DEVELOPMENT OF A CALCIUM-BASED SORBENT FOR HOT GAS CLEANUP

Semi-Annual Technical Progress Report

April 1, 1997 - September 30, 1997

T. D. Wheelock, K. Constant, and L. K. Doraiswamy
Principal Investigators

T. Akiti and J. Zhu
Graduate Assistants

Aurelia Amanda and Rachel Roe
Summer Interns

Issued: September, 1997

Chemical Engineering Department,
Materials Science and Engineering Department, and
Center for Coal and the Environment
2114 Sweeney Hall
Iowa State University
Ames, Iowa 50011-2230

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DEVELOPMENT OF A CALCIUM-BASED SORBENT FOR HOT GAS CLEANUP

Semi-Annual Technical Progress Report

April 1, 1997 - September 30, 1997

T. D. Wheelock, L. K. Doraiswamy, and K. Constant
Principal Investigators

ABSTRACT

Further review of the technical literature has provided additional information which will support the development of a superior calcium-based sorbent for hot gas cleanup in IGCC systems. Two general methods of sorbent preparation are being investigated. One method involves impregnating a porous refractory substrate with calcium while another method involves pelletizing lime or other calcium containing materials with a suitable binder. Several potential substrates, which are made of alumina and are commercially available, have been characterized by various methods. The surface area and apparent density of the materials have been measured, and it has been shown that some of the high surface area materials (i.e., 200-400 m^2/g) undergo a large decrease in surface area when heated to higher temperatures. Some of the lower surface area materials (i.e., 1-30 m^2/g) have been successfully impregnated with calcium by soaking them in a calcium nitrate solution and then heat treating them to decompose the nitrate. Potentially useful sorbents have also been prepared by pelletizing type I Portland cement and mixtures of cement and lime.

<u>TABLE OF CONTENTS</u>

<u>Page</u>

EXECUTIVE SUMMARY

The principal objective of this project is the development of a superior calcium-based sorbent for use in hot gas cleanup in IGCC systems. The sorbent should be capable of removing H_2S and COS from hot coal gas and should withstand repeated loading and regeneration. Progress has been made in several areas including a further review of the technical literature. By extending the review to publications concerned with the development of synthetic calcium-based sorbents for sulfur oxides, several publications which will assist the development of similar sorbents for H_2S were discovered.

Several porous alumina substrates for impregnation with calcium were collected and characterized by measuring the surface area and apparent density of the materials. Two broad classes of materials were identified. One class has a large surface area indicative of a large network of small diameter pores while another class has a small surface area and a network of relatively large diameter pores. Subjecting the first class of materials to a heat treatment at temperatures as high as 1100°C reduced the surface area of the materials greatly and also increased the apparent density of the materials.

Several of the porous substrates with the larger diameter pores were impregnated with calcium by soaking the materials in a concentrated solution of calcium nitrate under boiling conditions. The nitrate was then decomposed by heating the materials to 1100°C. The resulting deposition of calcium oxide within the pore structure produced a weight gain which varied with treatment conditions. In most cases a weight gain of 12 to 16% was observed when a calcium nitrate solution having a concentration of 20 mole % was employed.

Several potential sorbents were prepared by pelletizing type I Portand cement either alone or mixed with various amounts of calcium oxide or calcium carbonate. Some of the pellets were cured for 6 days while others were cured for 28 days in a humid environment before testing. Preliminary tests of sorbent capacity were conducted by employing high temperature thermogravimetric analysis to measure the gain in weight of the sorbent as carbon dioxide was passed over the material. Adsorption was rapid at first and then more gradual. After 2 hr the gain in weight was typically in the range of 12 to 14% when the tests were conducted at 850°C. Little or no adsorption was observed at 900°C.

INTRODUCTION

This research project is directed towards the development of a superior calcium-based sorbent for hot gas cleanup in integrated coal gasification, combined-cycle (IGCC) systems for generating electric power. The main goal is the development of a rugged and regenerable sorbent capable of removing all but traces of hydrogen sulfide from coal gas at temperatures in the range of 1025 to 1325°K (1450 to 1920°F). Two general methods are being investigated for creating potential sorbents. One method involves impregnating porous refractory substrates such as alumina catalyst carriers with calcium oxide. The other method involves pelletizing lime with other materials followed by heat treatment to produce porous composites such as $CaO \cdot Ca_2SiO_4$.

An extensive body of technical literature is being reviewed in order to build on previous work. A number of commercially available substrates have been collected and are being characterized. Various methods of impregnating the substrates with calcium have been tested, and one method in particular seems to work well. This method will be utilized for

preparing a series of potential sorbents for testing in the future. The ground work for the preparation of potential sorbents by pelletization and heat treatment is being laid. Several batches of pellets have been prepared by pelletizing type I Portland cement either by itself or in mixtures with calcium oxide or calcium carbonate. Initial adsorption tests have been conducted with carbon dioxide. Details of this work are presented below.

<u>LITERATURE REVIEW</u>

It was reported previously that a computerized search of *Chemical Abstracts* produced only a small number of publications which dealt with the development of synthetic, calcium-based sorbents for hydrogen sulfide (1). Since then, another computerized search of *Chemical Abstracts* has been conducted for synthetic, calcium-based sorbents which are designed to remove sulfur dioxide from hot combustion products. Any calcium-based material capable of removing sulfur dioxide from a hot gas should also be capable of adsorbing hydrogen sulfide. The second search turned up several publications containing information which will aid the development of sorbents for hydrogen sulfide. The reports of greatest interest are reviewed below.

