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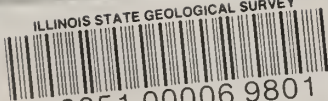
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Final Technical Report

**A METHOD  
FOR IMPROVING SULFUR CAPTURE  
USING COAL/SORBENT PELLETS**

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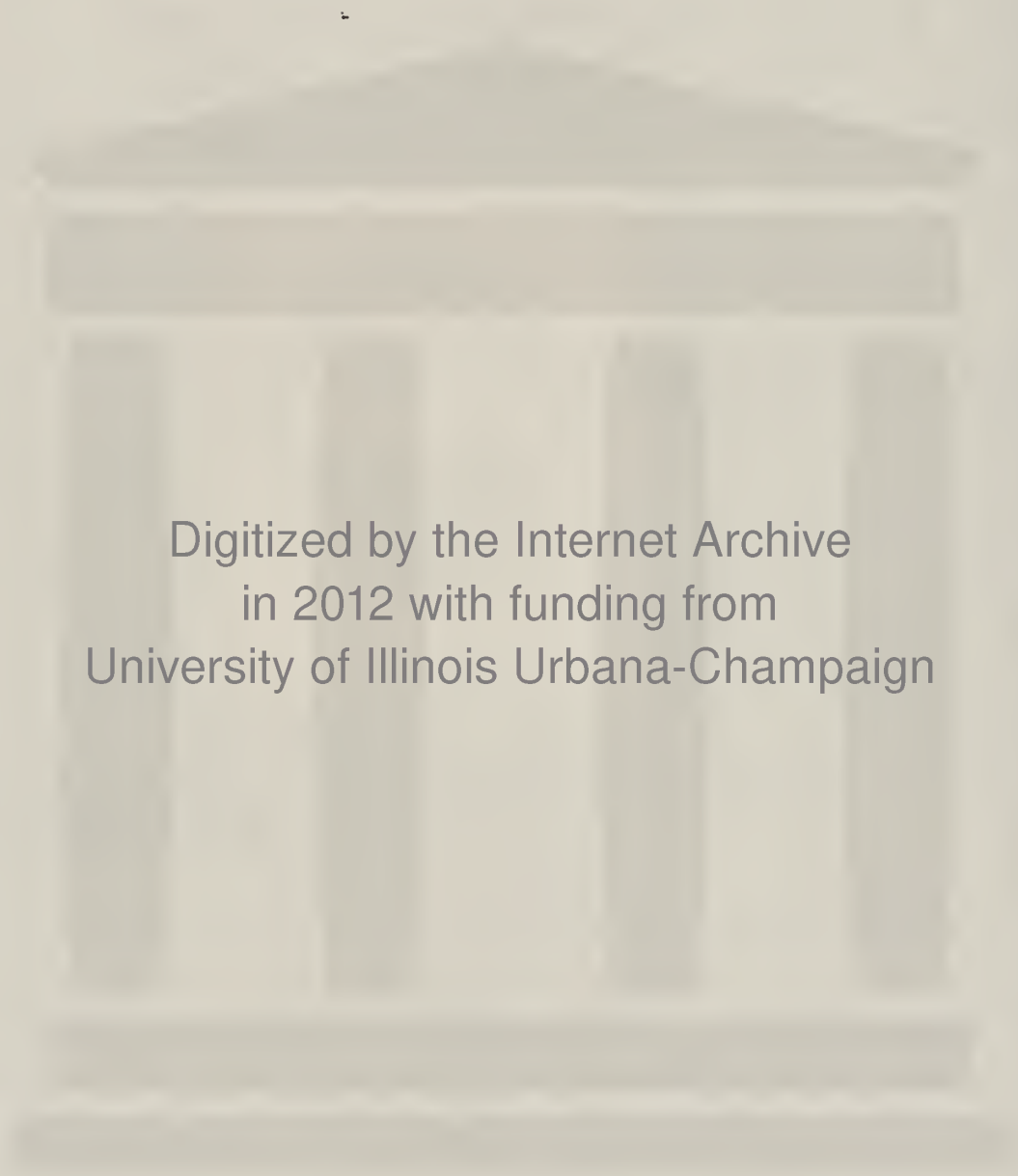
Illinois State Geological Survey

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through the  
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**FINAL TECHNICAL REPORT**  
September 1, 1989 through August 31, 1990

Project Title: A METHOD FOR IMPROVING SULFUR CAPTURE USING COAL/SORBENT PELLETS

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**ABSTRACT**

Current coal mining and processing procedures produce significant quantities of fine coal with limited marketability. The objective of this work was to utilize these fines to economically produce a fuel which will meet anticipated sulfur dioxide emission levels. To accomplish this, the process of pelletizing fine coal with a sulfur capturing sorbent such as calcium hydroxide was studied. Two potential applications were considered - fluidized-bed combustors and industrial stoker boilers. Carbonation, which is the reaction of calcium hydroxide with carbon dioxide to produce a bonding matrix of calcium carbonate, was investigated as a method for improving pellet quality and decreasing binder costs.

Test results indicate that carbonation significantly improves compressive strength, impact and attrition resistance and essentially waterproofs pellets having a 14% lime content. Binders such as corn starch or molasses do not produce waterproof pellets capable of withstanding rainfall that might occur during outdoor storage.

Combustion testing of carbonated pellets prepared using a mixture of IBC-106 and 14% lime (2:1 Ca/S ratio) indicate sulfur captures as high as 80% are achievable at 850 °C, the approximate operating temperature for fluidized-bed combustors. This sulfur capture would allow many high sulfur Illinois coals to be burned at the year 2000 compliance SO<sub>2</sub> emission limit of 1.2 lbs SO<sub>2</sub>/10<sup>6</sup> Btu. Combustion tests conducted at 1350 °C, using a quadrupole gas analyzer to continuously monitor SO<sub>2</sub> and CO<sub>2</sub> emissions, indicate appreciable initial sulfur captures. However, continued exposure to this relatively high temperature results in the release of captured sulfur. The higher temperature testing indicates sulfur capture for coal/sorbent pellets in stoker boilers can be improved by reducing residence time in the high temperature zone or by lowering the maximum temperature to which the pellets are exposed.

## EXECUTIVE SUMMARY

Modern mining methods have resulted in the generation of an increased amount of fines. In many cases, these fines are not processed because there is a limited market for fine coal. Disposal represents not only a lost opportunity for profit but also an increased waste disposal cost. If a pelletization method can be developed to economically produce a clean burning fuel, marketability of these fines would increase substantially. To accomplish this, the process of pelletizing coal with a sulfur capturing sorbent such as calcium hydroxide is being studied.

Previous attempts at forming coal/sorbent pellets have required use of a binder such as soya residue or cornstarch to develop pellets of acceptable strength. For this work, carbonation is being investigated as a method to reduce the need for these binders. Carbonation is the reaction of calcium hydroxide or calcium silicates (cement) with carbon dioxide to produce a bonding matrix of calcium carbonate (and silica gel when cement is used).

This research project consisted of four tasks. In Task 1 (carbonation), the objective was to determine methods of producing finely crystalline reaction products by carbonation of lime (calcium oxide which reacts with water to form calcium hydroxide) and portland cement in water. In Task 2 (sorbent testing), the goal was to use a thermogravimetric analyzer to determine the sulfation capacities of selected sorbents prepared in Task 1, and, if different crystal sizes and structures influenced sulfur capture.

In Task 3 (pellet formation), carbonation of coal/calcium hydroxide pellets was investigated and pellets were prepared for combustion tests. In Task 4 (combustion testing), the objective was to determine the sulfur capture of the carbonated coal/sorbent pellets.

The results for Task 1 indicate carbonation can be an effective method to reduce the crystal size of the carbonate reaction products. The test results also indicated that, under similar conditions, lime carbonates at a much faster rate than cement. This increased rate could result in a less expensive pellet carbonation procedure.

