lime weight ratio requirement. At a flyash/lime ratio of 1, the product of pressure hydration at 120°C for 2 h showed 45% lime conversion. The atmospherically hydrated product at the same flyash/lime ratio never achieved the 45% lime conversion.

The present work also included pressure hydration of diatomaceous earth/CaO slurry at 150 and 230°C for about 1 h. No significant increase in reactivity (lime conversion) was achieved by pressure hydration of diatomaceous earth with lime.

Parametric tests were conducted to pressure hydrate the lime with flyash. There is an optimum hydration time for each hydration temperature. At 230°C,

the maximum reactivity (lime conversion) was obtained with about 1 h hydration of flyash/lime at a ratio of 2.3. The optimum hydration time became 4 h at 180°C, and 5 h for 150°C. When the flyash/lime ratio decreased from 2.3 to 1, the optimum hydration time shifted from 5 h to 1 h at 150°C.

The reactivity of pressure hydrated flyash/lime correlated quite well with B.E.T. surface area. Higher surface area hydrates, generally produced at medium temperatures (150-180°C), optimum hydration time, and relatively high flyash/lime ratio (e.g., 2.3), usually possess greater reactivity toward SO₂.

The crystal morphology of the pressure hydrated flyash/lime mixtures was examined by scanning electron microscope (SEM) and x-ray diffraction. Compared with B.E.T. surface area and reactivity data, two factors were found necessary for the hydrates to readily react with SO₂ under conditions encountered in a dry injection FGD process: large sorbent surface area and amorphous surface structure. Usually, highly reactive hydrates have a large surface area and a gel-like amorphous crystal surface. For one hydrate sample prepared at 230°C, even though the measured B.E.T. surface area was high

(17 m²/g), the reactivity was poor (16 lime conversion). SEM pictures show that, instead of gel-like amorphous materials, a framework of distinct need shaped crystals was found. This finding seemed to indicate that the reactivity of hydrates was a function of crystal structure, which could be affected by hydration temperature.

Conclusions

Experimental results from this study indicate that the waste solids from boiler limestone injection process can be reactivated by atmospherically hydrating them under conditions which permit the reaction of calcium with silica to form large surface area hydrates. New crystals (calcium/aluminate/silicate/sulfate hydrates) were found in the reactivated BLIS samples. The reactivity of the hydrated BLIS samples increases with the time and temperature used for hydration, and correlates well with surface area; i.e., increases with increasing surface area. The reactivity of these hydrated BLIS samples is sensitive to the relative humidity of flue gas, with the SO₂ reactivity increasing with relative humidity.

Siliceous materials from sources other than flyash were found effective

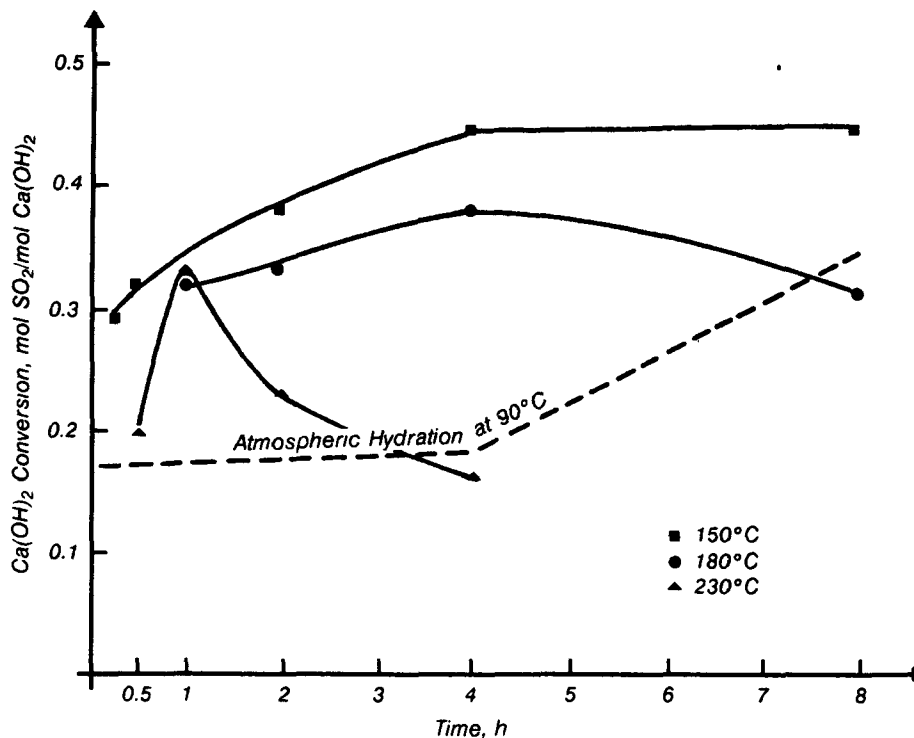


Figure 3. Combined time and temperature effects of pressure hydration on the reactivity of sorbent prepared at the weight ratio of flyash to Ca(OH)_2 of 2.3:1; sand-bed reactor conditions: relative humidity 60%, temperature 64°C, SO_2 concentration 500 ppm; pressure hydrator conditions: temperature 150°C, 2h.

enhancing the reactivity of the sorbents produced by slurring with lime at elevated temperatures. Among the siliceous materials tested, natural grade diatomaceous earth and bentonitic clay were found to be the most effective in producing reactive hydrates with lime. The most reactive hydrates were produced by slurring siliceous materials with lime at a silica/CaO ratio of about 1. It is postulated that calcium silicate hydrates were formed during the slurring process. The high reactivity of the slurring product can be partially attributed to the large surface area of calcium silicate hydrate and its high water retaining capability.

Additives such as sodium hydroxide, sodium phosphate, ammonium phosphate, and phosphoric acid can be added to the flyash/lime slurry to enhance the reactivity of the produced hydrates. The maximum reactivity enhancement effect was obtained by using 4 to 8 mol % (versus Ca) additives.

Very reactive sorbents for dry injection SO_2 removal from flue gas can be produced by pressure hydration of flyash with lime. Pressure hydration fosters the formation of hydrates from flyash/lime slurry in much less time than does atmospheric hydration. Hydration time, temperature, and flyash/lime ration are the three major parameters which affect

the reactivity of the hydrates. Matrices of optimum pressure, hydration time, temperature, and flyash/lime ratio for dry injection SO_2 removal purpose are needed for commercial application. SEM and x-ray diffraction studies demonstrated the formation of hydrates of different morphologies by using different flyash/lime ratios and changing the conditions of pressure hydration. Both high B.E.T. surface area and amorphous surface structure are necessary characteristics for the hydrates to be reactive with SO_2 . Although hydrates with well-defined, needle-shaped crystals have a large surface area, they are not reactive with SO_2 .

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The complete report, entitled "Evaluation of FGD Dry Injection Sorbents and Additives: Volume 1. Development of High Reactivity Sorbents," (Order No. PB 89-208 920/AS; Cost: \$23.00, subject to change) will be available only from:

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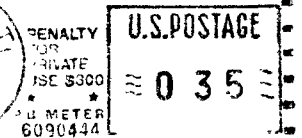
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