The work of Snyder *et al.* (2,3) is of particular interest because it involved preparing synthetic sorbents for sulfur dioxide by impregnating alumina supports with lime. One of the supports was a commercially available high purity alumina catalyst support in the form of 1/8 in. by 1/8 in. cylindrical pellets. A second support was prepared by heat treating pure boehmite granules to 1100-1500°C to form α-Al_2O_3. A third support was prepared by heat treating bauxite (70% Al_2O_3, 30% SiO_2) to 1100-1500°C. The supports were impregnated by placing them in an aqueous solution of calcium nitrate and subsequently soaking them under

reflux conditions for 8 hr. The pellets or particles were then heated to decompose the calcium nitrate, and with further heating to 1100°C calcium aluminate was produced. The amount of calcium introduced into the supports was directly proportional to the concentration of calcium in the impregnating solution. Although up to 15 wt.% CaO was introduced by this technique, it was found in subsequent tests of the sorbents that the sulfation rate decreased markedly as the addition of lime increased. The sulfation rate was also found to depend on the initial pore size of the support. Heat treating the boehmite support at 1500°C before impregnation produced larger pores and a higher sulfation rate after impregnation than was observed when the support was heat treated at 1200°C. Although the synthetic sorbents did not have as large a capacity for adsorption as natural limestones, they had a greater resistance to attrition. This was demonstrated by fluidizing the granular boehmite support for 10 hr in one test and granular Tymochtee dolomite in another test. In general the overall results obtained with the bauxite supported sorbent were less favorable than those achieved with the other materials.

Snyder *et al*. (2,3) believed that the CaO introduced into the alumina supports reacted with the alumina at high temperature to form calcium aluminates. When the sorbents were treated subsequently with a gas mixture containing sulfur dioxide and oxygen, the following reaction took place:

$$CaO \cdot nAl_2O_3 + SO_2 + \frac{1}{2}O_2 = CaSO_4 + nAl_2O_3 \tag{1}$$
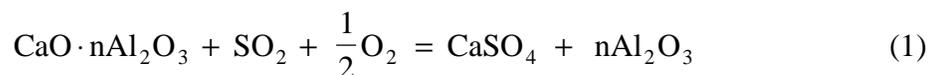
where n was either 1 or 2. In other words, free $CaSO_4$ was produced. During regeneration the $CaSO_4$ was decomposed by a reducing gas, and the resulting CaO recombined with the alumina to reform the calcium aluminates. When the sorbents were subjected to a number of adsorption and regeneration cycles, the sorbent prepared from the commercial catalyst

support was not affected noticeably. However, the capacity of the sorbent prepared with the boehmite support declined appreciably from cycle to cycle.

The potential for a silica supported lime sorbent was explored by Yang and Shen (4) who utilized a commercially available granular silica gel as a support. The granules were spherical in shape and ranged between 6 and 16 mesh in size. The total surface area of the silica gel was 720-760 m^2/kg and the pore volume was 4.3 x 10^{-4} m^3/kg. The granules were impregnated with an aqueous solution of calcium acetate or calcium nitrate and then heat treated at 1000° or 1075°C for 4 hr. After heat treatment at the lower temperature, the calcium was present mainly as CaO, whereas after heat treatment at the higher temperature, the calcium seemed to be present as β-$CaSiO_3$. The material heat treated at the lower temperature exhibited a much higher sulfation rate than the material heat treated at the higher temperature when the materials were tested with a gas mixture containing 0.25% SO_2, 5% O_2, and 5% H_2O at 900°C. The maximum CaO content was 7.7% for the prepared sorbent.

Yang and Shen (4) also investigated the use of pure, unsupported calcium silicates as regenerable sorbents for sulfur dioxide. Samples of $CaSiO_3$, β-Ca_2SiO_4, γ-Ca_2SiO_4 and Ca_3SiO_5 were tested and compared with pure CaO. Both $CaSiO_3$ and β-Ca_2SiO_4 reacted more rapidly at 850-900°C with sulfur dioxide and oxygen than pure CaO reacted. Moreover, these silicates displayed a larger capacity for sulfation on a molar basis than the CaO displayed, and these silicates were regenerated more rapidly than CaO was regenerated. By comparison, γ-Ca_2SiO_4 and Ca_3SiO_5 reacted much more slowly than the other materials. An analysis of the reaction products indicated that calcium was chemically bonded to both silica and sulfate in the sulfated $CaSiO_3$ while silica was not chemically bonded to calcium sulfate in

the sulfated Ca_2SiO_4. After regeneration of the sulfated silicates, the crystal structures of $CaSiO_3$ and Ca_2SiO_4 were restored.

Several reports are of interest because they deal in one way or another with pelletized calcium-based sorbents. Some of these reports were reviewed previously (1). The search of sorbents for sulfur dioxide produced additional reports of interest. Kamphuis *et al*. (5) reported on the testing and regeneration of sorbents produced by pelletizing limestone particles with binders. The sorbents had "absorption capacities higher than those of the most reactive limestone types, as well as attrition resistances equaling those of the hardest natural rock types." The pellets were described as having an open microstructure, and the method of preparation was described as a relatively inexpensive one. Unfortunately, few details were provided concerning the method of preparation.

A similar method of sorbent preparation was used by Zhang *et al*. (6). Limestone was crushed to produce particles smaller than 90 μm which were then pelletized with binders and additives to produce 2 mm diameter pellets. A new machine was devised for pelletization, and the method was described as low cost. Again no further details were provided about the method of preparation. However, the sorbent was reported as having an improved microstructure with good mechanical strength and large adsorption capacity. It was also reported to be easily regenerated.