Work performed in Task 2 indicates that carbonation can be an effective method for increasing the sulfation capacities of lime and portland cement (sulfation testing gives an indication of the sorbent's potential to capture sulfur). The sulfation capacities of the feed lime and cement were 56 and 40%, respectively. Carbonation was able to produce sorbents with sulfation capacities over 90% for lime and greater than 80% for cement. Scanning electron microscope (SEM) analyses indicated that for lime this increased sulfation capacity is most likely due to a reduction in crystal size rather than creation of a specific crystal form. For cement, the increased sulfation capacity is likely due to a decrease in crystal size and also to the fact that, when carbonated, the calcium carbonate formed is on the outer surface of the less reactive, low-lime silica gel. This would increase the exposure of the calcium to the sulfur gas and thus increase sulfation capacity. Although carbonation testing indicates that

the sulfation capacity of cement can be appreciably improved, calcium hydroxide is a superior sorbent for carbonation due to its greater sulfation capacity and because cement has an appreciable inert content (approximately 35%).

The results of Task 3 indicated that carbonation is an effective method to improve pellet quality and potentially reduce binder costs. Results showed that for pellets with a calcium hydroxide level of 13.1% or greater, carbonation can significantly improve compressive strength, increases impact and attrition resistance and essentially waterproofs the pellets. Binders such as corn starch or molasses do not produce waterproof pellets capable of withstanding rainfall that might occur during shipping or outdoor storage. This weatherproofing is likely due to the formation of a cementitious matrix of calcium carbonate which binds the pellets together.

In a test performed using 3.5 % corn flour (approximately 90% corn starch by weight on a dry basis) as a binder and a 3050 psi compaction force, pellets were formed with compressive strengths, attrition resistance and impact resistance comparable to carbonated 17.4% (2:1 Ca/S) calcium hydroxide pellets. However, when immersed in water, the corn flour pellets totally fell apart within 5 minutes. Similar behavior was observed for the uncarbonated pellets of 17.4% calcium hydroxide. When these pellets were carbonated for one hour though, they showed no visible signs of deterioration in 24 hours. Compressive strength testing did, however, show a loss of strength. The pellets retained about 1/3 of their original strength (151 lbs to 48 lbs crushing force), but still had sufficient integrity to withstand handling. A relevant factor to note is that binder costs per ton of coal pelletized are comparable for both 3.5% corn flour and 17.4% calcium hydroxide at \$8.75 and \$10.58, respectively. Calcium hydroxide, of course, has the advantage of being a sulfur capturing sorbent.

Combustion tests were conducted to evaluate coal/sorbent pellets as feed for fluidized-bed combustors (FBC) and industrial stoker boilers. Pellets were prepared using IBC-106 (3.77% total sulfur, 9% ash) from the Illinois Basin Coal Sample Program. Variables investigated included temperature, sorbent, the effect of carbonation on sulfur capture and the benefits of physical cleaning. Combustion tests were conducted using a high temperature furnace coupled with a Quadrupole Gas Analyzer (QGA) to monitor the release of  $\text{SO}_2$  and  $\text{CO}_2$  during combustion. For each test, the furnace was brought to the desired combustion temperature before placing the pellets in the hot zone. Combustion and monitoring of gases began immediately.

Two sorbents were evaluated, lime ( $\text{CaO}$ ) and calcium hydroxide ( $\text{Ca(OH)}_2$ ). The lime was added to a coal slurry and mixed for two minutes before filtration. The mixing allowed the lime sample to hydrate, so both samples tested were calcium hydroxide, although formed under different conditions. The calcium hydroxide tested is a commercially available sample prepared from the lime tested. The results for both sorbents were similar, indicating no distinct advantage for either, other than the fact

that lime is slightly cheaper than calcium hydroxide on the basis of calcium content.

Results from tests varying lime addition and temperature indicate sulfur captures as high as 80% are achievable using 2:1 Ca/S (14% lime) pellets at 850 °C, the approximate operating temperature for many fluidized bed combustors. This sulfur capture would allow many high sulfur Illinois coals to be burned at the year 2000 compliance SO<sub>2</sub> emissions limit of 1.2 lbs SO<sub>2</sub>/10<sup>6</sup> Btu.

For stoker boilers, temperatures are much higher than for FBC's. Flame temperatures of 1350 °C are common, although temperature gradients are likely in the bed. For combustion tests at 1350 °C, sulfur captures were low with a best result of 22.8%. However, output from the quadrupole gas analyzer indicates appreciable initial sulfur captures, although continued exposure to high temperatures results in release of this sulfur. The CO<sub>2</sub> emissions data from the QGA, though, did indicate most of the carbon is burned before appreciable sulfur is released. This indicates improved sulfur capture can be attained in stoker boilers for coal/lime pellets by reducing the time the pellet spends in the hot zone.

The effect of carbonating pellets on sulfur capture was also investigated. Generally, it is accepted that calcium carbonate is not as effective at capturing sulfur as calcium hydroxide. This being the case, there was some concern that carbonating the pellets would result in a substantial decrease in sulfur capture. The data gathered do seem to indicate some loss in sulfur capture but not an excessive amount (<5% on average). Because the calcium hydroxide is quite fine to begin with, the carbonated crystals formed are also likely to be quite fine which would lessen the differences between the two sorbents.

The effect of physical cleaning on sulfur capture was also investigated. Samples of IBC-106 were ground to 90% minus 90 microns and cleaned by froth flotation. In this step, total sulfur was reduced from 3.76% to 3.14%. Ash was reduced from 9% to 5%. The lime content for both samples was kept constant so the Ca/S ratios for the physically cleaned samples increased from 1:1 and 2:1 to 1.2:1 and 2.4:1, respectively. The data indicated no significant improvement in sulfur capture at 850 °C. Sulfur capture was largely dependent on the Ca/S ratio. At higher temperatures, 1100 °C and 1350 °C, there was some evidence of improved sulfur capture for the physically cleaned coal.

In summary, work to date indicates carbonation is an effective method to improve pellet quality and potentially decrease binder costs. Carbonated coal/sorbent pellets can be burned to achieve high sulfur captures (approximately 80%) at 850 °C with a 2:1 Ca/S ratio of lime addition. For higher temperatures, appreciable initial sulfur captures are possible, but this sulfur is released with continued exposure to high temperatures. For stoker boilers, the implication is that sulfur captures can be improved by reducing pellet residence time in the high temperature region (possibly sacrificing some carbon burnout) and/or reducing the maximum temperatures to which the pellets are exposed.



## OBJECTIVES

The objective of this work was to economically produce a clean-burning fuel from fine Illinois coal. An integrated process was investigated including a physical coal cleaning step, pelletization with lime (CaO), calcium hydroxide or calcium silicates (cement) and combustion testing to determine sulfur capture efficiency. Pellets were evaluated as feed for either fluidized-bed combustors or industrial stoker boilers.

Previous attempts at forming coal/sorbent pellets have required the use of a binder such as soya residue or cornstarch to develop pellets of acceptable strength. In this study, carbonation was investigated as a method to reduce the need for these binders. Carbonation (reaction with CO<sub>2</sub>) of lime and calcium silicate compounds results in the formation of a cementitious matrix of calcium carbonate and a low lime silica gel (when cement is used). In addition, by adjusting carbonation parameters, the reaction products and crystal sizes can be influenced. With proper conditions, extremely fine (<1 micron) crystals can be produced which could be highly reactive with sulfur during combustion.

To accomplish these goals, research was conducted consisting of the following four tasks:

1. CARBONATION -- to investigate methods of producing finely crystalline reaction products by carbonation of lime and portland cement.
2. SORBENT TESTING -- to determine the sulfation capacities of selected sorbents.
3. PELLET FORMATION -- to investigate carbonation as a method for reducing binder costs and to prepare pellets for combustion testing.
4. COMBUSTION TESTING -- to determine the sulfur capture potential of coal/sorbent pellets at temperatures ranging from 850 °C to 1350 °C.