While pelletization of limestone fines is one method of preparing a macroporous sorbent, another method is that described by Sasaoka *et al*. (7). These workers exposed limestone particles to acetic acid vapors which caused the particles to swell. The particles were subsequently dried and calcined at 850°C to produce macroporous calcium oxide. This

material was then tested as a regenerable sorbent for both SO_2 and H_2S. It was concluded that swelling improved the reactivity of the material for either gas.

A rather unusual method of sorbent preparation was reported by Duisterwinkel (8) and Wolff (9). The method is based on a sol-gel process which produces 3 mm diameter spherical particles consisting of 5-8 wt.% CaO on a γ-Al_2O_3 support. After calcination at high temperature calcium aluminates are formed. The sorbent is made by first dispersing pseudo boehmite (AlOOH $\cdot$ xH_2O) powder in an aqueous solution of nitric acid and urea to produce a sol. The sol is then added dropwise to a two layer system consisting of an upper layer of a nonpolar liquid such as kerosene and a lower layer of ammonia in water. As the drops sink through the nonpolar layer they become spherical and when they interact with the aqua ammonia they gelate. Calcium can be incorporated during gelation by adding calcium nitrate to the ammonia solution. The gel is heated to evaporate water and decompose the calcium nitrate.

Wolff (9) reported that after the material had been calcined at 850°C for 10 hr, the resulting γ-Al_2O_3 support was found to have a surface area of 100 m^2/g and a pore volume of 0.3 ml/g. It appeared that CaO $\cdot$ 2Al_2O_3 was the most likely material formed at 850°C. The crushing strength and attrition resistance of the prepared sorbent were much greater than that of lime. Also when the sorbent was subjected to repeated cycles of sulfation and regeneration at 850°C, the properties of the sorbent changed very little. Even continuous heating of the sorbent for 500 hr at 850°C caused only a relatively small decrease in surface area to 80 m^2/g. However, heating the sorbent for 10 hr at 950°C reduced the surface area to 42 m^2/g and

reduced the capacity of the material for adsorbing sulfur dioxide somewhat. Heating the sorbent to 1200°C reduced its surface area to 10 m^2/g and rendered it unsuitable.

Deng and Lin (10) also applied a sol-gel process to produce both calcium-based and copper-based sorbents, but their process differed somewhat from that described above. The sol-gel technique was used to prepare a γ-alumina support which was then impregnated with a solution of calcium chloride or copper chloride. The impregnated materials were dried and then calcined at 550°C for 6 hr. The CaO content of the prepared sorbents ranged from 10 to 30 wt.%, and as the calcium content increased, the surface area decreased from 258 to 182 m^2/g and the pore volume decreased from 0.36 to 0.23 cm^3/g. When the sorbent containing 10 wt.% CaO was heated at 850°C for 168 hr, its surface area decreased to 109 m^2/g and its pore volume decreased to 0.27 cm^3/g. These properties were not greatly affected by repeated sulfation and regeneration at 850°C.

RESULTS AND DISCUSSION

Porous Alumina Substrates

A number of porous alumina substrates or catalyst carriers have been obtained and are being evaluated as potential supports for calcium-based sorbents. The substrates are generally in the form of small spherical or cylindrical beads or pellets. Some of the more promising materials are listed in Table 1 together with their significant properties. Many of the property values were supplied by the manufacturers. However, the surface area and apparent density of the materials have been measured as part of the present research effort, and the results are given in the two right hand columns of the table. It can be seen that the locally measured values agree well with the values reported by the manufacturers.

The surface area was measured with a Leeds and Northrup surface area analyzer based on the BET method of gas adsorption. The apparent density was determined by using a Quantachrome Multipycnometer to measure the apparent volume of the pellets. The as-received materials were also examined by X-ray diffractometry which revealed a fairly complex crystal structure resulting from a synthesis route that produced an unstable low temperature phase of alumina. This phase would transform to corundum at high temperature.

A comparison of the materials received from Alcoa and Norton indicates a wide variation in properties. The samples received from Alcoa had a large surface area indicating a large network of small diameter pores, while the samples from Norton had a low surface area and a network of relatively large diameter pores. Furthermore, the Alcoa samples had a relatively low apparent density compared to that of the Norton samples which suggests that the closed pore volume of the Alcoa samples was larger than that of the Norton samples.

Since the sorbents would be expected to withstand high temperatures in service and during regeneration, the temperature stability of the porous carrier is an important property. In order to evaluate the temperature stability of the Alcoa samples, small portions of each were heat treated at 450, 600, 750, 900, 1000, and 1100°C. The surface area and apparent density of the treated materials were then determined and the results are shown in Figures 1

Table 1. Alumina carriers and their properties

| Sample No.	Made by	Surface areas, m^2/g	Pore diam., μm	Apparent porosity, %	Apparent density, g/cm^3	Particle density, g/cm^3	Measured[a] area, m^2/g	Measured[a] apparent ρ, g/cm^3
DD431	Alcoa	343	--	--	--	--	412	2.21
DD831	Alcoa	339	--	--	--	--	372	2.45
DD660	Alcoa	406	--	--	--	--	417	2.43
Cl 750	Alcoa	196	--	--	--	--	229	2.54
SA3232	Norton	29.5	1.1	67.5	3.23	1.05	30.0	3.20
SA5205	Norton	0.01	136.1	48.4	3.59	1.85	0.01	3.56
SA5262	Norton	0.8	3.7	67.4	3.97	1.29	0.8	4.01
XA69257	Norton	8.4	3.4	70.9	3.74	1.09	7.6	3.75

[a]Measured at Iowa State University
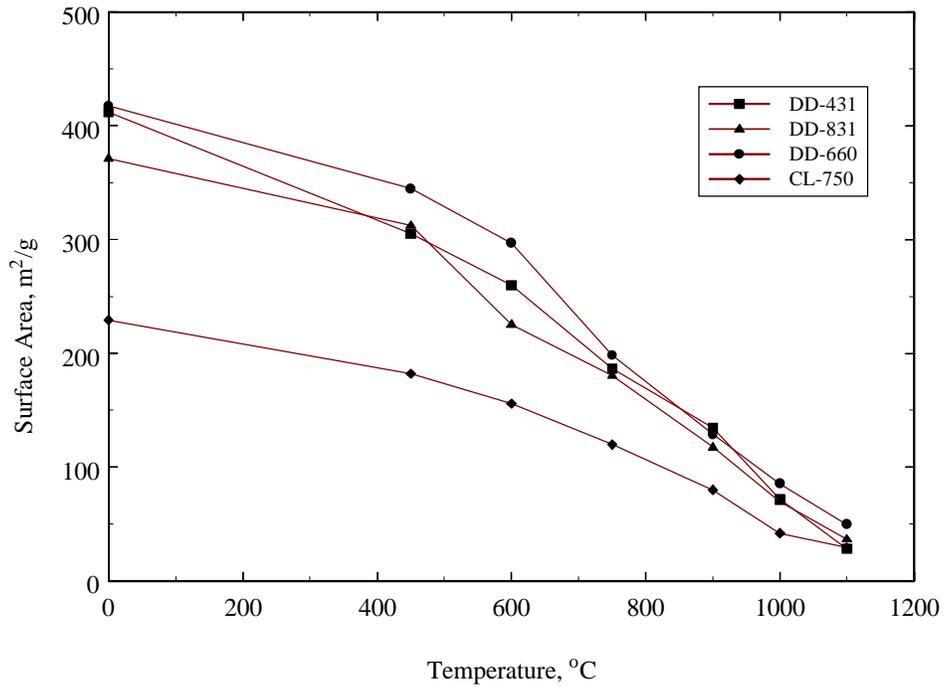
Figure 1.   Surface area of alumina samples versus temperature.
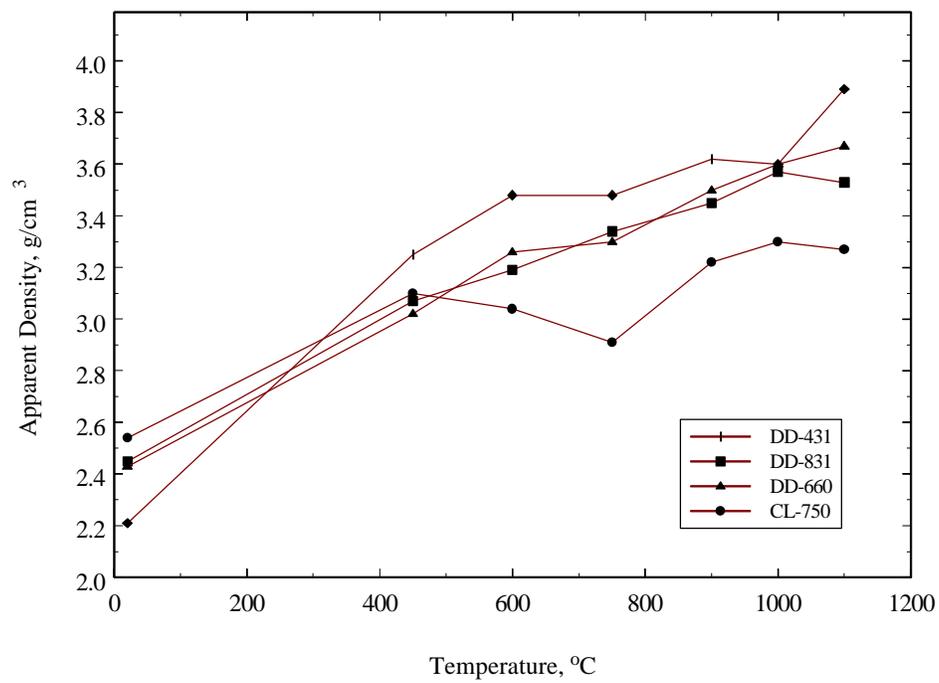

Figure 2.   Apparent density of alumina samples versus temperature.

and 2. It can be seen that the surface area of all of the samples decreased steadily as the treatment temperature was increased while at the same time the apparent density increased. These results show that the pore structure changed markedly as a consequence of the heat treatment. It is likely that smaller diameter pores disappeared while larger diameter pores may have increased in size. The overall consequences of these changes on the utility of the materials as sorbent carriers can only be determined by infusing the heat-treated materials with lime and conducting adsorption tests. The effect of the heat treatment on the Norton materials will be studied in the future.

Impregnation of Alumina Substrates

Various techniques for impregnating porous alumina substrates with calcium were investigated. The most successful method was the one used previously by Snyder *et al*. (2,3). This method involved boiling the selected substrate in an aqueous solution of calcium nitrate for several hours to infuse the pore structure with the calcium salt followed by a heat treatment to decompose the nitrate. The heating rate was carefully controlled to prevent spalling, and the treatment was concluded by holding the material at 1100°C for 2 hr.