## BACKGROUND

Environmental concerns about acid rain, due in part to sulfur emission during coal combustion, have prompted research to determine methods of reducing these emissions. A method being investigated to accomplish this is the use of calcium based sorbents to act as sulfur capture agents during combustion. One application of this approach has been to mix coal with lime and some form of binder to make pellets as feedstock for industrial stoker boilers. Drawbacks of this approach are moderate sulfur captures for the relatively high temperature stokers and high binder costs. Parallel to this work, advanced physical fine coal cleaning processes are being developed to more efficiently reduce inorganic (pyritic) sulfur levels prior to combustion. These fine coal cleaning processes have potential application not only in future work to deep clean a finely ground preparation plant product, but also for recovering the fine coal (-100 mesh) currently rejected in many plant waste streams.

Each year 2-3 million tons of these fines are disposed of in Illinois due to limited marketability and questions of recoverability (Bhagwat, 1989).

Waste coal fines present several advantages toward producing a clean-burning fuel. One, the particle size of the coal is already quite fine and significant amounts of pyrite and other mineral matter are liberated and would be rejected by advanced froth flotation. Two, evidence gathered at the ISGS indicates that the fines fraction from a preparation plant often has significantly lower levels of organic sulfur than the coarse coal from the plant (Lytle, 1989). This is most likely due to differences in maceral composition. Lastly, since the coal in many cases is being disposed of, mining costs are essentially zero. In fact, waste disposal costs would be lessened which would further improve process economics. The combination of these factors indicate potential for plant waste fines as an economical clean-burning fuel source for fluidized-bed combustors and stoker boilers. This would significantly increase their marketability and help improve the overall economics of mining and processing coal.

## RESULTS AND DISCUSSION

**Task 1. Carbonation** -- The objective for this task was to vary carbonation conditions with the intent to produce different carbonate crystal structures and sizes. To accomplish this, CO<sub>2</sub> gas was bubbled through mixtures of lime or portland cement in water. Also, some tests were performed with cement in water/methanol mixtures. Sample sizes were varied to influence carbonation rate and crystal sizes and structures. A scanning electron microscope (SEM) was used to inspect and photograph selected samples. The purpose of this task was largely to prepare samples to be used in Task 2.

### Procedures

Experiments were conducted in magnetically stirred 1000 ml volumetric flasks. A ceramic frit connected to a CO<sub>2</sub> tank was placed in each flask and a valve was used to regulate the flow of CO<sub>2</sub> at 1.4 standard cubic feet per hour.

For each test, CO<sub>2</sub> is bubbled through 500 ml of stirred solution until it is saturated with CO<sub>2</sub> (>1 hour). After the system is saturated, the lime or cement is added to the liquid and CO<sub>2</sub> is continuously bubbled through the stirred solution for the prescribed length of time. For lime, sample sizes were 6.8, 13.7, 27.4, and 54.7 grams. For cement, sample sizes were 12.5, 25, 50, and 100 grams. After carbonation, the sample is vacuum filtered and rinsed twice with methanol to remove any remaining water. The sample is dried under vacuum at 60 °C and stored in a desiccator until analysis.

For cement, the extent of carbonation was determined by placing a weighed portion of each sample into a ceramic crucible. The sample is dried at 105, 350, 500 and 900 °C for 24 hours with the weight loss being recorded for each step. Between 105 °C and 350 °C any water or cement hydration

products are evolved. Between 350 °C and 500 °C both vaterite and small amounts of calcite are calcined. From 500 °C to 900 °C, calcite is calcined. Samples analyzed by x-ray diffraction showed no signs of vaterite so weight loss between 350 °C and 900 °C was used to calculate percent carbonation.

For the carbonated lime samples, the extent of carbonation was determined using information obtained from a Cahn balance. As part of the procedure for sulfation capacity testing (see below) weight loss due to dehydration and calcination was determined. After allowing for weight loss due to dehydration, weight loss from calcination was used to determine extent of carbonation.

## Results

The results from carbonation testing, shown in Figures 1,2 and 3, indicate that lime carbonates much more readily than cement. For lime, the 6.8 gram sample was 100% carbonated in five minutes. For cement, similar results were not achieved in a 2.5 hour carbonation period. Reaction times for the cement samples were further slowed when using water/methanol mixtures. This increased reactivity for lime indicates an advantage for lime when used as a binder. The increased rate would lead to shorter carbonation times and consequently permit a smaller sized reactor to be used. Results of SEM work will be discussed in conjunction with Task 2 data.

**Task 2. Sorbent Testing** -- The objective of this task was to use a thermogravimetric analyzer to determine the sulfation capacities of lime and cement samples carbonated in Task 1. Sulfation testing gives an indication of a sorbent's potential to capture sulfur. This procedure was used to evaluate carbonation as a method to improve sulfur capture and to determine if certain crystal forms produced in Task 1 resulted in more effective sorbents. If testing indicated certain crystal forms were desirable, attempts would be made to produce these crystals in the carbonated coal/sorbent pellets. Sulfation testing, however, does not accurately reproduce thermal history in an actual system, so these tests were used only as an indication of potential for SO<sub>2</sub> removal and to determine potential trends among carbonated sorbents.

### RG Cahn Balance Test Procedure (Sulfation Capacity Tests)

A Cahn RG microbalance was used to determine the sulfation capacities of the carbonated sorbents. A typical experiment proceeded as follows. The microbalance reactor is calibrated and purged with nitrogen before each experiment to ensure that accurate weight measurements are obtained. The sample is heated in a 2 l/min flow of nitrogen at a constant rate (20 °C/min) to 850 °C. During heat-up, the weight loss occurring as a result of CO<sub>2</sub> evolution (calcination) is monitored. For the lime samples, weight loss due to dehydration is also monitored. Because the samples to be tested have undergone various degrees of carbonation, sample sizes were chosen such that, after weight loss, the sample weighed approximately 20

mg. After the weight stabilized, the reaction gas mixture containing 0.3% SO<sub>2</sub>, 5% O<sub>2</sub> and 20% CO<sub>2</sub> in N<sub>2</sub> was introduced at a flow rate of 2 l/min. The increase in weight due to sulfation was recorded continuously for 90 minutes, after which time, sulfation was essentially complete. At the end of the reaction time, the gas was switched to nitrogen and the reactor was cooled to room temperature.

### Dupont TG Test Procedure (Pyrolysis Testing)

Weight loss profiles were obtained with an Omnitherm thermogravimetric analyzer (TGA) coupled with an Omnitherm QC25 Programmer/Controller. The TGA system was interfaced with an IBM PC-XT computer through a Keithley DAS series 500 data acquisition system to provide automated data collection and storage. The unit was programmed for a heating rate of 20 °C per minute, going from ambient to a maximum of 950 °C. Tests were run with a nitrogen gas flow of 100 cc/min. Weight losses from samples with starting weights of approximately 30 mg were monitored continuously by computer, with weight loss curves, as well as rate of loss curves, available on command.

### Cahn Balance Results

Sulfation capacity tests were performed on lime and cement samples prepared in Task 1. Samples were selected to represent a range of carbonation conditions and carbonate contents. The results (Tables 1 and 2) indicate carbonation is an effective method to improve sulfation capacity. Carbonated lime was found to have a higher potential for sulfur capture than the carbonated cement samples tested. The sulfation capacities of the feed lime and cement tested were 56 and 40%, respectively. Carbonation was able to produce sorbents with sulfation capacities over 90% for lime and greater than 80% for cement.

For the lime data in Table 1, carbonated samples were selected from all four of the sample sizes tested. Also, results are shown for the feed lime and for the commercially available calcium hydroxide prepared using this lime. The data showed that the more fully carbonated samples have the highest capacity to capture sulfur, which is even above that for the commercially available calcium hydroxide prepared using this lime. This increased reactivity for a carbonate is most likely due to carbonation decreasing the crystal size of the sorbent. For carbonates, sulfation capacity is largely a function of particle size (Rostam-Abadi, 1986).

There is, however, no indication of any trends showing different capacities to capture sulfur among the carbonated lime samples. For example, the 6.8 gram sample, 100% carbonated in 5 minutes, had a 91% sulfation capacity. The 54.7 gram sample, which took greater than 2 1/2 hours to fully carbonate, had a 93% sulfation capacity.