The results of treating each of the Norton samples with a 20 mole % $Ca(NO_3)_2$ solution for 4 hr. are indicated in Table 2. The treatment was repeated three times for each material. The overall gain in weight of the material from start to completion of the heat treatment is indicated. The gain in weight should correspond to the amount of calcium oxide deposited within the pore structure of a given substrate. The indicated gain in weight was not corrected for the small loss on ignition which the materials experienced when heated to

Table 2. Gain in weight of Norton carriers with 20 mole % $Ca(NO_3)_2$ cured for 4 hr.

Sample No.	Weight gain, %				L.O.I.[a] %
	Trial 1	Trial 2	Trial 3	Average	
SA 3232	11.9	12.5	12.3	12.2	0.5
SA 5205	2.5	2.6	2.6	2.6	0.1
SA 5262	12.8	12.7	13.1	12.9	0.1
XA 69257	16.3	16.3	15.9	16.1	1.1

[a]Loss on ignition when original material was heated to 1100°C.

1100°C without first being infused with calcium nitrate. The results show that three out of four samples experienced a weight gain of 12 to 16% as a consequence of the impregnation treatment. The one exception was sample SA 5205 which gained only 2.6%. This material had a very small surface area and very large pores.

To further investigate the calcium nitrate infusion procedure, a series of tests was conducted in which the concentration of calcium nitrate and the time of exposure to the boiling and refluxing solution were varied. In each case the same heat treatment was applied. The results are indicated in Table 3. It can be seen that in two cases there was a slight increase in sample weight gain when the time of exposure to the boiling solution was increased from 4 to 8 hr. However, in one case the sample weight gain was actually lower when the time was increased. Therefore, little was gained by increasing the time. It can also be seen that reducing the concentration of the calcium nitrate solution from 20 to 10 mole % reduced the sample weight gain appreciably showing that less calcium oxide was deposited in the substrates.

Table 3. Properties of Norton carriers impregnated with CaO under different treatment
          conditions

Sample No.	Ca(NO$_3$)$_2$ mole %	Reflux, hr.	Wt. Gain, %	Apparent ρ, g/cm^3	Apparent porosity, %
SA 3232	na	0	---	3.20	67.5
	20	4	12.2	2.99	60.9
	20	8	12.7	2.86	58.7
	10	4	8.8	2.88	60.4
SA 5262	na	0	---	4.01	67.4
	20	4	12.9	3.50	58.4
	20	8	13.7	3.61	61.2
	10	4	8.3	3.51	58.2
XA 69257	na	0	---	3.75	70.9
	20	4	16.1	3.35	62.1
	20	8	15.9	3.32	62.0
	10	4	10.3	3.43	65.0

Similar tests will be conducted with the Alcoa samples in the future. Of course, the

ultimate test will be to measure the effectiveness of the impregnated samples as sorbents for

hydrogen sulfide.

Pelletized Portland Cement

Due to the encouraging results with Portland cement pellets reported by Yoo and

Steinberg (11), further study of this material as a sorbent was undertaken. A sample of type I

Portland cement powder was obtained, and a series of pelletized samples was prepared with a

small drum pelletizer. The procedure involved placing a known amount of dry powder in the

drum, and as the drum revolved a controlled amount of water was added as a fine spray. With

the right amount of water, the powder balled up into spherical pellets which could be handled.

The pellets were air-dried at room temperature for 20 hr and then soaked in water for 5 min.

After excess water was removed from the surface of the pellets, the pellets were cured at room temperature in a chamber having an atmosphere saturated with water vapor. The curing time was either 6 days or 28 days. Pellets which had been cured for 6 days were subsequently heat treated at 1100°C for 2 hr before conducting adsorption tests, whereas pellets cured for 28 days were not heat treated before testing. The pellets cured for the longer time were stronger than those cured for the shorter time, and they were solid throughout, whereas the pellets cured for the shorter time had a hard shell and powdery interior. When some of the heat-treated pellets which had been cured for 6 days were exposed to the laboratory atmosphere for about a week, they developed cracks probably because of adsorbing moisture from the atmosphere. Similar cracking did not occur when some of the pellets which had been cured for 28 days were heat-treated and then exposed to air.

In some cases a specific amount of calcium oxide powder or calcium carbonate powder was mixed with the cement powder before pelletization. To prepare pellets with either 1 or 10 w/w% CaO, calcium oxide was used, while to prepare pellets with 20 w/w% CaO, calcium carbonate was added. Pellets made with 10 wt.% CaO or less were kept in the rotating pelletizer for 1 hr, whereas those made with a relatively large amount of calcium carbonate were removed after 10 min because the pellets grew large very rapidly. The pellets made with calcium carbonate were softer than the others and had to be handled more carefully. Pellets made with 10 wt.% CaO or less were sized by screening shortly after leaving the pelletizer, while those made with calcium carbonate were air dried overnight before screening.

Table 4. Sorbents formulated with type I Portland cement (PC-I) and CaO

Identification No.	Sorbent formulation	Curing time, days	Thermal treatment
I	PC-I	6	1100°C for 2 hr
II	PC-I + 1% CaO	6	1100°C for 2 hr
III	PC-I + 10% CaO	6	1100°C for 2 hr
IV	PC-I + 20% CaO	6	1100°C for 2 hr
V	PC-I	28	None
VI	PC-I + 1% CaO	28	None
VII	PC-I + 10% CaO	28	None
VIII	PC-I + 20% CaO	28	None

A summary of the different sorbent formulations is indicated in Table 4. Sorbents I and V were made entirely of type I Portland cement, whereas the other sorbents also contained added calcium. The prepared sorbents after being heat treated at 1100°C were examined by x-ray diffractometry, and in all cases tricalcium silicate appeared to be the predominant species present. Calcium oxide was observed in all of the sorbents made with either 10 or 20 wt.% CaO.