Inspection of SEM photos of these two samples (Figures 4 and 5) do indicate differences in crystal structure, although the sulfation capacities are similar. The results suggest that increased sulfation

capacity is more dependent upon carbonation reducing crystal size rather than changing crystal form.

The data for cement carbonation presented in Table 2 also indicated a trend towards increased sulfation capacity with increased carbonation. Sulfation capacities ranged from 40% for the feed cement to 86% for the 100 g, 24 hour sample. (Denotes 100 gram sample carbonated 24 hours). This increase is likely due to two factors. First, the carbonation reaction involves conversion of calcium silicates (cement) to calcium carbonate and a low lime silica gel. The carbonate reaction product forms on the outer surface of the less reactive silica gel which should lead to greater exposure to the sulfur gas and therefore, increased sulfation capacity. Also, the carbonate crystals formed should be finer leading to a further improvement in sulfation capacity. However, these results are not as promising as those obtained for lime. When this information is considered along with the fact that cement has an appreciable inert content (approximately 35%), it is apparent that lime is a more desirable carbonated sorbent than cement.

### TG Results

Six cement samples carbonated in Task 1 were analyzed by TG to determine weight loss profiles. Differing weight loss profiles could be an indication of differing crystal size and structure. The results (Figure 6) show similar profiles for all but the 25 gram sample carbonated in methanol.

Inspection of SEM photographs of these samples does indicate differing crystal structures as seen in Figures 7 and 8. The sample carbonated in methanol has a much more needle-like structure than, for instance, the 100 g, 24 hour sample. However, sulfation capacity tests (Table 2) do not indicate that the needle-like crystals produced increased sulfur capture, if anything just the opposite seems to be the case. This work was preliminary in nature and minimally informative, so, no follow up work was performed.

**Task 3. Pellet Formation** -- The objective of this task was to investigate carbonation as a method to decrease the need for binders such as corn starch or molasses often used when forming coal/sorbent pellets. Promising carbonation conditions would be used to prepare pellets for Task 4 (Combustion Testing). Because of the results obtained in Tasks 1 and 2 and initial results obtained in this task, reduced emphasis was placed on testing cement. Increased emphasis was placed on comparing lime vs. calcium hydroxide for the potential to reduce overall process costs. The coal used for all tests is IBC-106 from the Illinois Basin Coal Sample Program.

### Formation Procedures

Pellets were formed using a 1/2 inch (inside diameter) stainless steel cylindrical mold and piston. Samples were compacted using a laboratory

Carver hydraulic press and pellets were approximately 1/2 inch in diameter by 3/8 inches in height. Standard formation procedure was to place the sample in the mold, compact with the desired pressure for 10 seconds, and then remove the pellet from the mold.

Prior to reconstitution, samples of IBC-106 were wet-ground to a particle size of 90% passing 90 microns in a laboratory rod mill. The ground sample was then split using a rotary wet splitter and stored in sealed containers until used.

For most samples, the sorbent/binder is added to the slurry sample, shaken by hand for two minutes, and filtered using a Buchner funnel. (When lime is added in this manner it reacts with water to form calcium hydroxide - for further information see mixing section). The sample is then dried to the desired moisture content and thoroughly mixed before pelletizing. For the results in section two, the coal/sorbent blend was forced through an 8 mesh sieve before pelletization to improve mixing.

### Carbonation Procedure

Carbonation testing was conducted using a desiccator connected to a CO<sub>2</sub> source, a weather balloon and a vacuum line. The procedure followed was to fill the weather balloon with CO<sub>2</sub>, close the valve, place the pellets in the desiccator, evacuate the desiccator using the vacuum line, then open the valve to the weather balloon to introduce the CO<sub>2</sub> into the desiccator. The samples are removed at the end of the desired carbonation time.

\*NOTE: Data obtained in Tables 3, 4, 5, and 6 were obtained before a vacuum drier was obtained. Samples were dried to the desired moisture for pelletization using an air drier set at 95 °F. Samples in Tables 11-14 were prepared using a vacuum drier set at a temperature of approximately 70 °C and a gauge pressure of minus 29 inches Hg.

Compressive strength testing - Compressive strength is measured using a Tinius-Olsen compressive strength testing machine. The planar ends of the cylindrical pellets are placed between two parallel plates, a load is applied and compression to failure recorded. Results reported are an average of 3 results.

Attrition Resistance - For attrition resistance testing, 6 pellets are weighed, placed on a 20 mesh sieve and shaken for 20 minutes using a conventional Ro-Tap sieve shaking machine. The weight of the pellets remaining on the sieve after 20 minutes is recorded and the percent loss calculated.

Drop Testing - Drop tests are conducted by dropping pellets onto a concrete floor at specified heights and noting when an agglomerate breaks into two or more pieces. Minor chipping around the edges is not considered failure. Initial test height is 18". If a pellet survives 25 drops at this height, the height is increased to 36" and another pellet

tested. If the pellet survives 25 drops at this height, a new pellet is tested at 72". Results reported are the average of 3 tests.

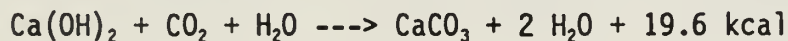
Weatherability - Weatherability tests are conducted by immersing 3 pellets in water for 24 hours and then measuring compressive strength in the manner described previously.

## Results

Research indicates carbonation can be an effective method to improve pellet characteristics such as compressive strength, weatherability, resistance to attrition and impact (drop testing). Important variables investigated were: percent moisture, binder type (lime, calcium hydroxide, or cement), binder level, and extent of carbonation time. Results from this test program will be presented in two sections. The first will discuss the effects of proper moisture content, compaction force on strength development, and the effectiveness of various binders and binder levels. The second section discusses results from a characterization program conducted to further determine the benefits of carbonation.

### Section One

Moisture is an important variable influencing strength development due to carbonation. For calcium hydroxide the reaction is as follows:



As seen, moisture is required for the reaction to occur. However, if too much moisture is present in a pellet, the pore spaces are filled and CO<sub>2</sub> must diffuse through the water to reach the calcium hydroxide and react. This severely slows the rate of reaction. The ideal situation is when there is just enough moisture to coat the coal and calcium hydroxide particles. This allows the CO<sub>2</sub> to diffuse into the pellet and react with the calcium hydroxide to form a cementitious matrix of calcium carbonate.

An example of the importance of proper moisture may be observed in Table 3. For this work, a 14% lime (2:1 Ca/S ratio) coal/lime mixture was split and dried to 3 different moisture levels. (NOTE: 14% lime is slightly higher than 2:1 Ca/S ratio for this coal. However, there is a loss during mixing due to solubility which brings the ratio close to 2:1. For more information see the mixing section.) Pellets were then formed using a 3050 psi compaction force. After formation and before carbonation pellet moisture contents were 32, 28, and 22%, respectively (handling, and pellet formation reduce moisture content). Table 3 shows that there is significant strength development for the 32% and 28% moisture samples. However, for the 22% moisture sample, no appreciable increase in strength is observed. This is possibly due to a lack of sufficient moisture for the reaction to occur. More work is required though to fully determine optimum moisture condition for carbonation of coal/calcium hydroxide mixtures.

Potential effectiveness of carbonation at these higher moisture levels (approximately 30%) is an indicator of a potential low cost reconstitution method because such a moisture level is achievable by vacuum filtration. If extrusion is the desired reconstitution technique, the extruder could be used to squeeze the pellets to the required moisture levels. If, as will be investigated in next year's work, burning coal can be used as a CO<sub>2</sub> source for carbonation, the pellets can be carbonated and partially dried simultaneously.

Optimum carbonation time was not determined because it is a function of CO<sub>2</sub> concentration and was outside the scope of this year's efforts. However, work was done to investigate this variable. Table 4 shows results for a 2:1 Ca/S ratio lime sample compacted with pressures ranging from 610 to 6100 psi. As may be observed, little if any, strength development occurs after 1 hour. This result is in accordance with other work done earlier in the year which showed little benefit for extended carbonation time. More work investigating this variable will be done next year.