The sorbents were tested by measuring their gain in weight when exposed to an atmosphere of pure carbon dioxide. The tests were conducted with a Seiko SSC/5200H thermogravimetric analyzer (TGA). The apparatus would accommodate only a single -6/+5 mesh pellet with a diameter of about 3.6 mm. After loading, the apparatus was heated at a rate of 10°C/min while using a nitrogen flow rate of 40 ml/min. Once at the desired temperature, the gas flow was switched to 100 ml/min of pure carbon dioxide. As adsorption took place, the temperature and gas flow rate were held constant and the weight of the pellet

was recorded. After 2 hr, the gas flow was switched back to nitrogen and the apparatus was allowed to cool.

The first series of tests was conducted to determine the effect of temperature on the rate of adsorption of carbon dioxide by the sorbent containing 1 wt.% CaO which had been cured for 6 days. The results presented in Figure 3 indicate that the sample treated at 850°C experienced the largest gain in weight (12.1%) in 2 hr while the sample treated at 900°C experienced almost no gain in weight. This result indicated that 900°C is probably close to the equilibrium decomposition temperature for the reaction product formed by the adsorption of carbon dioxide on type I Portland cement under a partial pressure of 1.0 atmosphere.

The second series of tests was conducted to determine the effect of CaO concentration on the rate of adsorption of carbon dioxide at 850°C using samples which had been cured for 6 days and heat-treated at 1100°C. The results presented in Figure 4 show that the samples which contained any amount of added lime adsorbed carbon dioxide at a much higher rate than the sample with no added lime. However, there was little difference among the results achieved with 1, 10, or 20 wt.% CaO. Therefore, it appeared that the principal effect of the added lime was to modify the microstructure of the pellets so that the interior was more readily accessible to carbon dioxide.

The third series of tests was carried out to observe the effect of several cycles of loading and regeneration on the capacity and regenerability of sorbent II which contained 1 wt.% CaO and had been cured for 6 days. The sample was loaded with carbon dioxide at 850°C over a 2 hr period and then was regenerated by passing nitrogen over it at the same temperature for about 1.5 hr. The results are indicated below for three cycles.
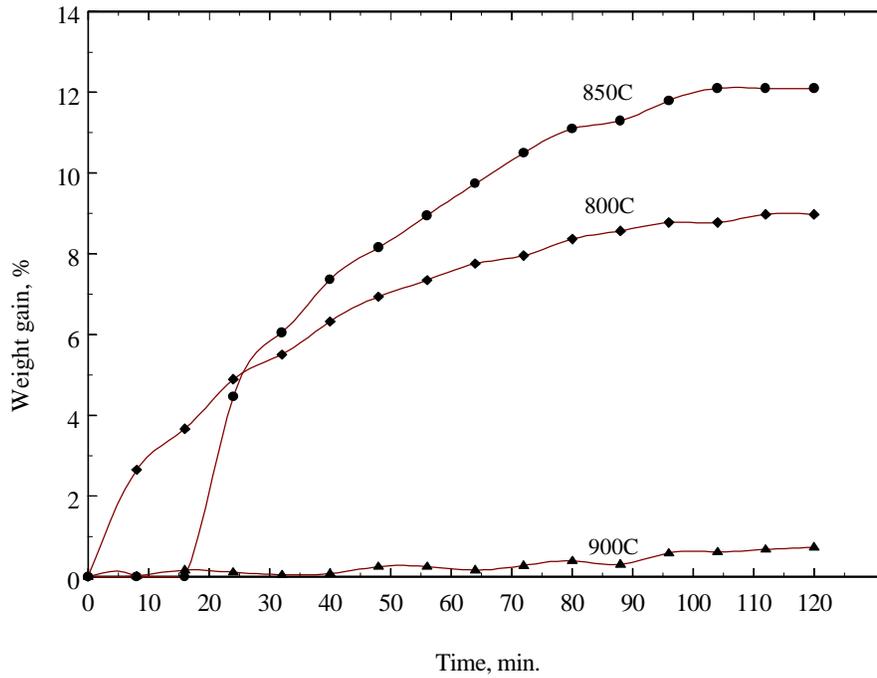
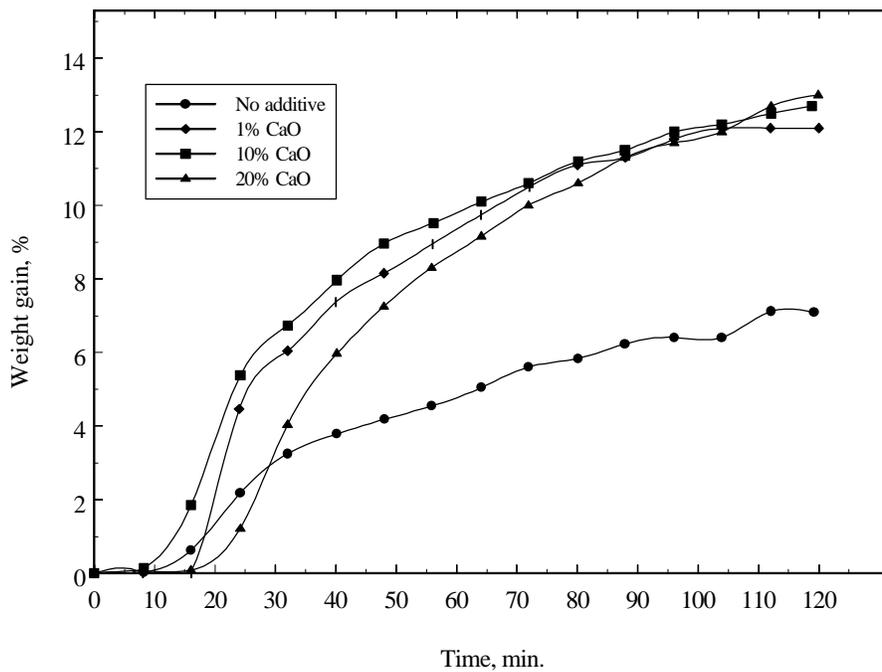Figure 3.   Effect of temperature on adsorption of CO_2 by PC-I with 1% CaO cured for 6 days.