Once a proper moisture level and one hour carbonation period were established, a series of tests was conducted to determine the effect of carbonation on improving compressive strength. For the tests in this series, the mixtures were prepared and dried to approximately 30% moisture before pelletizing. Compaction forces ranged from 610 to 6100 psi. IBC-106 pellets formed with no binder as well as pellets formed with 1:1 and 2:1 Ca/S ratios of lime and cement added were tested. Also, for comparative purposes, additional pellets to which corn flour had been added were tested.

Table 5 indicates that lime, cement, and corn flour addition increase compressive strength. However, only the 2:1 Ca/S ratio lime sample shows an increase in strength due to carbonation. This sample does show an approximate 100% increase in strength after 1 hour of carbonation. Selected results from Table 5 are shown graphically in Figure 9. A discussion of each binder system follows.

IBC-106 only - Agglomerates of coal only were prepared covering a range of moisture contents and compaction pressures to establish baseline levels. Results from these tests are listed in Table 6. As may be observed, strength development is largely independent of moisture content and is a function of compaction pressure.

IBC-106/lime - Samples of IBC-106 and lime (see Table 7 for analyses) were evaluated for compressive strength at 14% lime addition (2:1 Ca/S ratio) and at 7.0% lime addition (1:1 Ca/S ratio). The results in Table 5 indicate an approximate 100% increases in compressive strength for the 14% lime addition agglomerates.

Table 5 also shows that for the 7.0% lime mixture compressive strengths were above those for the mixtures containing only coal; however, carbonation did not increase compressive strength for either mixture. This is probably due to the presence of an insufficient amount of lime to form a bonding matrix when carbonated.



IBC-106 cement - Samples of IBC-106 and cement (see Table 8 for analyses) were pelletized at two Ca/S ratios; 1:1 (10.5% cement) and 2:1 (21% cement). The results indicate increases in compressive strength above that for the mixtures containing only coal; however, carbonation did not increase compressive strength for either mixture. This could be due to insufficient mixing. Because the cement was air dried to the desired moisture content, which can take several hours when air dried as these samples were, it has a chance to partially hydrate. During final mixing before agglomerate formation, it was noticed that a reasonable amount of the cement had clumped together in small lumps and hardened. This indicates a lack of sufficient mixing which would hinder strength development.

Strength development for cement was expected to be at least equivalent to that for lime. However, because of the success obtained with lime and the fact that cement has a reasonable amount of inherent ash, reduced emphasis was placed on any further work with cement.

IBC-106/corn flour - IBC-106/corn flour agglomerates were prepared to better evaluate the effectiveness of carbonation as a method to reduce binder requirements. For this work, 3.5% corn flour was added to an IBC-106 filter cake, mixed, dried to 30% moisture and pelletized. A 3.5% corn flour level (12.5 ¢/lb) was chosen because the cost per ton of coal (\$8.75) is comparable to the expense for 15% lime addition (\$10.08). The corn flour used was approximately 90% corn starch by weight. It also contained protein (8.5%) and minor amounts of ash, crude fiber and oil. The results in Table 9 show significant increases in compressive strength for the 610 and 3050 compaction pressures. Strength appears to decline at the 6100 compaction pressure; however, this could be due to scatter in the data.

## Section Two

A test program was conducted to follow up on the results in Section One and to further quantify the potential benefits of carbonation. Compressive strength, attrition resistance, weatherability and drop testing were conducted on a number of binder systems. IBC-106 and mixtures with lime, calcium hydroxide, (see Table 9 for analyses), corn flour and a corn flour/lime mixture were tested. For informational purposes, binder costs are listed in Table 10. The calcium hydroxide is the commercially available sample prepared from the feed lime tested. The results of the program are discussed by test category.

Compressive strength testing - Compressive strengths (Table 11) ranged from a low of 19 lbs for the pellets prepared using IBC-106 only to 151 lbs for the carbonated 2:1 Ca/S calcium hydroxide sample. (NOTE: For calcium hydroxide addition, loss due to solubility was not accounted for. Based on work with lime, calcium hydroxide levels are likely to be about 6% less than stated.) The 151 lbs attained by this sample was a three fold increase over the uncarbonated strength of 49 lbs. The second highest compressive strength was obtained using the 3.5% corn flour mix.

The general trend for the data is that the 1:1 Ca/S samples show no increase in strength due to carbonation, but the 1.5: 1 and higher samples, however, do show a considerable improvement in strength. The 1:1 Ca/S lime/1% corn flour sample mix also had an improvement in strength due to carbonation. This is possibly due to the corn flour providing a better surface to which the lime may bond.

The carbonated 2:1 Ca/S lime sample did not develop a level of strength comparable to the sample with an equivalent ratio of calcium hydroxide, but it did have an approximate 2-fold increase in strength over the uncarbonated sample (27 to 52 lbs). The reason for this lower strength is not known because other samples of 2:1 Ca/S lime have developed strengths as high as 122 pounds with a 1-hour carbonation period. Most likely, the sample was not well mixed which decreased the initial strength and limited the potential for further strength development. This lower compressive strength indicates that the results reported for attrition resistance, weatherability, and drop testing would be improved if the sample had obtained full strength.

Attrition resistance testing - Results for attrition resistance (see Table 12) closely follow the trends seen for compressive strength. However, the best results were obtained by the 3.5% corn flour mixture with only 6% loss to the fines fraction. The carbonated 2:1 calcium hydroxide sample was a close second with only a 13% loss. The poorest result was for the IBC-106 sample with a 100% loss to the fines.

As was the case for the compressive strength tests, the 1.5:1 and 2:1 Ca/S ratio samples and the 1:1 Ca/S lime/corn flour mixture showed improvements with a one hour exposure to CO<sub>2</sub>.

Drop Testing - Drop tests results (Table 13) also followed the trends of the compressive strength and attrition resistance testing. Best results were obtained for the 3.5% corn flour mixture followed closely by the carbonated 2:1 Ca/S calcium hydroxide sample. Both of these samples required drop heights of 72" before pellet breakage was observed. The only other samples to survive 25 drops at 18" were the 2:1 Ca/S lime and 1.5:1 Ca/S hydrated lime samples at 36".

Weatherability - The benefits of carbonation are most readily apparent from the weatherability test (Table 14). All samples other than the carbonated 2:1 Ca/S lime, 1.5:1 Ca/S calcium hydroxide and 2:1 Ca/S calcium hydroxide pellets dissolved within 5 minutes of their immersion in water. The carbonated pellets mentioned, however, maintained their integrity for 24 hours and retained on the order of 1/3 of their original compressive strength. This ability to maintain strength is probably due to the formation of a cementitious matrix of calcium carbonate that holds the pellet together. The 1:1 Ca/S samples likely do not have enough lime or calcium hydroxide to form a bonding matrix. Improved resistance to water penetration is an important quality if pellets are shipped in open rail cars. If a sudden rain storm is enough to severely degrade pellet quality, this would cause severe handling problems when unloading the rail car.

Mixing - To determine if a cost savings could be realized by utilizing lime in place of calcium hydroxide and also to determine the effect of lime addition on filtration rate, the following mixing procedure was established. Lime (CaO) is added to a coal slurry of 10-15% solids by weight (110 g coal). The sample is then mixed for two minutes prior to filtration. The scenario envisioned was that of adding lime to the coal slurry as it is introduced into a filtration device. The lime could then hydrate and also be intimately mixed with the coal as it is filtered. Lime could also be used to increase filtration rate and reduce cake moisture.

The results indicate that lime does increase filtration rate and would most likely hydrate to form calcium hydroxide. The following tests were calculated to arrive at this conclusion.

The objective of the first test was to determine the extent of conversion of lime to calcium hydroxide and the loss of lime due to solubility in water. Lime, when placed in water, hydrates according to the following reaction:



Thus, one gram of lime would result in 1.32 grams of calcium hydroxide if the sample is fully hydrated and no lime is lost due to solubility in water. (Calcium hydroxide solubility  $\cong$  1 g/liter at room temperature).