Figure 4. Effect of CaO content on adsorption of CO_2 at 850°C by PC-I cured for 6 days.

Cycle No.	Adsorption wt. gain, %	Regeneration conversation, %
1	11.04	99.8
2	10.35	100.0
3	10.35	99.8

The extent of regeneration reported above represents the percent of the weight gain during adsorption which was lost subsequently during regeneration. It can be seen that after the first cycle there appeared to be no change in the capacity of the sorbent. Moreover, regeneration always seemed to be complete.

The fourth series of tests was conducted to see whether the initial heat treatment at 1100°C had an effect on the performance of the sorbent. Sorbent III with 10 wt.% CaO and a curing time of 6 days was selected for these tests. Two samples which had received the heat treatment and one sample which had not were used. The results presented in Figure 5 indicate that the initial rate of adsorption may have been slightly greater for the sample which had not been heat treated than for the other two samples. However, the difference in results for the two heat-treated samples was greater than the difference in results between the untreated sample and either heat-treated sample. Therefore, it appeared that the effect of the heat treatment was slight.

The fifth series of tests was conducted with samples which had been cured for 28 days and not been heat treated. The results in Figure 6 show that the sample with 1 wt.% CaO performed the same as the sample with no added lime. However, the sample with 10 wt.% CaO seemed to have a noticeably greater adsorption capacity than the others. It can be seen that the trends displayed in Figure 6 differ from those displayed in Figure 4. This
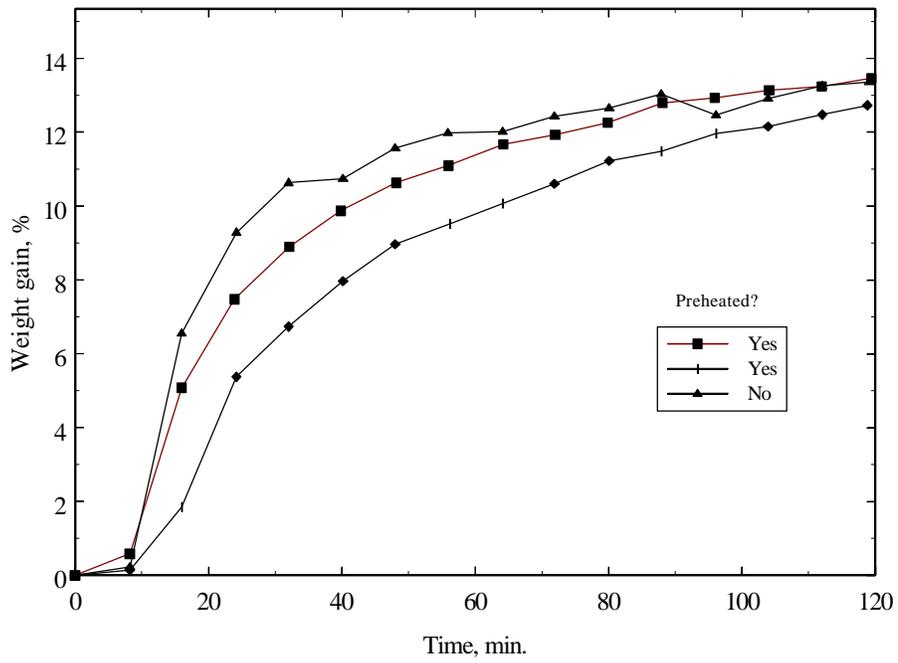
Figure 5.   Effect of preheating PC-I with 10% CaO cured for 6 days on adsorption of CO_2 at 850°C.
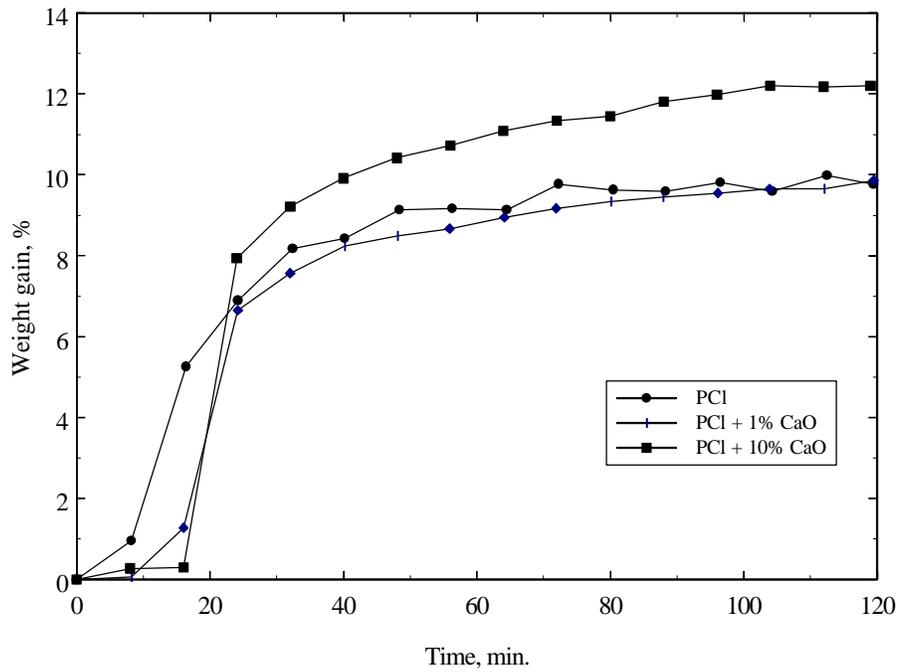