For this test, 16.55 grams of lime was added to approximately 700 ml of distilled water, mixed for two minutes and filtered under vacuum (gauge pressure of minus 20" Hg) in a 5 1/2" diameter Buchner funnel. To remove all the material from the sample container, distilled water was used resulting in a total filtrate volume of 1050 ml. Total filtration time was 10 minutes 30 seconds. After filtration, the sample was dried in an air-dry oven at 95 °F. The filtrate was analyzed for pH and calcium content; the filter cake was weighed and analyzed by TG under pyrolysis conditions.

The results are reported in Table 15 and show a loss of 1.05 grams of lime or 6.5% of the total. The TG test performed on the dry sample indicated the sample was 80% calcium hydroxide, 12.5% carbonate and 7.5% lime. The high degree of hydration was expected, but the degree of carbonation was not. The carbonation likely occurred during the period the sample was air dried (> 24 hours) and indicates that care must be taken during drying to prevent premature carbonation.

To determine the benefits of lime addition on filtration characteristics, another test was conducted. In this test, two 110 gram samples of coal (IBC-106, 90% minus 90 microns) were slurried with approximately 700 cc of tap water resulting in a slurry of 12.5% solids. This is in the same general range as that of a concentrate in a flotation launder. To one sample, 16.55 grams of lime (equivalent to a 2:1 Ca/S ratio for IBC-106) was added, mixed for two minutes and filtered. The other sample (without lime addition) was filtered as is. Both samples were filtered in the

Buchner funnels as described previously. Water was added to rinse each sample container resulting in filtrate volumes greater than 700 cc. The results (see Table 16) indicate a nearly two-fold improvement in filtration time for the sample with lime addition. Also, both samples were filtered for a total of 15 minutes and the cake moisture determined. The sample without lime had a cake moisture of 40%. For the sample filtered with lime cake moisture was 32.8%.

The results from these tests indicate that lime addition before filtration may present advantages when it comes to filtration characteristics, product moisture content and mixing that would balance the loss of soluble sorbent in water. One other item to consider from a plant operations point of view is the effect of buildup of lime in the plant recycle water. This build up would decrease loss of sorbent due to solubility. Its effect on flotation would also have to be determined. In the copper industry, lime is sometimes added to flotation circuitry to maintain a pH in the range of 10.4 for pyrite depression. On the negative side, lime addition could result in deposits on piping and other equipment which could be a problem. To determine the truly best pelletization method, factors not directly related to pellet formation, such as dewatering, flotation effects, and product handling problems must be addressed.

#### **Task 4. Combustion testing**

Combustion Testing - The objective of this task was to determine the sulfur capture potential of pellets prepared using procedures developed in Task 3. To evaluate carbonated coal/sorbent pellets as combustion feed, four variables were investigated: sorbent, temperature, the effect of carbonation of sulfur capture, and the benefits of precombustion pyrite removal (physical cleaning).

#### Equipment and Procedures

Because temperature is a critical factor influencing sulfur capture, considerable effort was expended to modify the combustion testing equipment to accurately measure pellet combustion temperature.

The apparatus used is shown in Figure 10 and consists of: a high-temperature furnace capable of operating at temperatures up to 1350 °C, a mullite combustion tube, a LFE computerized temperature controller, a Dycor quadrupole gas analyzer (QGA), a Compaq personal computer, and two gas wash bottles. A second oxidation zone (filled with CuO and held at 800 °C) was made in the mullite tube to assure that all the volatiles are oxidized during combustion to CO<sub>2</sub> and SO<sub>2</sub> prior to exiting to the tube. The combustion furnace temperature is controlled by a thermocouple located in the center of the furnace outside of the mullite tube. A second thermocouple was positioned inside the mullite tube adjacent to the pellet to obtain a more accurate temperature profile of the pellet as it burns. As the combustion gases exit the mullite tube a continuous sample is taken through a capillary tube (50 μm) and monitored for CO<sub>2</sub> and SO<sub>2</sub> by the QGA. The QGA, the LFE temperature controller, and the inside thermocouple are

connected to the Compaq PC which controls the data acquisition for each combustion experiment.

Combustion tests are performed using air with a flow rate of 560 cc/min. For each test the furnace is brought to the desired combustion temperature and the pellet placed in the furnace. (To fit into the combustion boat, the pellets used are 1/4 of the size produced in Task 3 or approximately 1/4" square). Combustion and monitoring of combustion gases by the QGA begins immediately. The main flow of combustion gas passes through the two consecutive gas wash bottles filled with hydrogen peroxide which traps the sulfur released during combustion. The trapped sulfur is precipitated as BaSO<sub>4</sub> and weighed to determine the amount of sulfur released during combustion. The residue from each combustion test is acid leached to determine residual sulfur and to allow a material balance to be performed for each test.

## Results

Each of the variables investigated; temperature, sorbent, carbonation and physical cleaning are discussed separately. Data from all tests are reported in Tables 17-19.

Sorbents - Two sorbents were investigated, lime and calcium hydroxide. The lime was added to the coal slurry as discussed in Task 3 (mixing section) which indicated that hydration does occur. Thus, both samples tested are calcium hydroxide, but formed under different conditions. Nonetheless, they will be referred to as lime and calcium hydroxide in the text. The calcium hydroxide used is the commercial version prepared from the feed lime tested. The results indicate similar sulfur capture for both sorbents at 850 °C. If there is an advantage, it lies with the lime. However, this difference could be due to differences in pellet quality or scatter in the data.

Another factor could be that the carbonated lime pellets increased in strength only from 32 to 53 lbs and calcium hydroxide pellets increased in strength from 78 to 145 lbs. There is some evidence that carbonation does decrease sulfur capture (discussed later in the carbonation section). Both the carbonated and uncarbonated strengths indicate significant differences in pellet quality. Because of this, it is difficult to determine if the lack of strength development is due to carbonation and not some other factor such as insufficient mixing.

Temperature - Two of the potential applications envisioned for coal/sorbent pellets are industrial stoker boilers and fluidized bed combustors. The operating temperature for these systems differ dramatically. Fluidized bed combustors commonly operate at a temperature of approximately 850 °C. Stoker boiler temperatures are much higher. Temperatures measured by optical pyrometer are often around 1350 °C. However, this temperature is a flame temperature and temperature gradients are likely in the bed. To evaluate coal/sorbent pellets for these two applications, combustion tests at temperatures of 850, 1100 and 1350 °C were performed.

The results at 850 °C indicate that a sulfur capture of 80.4% is achievable for a 2:1 Ca/S lime (14% by weight) ratio. This sulfur capture would allow this and many high sulfur Illinois coals to be burned at anticipated compliance SO<sub>2</sub> emission levels (1.2 lbs SO<sub>2</sub>/million Btu). Sulfur captures for a 1:1 Ca/S lime (7.5% by weight) were somewhat lower - 50.8%.

Sulfur captures for the two higher temperatures - 1100 °C and 1350 °C were, as expected, lower than for 850 °C. At 1100 °C, sulfur captures were 57.9% and 12.5% for the 2:1 and 1:1 Ca/S ratios, respectively. At 1350 °C, sulfur capture dropped further to 1.4 and 1.5 at the two ratios. These low captures are not surprising since calcium sulfate decomposes at less than 1350 °C.

Although measured sulfur captures at 1350 °C were very low for both Ca/S ratios, data gathered using the quadropole gas analyzer indicate that lime addition does result in appreciable initial sulfur capture. This sulfur is released, however, with continued exposure to high temperatures. This is illustrated in Figure 11, which is a plot of combustion time vs. ion current. The ion current is proportional to partial pressure. This figure shows that once a pellet is placed in the "hot zone" (at about 1 1/2 minutes in the figure) there is an immediate release of sulfur for the 0:1 Ca/S sample, reduced emissions for the 1:1 Ca/S pellet, and significantly reduced emissions for the 2:1 Ca/S ratio pellet. However, continued exposure to the 1350 °C temperature results in the release of this sulfur. Figure 12 is a similar plot of the 2:1 Ca/S pellet showing SO<sub>2</sub> and CO<sub>2</sub> (an indicator of combustion) emissions. As may be observed, by the time the sulfur is released, a significant amount of the pellet has burned. This indicates that increased sulfur captures for coal/sorbent pellets in stoker boilers may be possible by reducing the time the pellet spends in the "hot zone". This would be in accordance with work done by Consolidated Coal company in plant scale stoker tests. Their findings were that maximum sulfur capture occurred with higher grate speeds. This would result in reduced residence time in the stoker (Douglas, 1990).