Figure 6.   Effect of CaO content on adsorption of CO_2 at 850°C by PC-I cured for 28 days.

difference could have been due to an interaction between the added lime and the cement either during the curing stage or during the heat treatment which one set of samples received but not the other set.

These very preliminary results indicate that while Portland cement is a promising material for making an adsorbent, it will require an extensive study to determine the necessary conditions for producing a good sorbent for hydrogen sulfide because there are so many variables.

CONCLUSIONS

By extending the literature review to publications dealing with the development of synthetic calcium-based sorbents for sulfur oxides, several publications were found which will assist the development of similar sorbents for hydrogen sulfide. The characterization of available alumina substrates, which may prove suitable for impregnation with calcium, revealed materials with a wide range of surface areas and pore sizes. However, some of the higher surface area materials lost much of their surface area when heat treated at temperatures ranging up to 1100°C. Materials with a relatively large pore size and low surface area were successfully impregnated with calcium by soaking the materials in a concentrated calcium nitrate solution and then heat treating the product to 1100°C to decompose the nitrate. Other potential sorbents were prepared by pelletizing type I Portland cement and mixtures of cement and lime. Preliminary tests of the pelletized materials showed them to be effective sorbents for carbon dioxide at 850°C but completely ineffective at 900°C. Therefore, carbon dioxide should not interfere with their use for adsorbing hydrogen sulfide at 900°C and higher temperatures.

REFERENCES

1. Wheelock, T. D., L. K. Doraiswamy, K. Constant, T. Akiti, and J. Zhu, "Development of a Calcium-Based Sorbent for Hot Gas Cleanup," Semi-Annual Technical Progress Report, October 1, 1996, to March 31, 1997, Chemical Engineering Department and Center for Coal and the Environment, Iowa State University, Ames, Iowa.

2. Snyder, R. B., W. I. Wilson, I. Johnson, and A. A. Jonke, "Synthetic Sorbents for Removal of Sulfur Dioxide in Fluidized-Bed Coal Combustors," ANL/CEN/Fe-77-1, Argonne National Laboratory, Argonne, IL, June 1977.

3. Snyder, R. B., W. I. Wilson, I. Johnson, and A. A. Jonke, "Synthetic SO_2 Sorbents for Fluidized-Bed Coal Combustors," *Journal of the Air Pollution Control Association,* **27**, 975-981 (1977).

4. Yang, R. T., and M.-S. Shen, "Calcium Silicates: A New Class of Highly Regenerative Sorbents for Hot Gas Desulfurization," *AIChE Journal,* **25**, 811-819 (1979).

5. Kamphuis, B., A. W. Potma, and U. Spitsbergen, "Regenerative Sorbents for High Temperature Desulfurization of Coal Combustion Gases," Proceedings of the 6th Annual International Pittsburgh Coal Conference, Vol. 2, 1989, pp. 994-1003.

6. Zhang, H., X.-Y. Huang, X.-Y. Zhang, and B.-C. Wu, "Development of Advanced Synthetic Sulphur Sorbent for Fluidized Bed Coal Combustion," Proceedings of the 10th International Conference on Fluidized Bed Combustion, Vol. 1, 1989, pp. 591-595.

7. Sasaoka, E., M. A. Uddin, and S. Nojima, "Novel Preparation Method of Marcroporous Lime from Limestone for High-Temperature Desulfurization," *Ind. Eng. Chem. Res.*, **36**, 3639-3646 (1977).

8. Duisterwinkel, A. E., *Clean Coal Combustion with In Situ Impregnated Sol-Gel Sorbent,* Delft University of Technology, The Netherlands, 1991.

9. Wolff, E. H. P., *Regenerative Sulfur Capture in Fluidized Bed Combustion of Coal: A Fixed Bed Sorption Study,* Delft University Press, The Netherlands, 1991.

10. Deng, S. G., and Y. S. Lin, "Synthesis, Stability, and Sulfation Properties of Sol-Gel-Derived Regenerative Sorbents for Flue Gas Desulfurization," *Ind. Eng. Chem. Res.*, **35**, 1429-1437 (1996).

11. Yoo, H. J., and M. Steinberg, Calcium Silicate Cement Sorbent for H_2S Removal and Improved Gasification Process, Final Report, DOE/CH/00016-1494, Brookhaven National Laboratory, Oct. 1983.