Physical Coal Cleaning - Precombustion pyrite removal was investigated for potential improved sulfur reduction. Samples of IBC-106 were wet ground in a laboratory rod mill to 90% minus 90 microns and cleaned by froth flotation. The 3.76% total sulfur, 9% ash coal sample was cleaned to 3.1% total sulfur and 5% ash. The lime contents for both samples were kept constant at 7.0% and 14% by weight so Ca/S ratios were 1:1 and 2:1 for IBC-106 and 1.2:1 and 2.4:1 for physically cleaned IBC-106.

The data indicate that at 850 °C, sulfur captures are similar. For a 2:1 Ca/S ratio, sulfur capture for IBC-106 was 80.4%. For physically cleaned IBC-106 (2.4:1 Ca/S), sulfur capture was 76.7% (average of 3 runs - 71.6, 78.0 and 80.7%). For IBC-106 at a 1:1 Ca/S ratio, sulfur capture was 50.6%; and, for physically cleaned IBC-106 (1.2:1 Ca/S), sulfur capture was 54.9% (average of 55.2 and 54.5%).

At higher temperatures, there does appear to be a benefit from physical cleaning. At 1100 °C sulfur captures for IBC-106 at 1:1 and 2:1 Ca/S

ratios, were 57.4 and 12.5%. For physically cleaned IBC-106 sulfur captures for the 1.2:1 and 2.4:1 Ca/S ratios were 70.6 and 32.7%.

Sulfur captures at 1350 °C were less than 2% for all pellets except for the physically cleaned 2.4:1 Ca/S pellet which had a sulfur capture of 19.95% (average of 22.8 and 15.1%). This higher sulfur capture could be due to the pellet(s) being removed from the combustion furnace earlier than other samples, but the quadrupole plot indicates that the pellet(s) (in both cases) were not removed until CO<sub>2</sub> emissions had ceased. So there is some indication that pyrite removal improves sulfur capture at higher temperatures which should lead to improved results for stoker boilers.

Carbonation - Because calcium hydroxide is acknowledged to be a better sulfur capture sorbent than calcium carbonate, there is some concern about the effect of carbonation on sulfur capture. The results do indicate some decrease due to carbonation (<5% on average for all comparable results), but not an excessive reduction in capture. This is most likely due to the carbonate formed being very fine and to the intimate mixing throughout the pellet. Also, the pellet may not carbonate all the way to the center. Results are presented graphically in Figure 13. In this Figure, Ca/S ratios were adjusted to account for the loss of calcium hydroxide due to solubility during mixing (see Task 3) which results in Ca/S ratios of 0.94/1 and 1.88/1, respectively. Sufficient lime was added, however, to account for loss due to solubility so Ca/S ratios are 1:1 and 2:1 after accounting for this loss. The results indicate some decrease in sulfur capture due to carbonation for the calcium hydroxide samples at the 2:1 Ca/S level. However, the carbonated lime pellet achieved a sulfur capture equivalent to the non-carbonated calcium hydroxide sample. This could be to lime being a better sorbent, scatter in the data, or to the fact the lime pellets did not carbonate as much as the calcium hydroxide pellets (sorbent section). More tests need to be run to fully determine the effect of carbonation on sulfur capture. This will be done in the coming year.

## SUMMARY AND CONCLUSIONS

The purpose of this project was to investigate a method to economically produce a clean burning fuel from fine Illinois coal. Each year a significant amount of fine coal is disposed of at many Illinois preparation plants. Coal/sorbent pellets were evaluated as potential fuel for fluidized-bed combustors and industrial stoker boilers. Several findings in this year's work have the potential of improving the economics or effectiveness of coal/sorbent pellets.

Carbonation has been demonstrated as a potential method to improve pellet quality and reduce the need for additional binders such as corn starch or soya residue. Carbonation of lime, calcium hydroxide and cement were all considered. Lime and calcium hydroxide were considered to be superior sorbent/binders because of better binding characteristics, sulfation capacities, and because cement has a significant inert content (approximately 35%). In work performed by Battelle Columbus to prepare coal/hydrated lime briquettes (Conkle, 1983) economic analysis was performed

assuming a 6% by weight addition of soya residue. This amount of soya residue would cost \$7.80 (1983 dollars) per ton of coal briquetted. Carbonation as an alternative binding mechanism may be able to reduce these costs significantly.

Lime addition was investigated for its effect on filtration rate and cake moisture. An addition of 14% lime (equivalent to a 2:1 Ca/S ratio) was found to significantly increase the filtration rate and reduce cake moisture content. This represents a potential flowsheet consideration when determining point of lime addition.

For combustion testing, sulfur captures of 80% were achieved at 850 °C; the approximate operating temperature for many fluidized-bed combustors, using IBC-106/lime pellets. This sulfur capture would allow many high sulfur Illinois coals to be burned at the year 2000 compliance SO<sub>2</sub> emission limit of 1.2 lbs SO<sub>2</sub>/10<sup>6</sup> Btu. At a higher temperature of 1350 °C, sulfur captures were low. However, evidence gathered using a quadrupole gas analyzer indicates significant initial sulfur captures, but this sulfur was released with continued exposure to high temperatures. This indicates that sulfur capture using coal/sorbent pellets in stoker boilers may be improved if care is taken to reduce the time the pellets spend in the high temperature zone.



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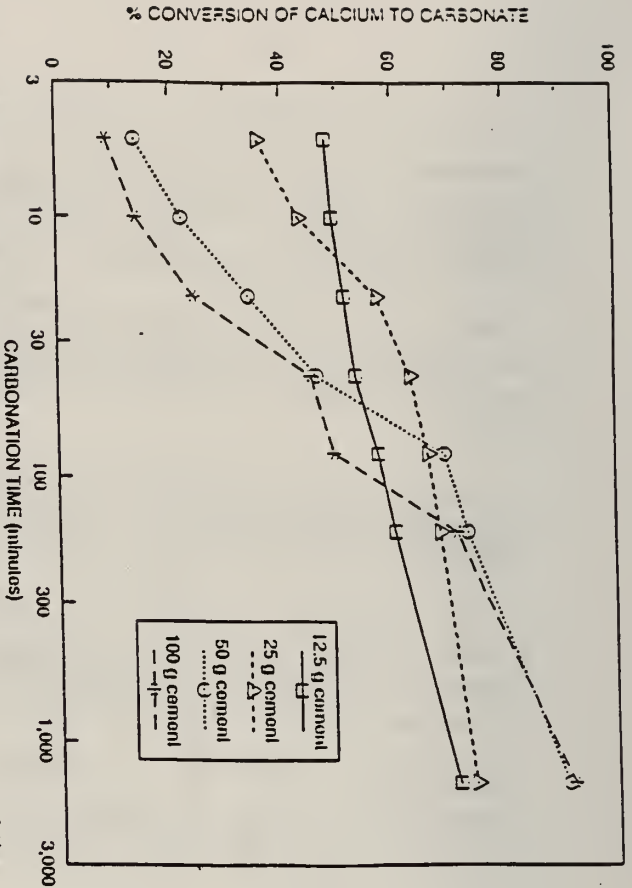


Figure 1.-Per cent conversion of calcium in portland cement to calcium carbonate as a function of time for samples carbonated in 500 ml of water.

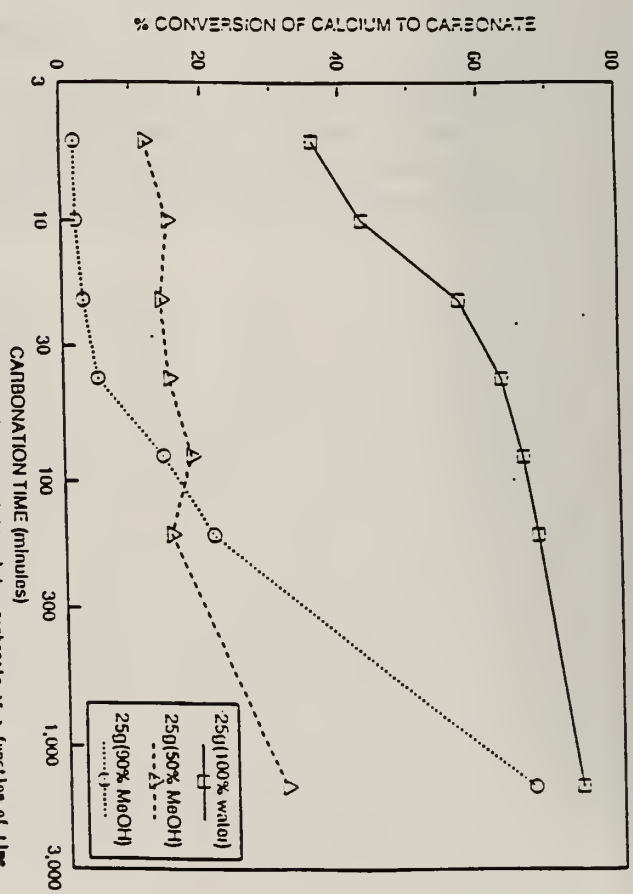


Figure 2.-Per cent conversion of calcium in portland cement to calcium carbonate as a function of time for 25g samples carbonated in 500 ml of water and water/methanol mixtures.

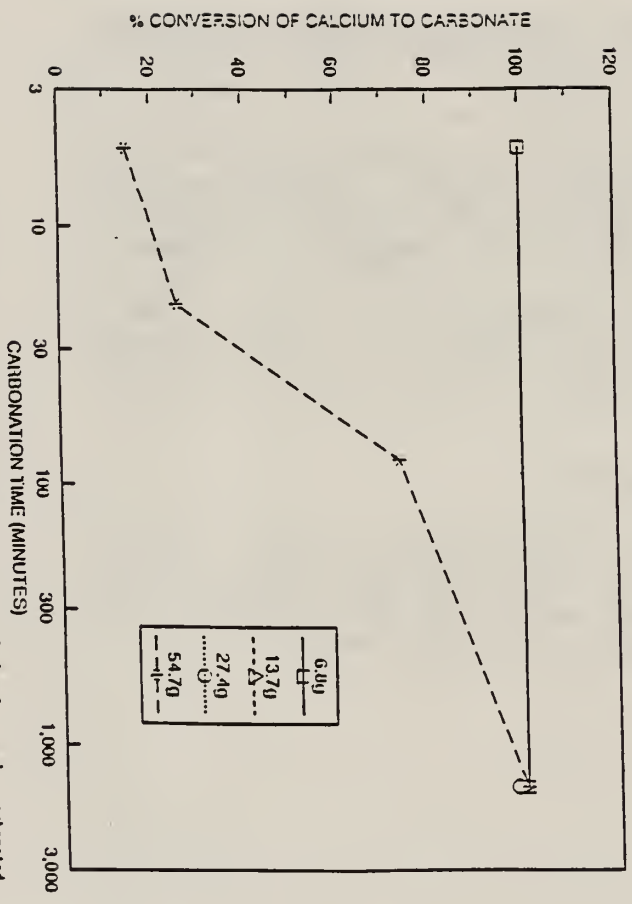


Figure 3.-Per cent conversion of time to calcium carbonate as a function of time for samples carbonated in 500 ml of water.

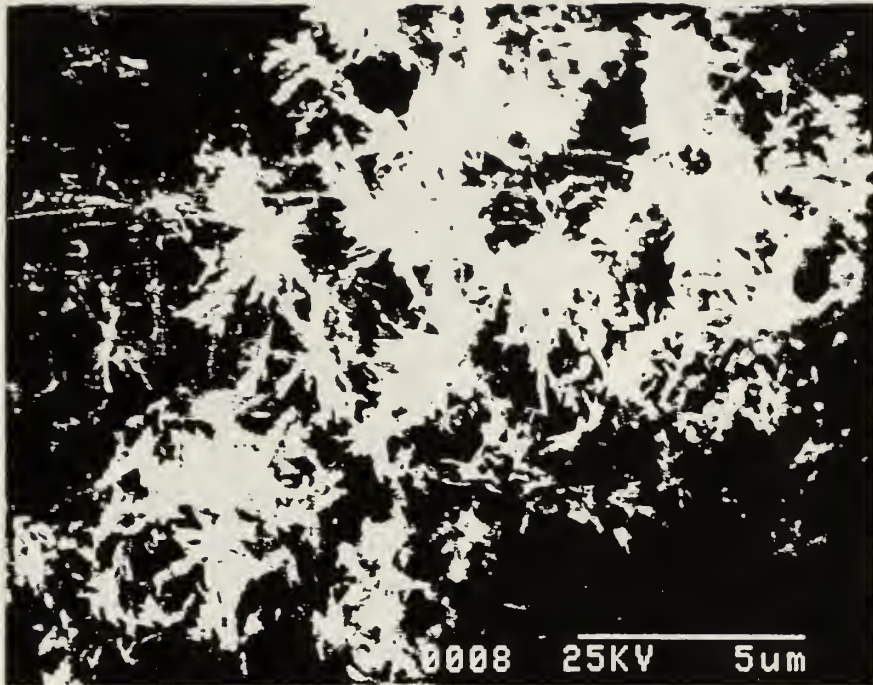


Figure 4.-SEM photomicrograph of the 6.8 gram lime sample carbonated five minutes.

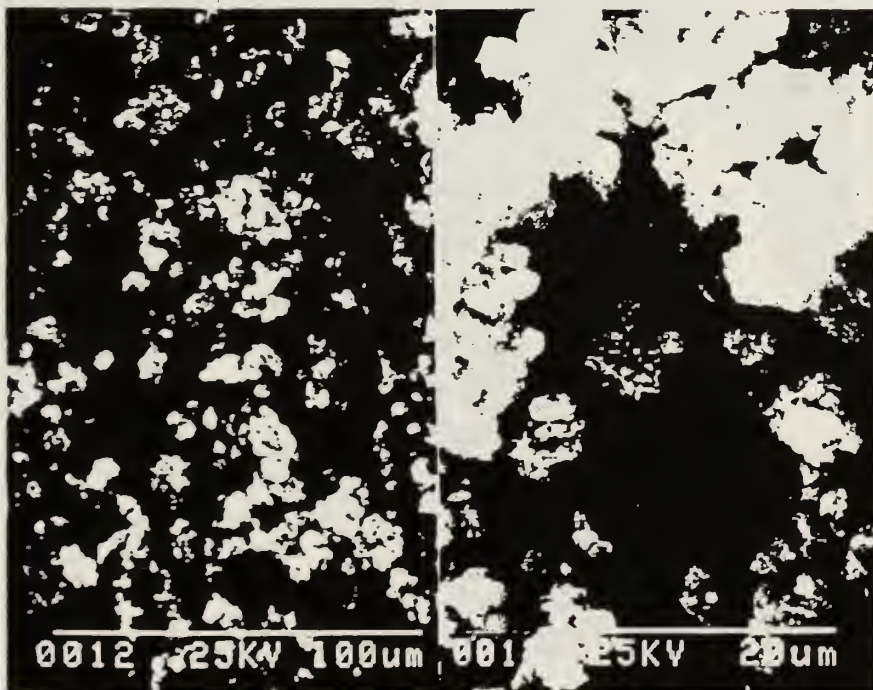


Figure 5.-SEM photomicrograph of the 54.7 gram lime sample carbonated 24 hours.

# PYROLYSIS OF CARBONATED PORTLAND CEMENT

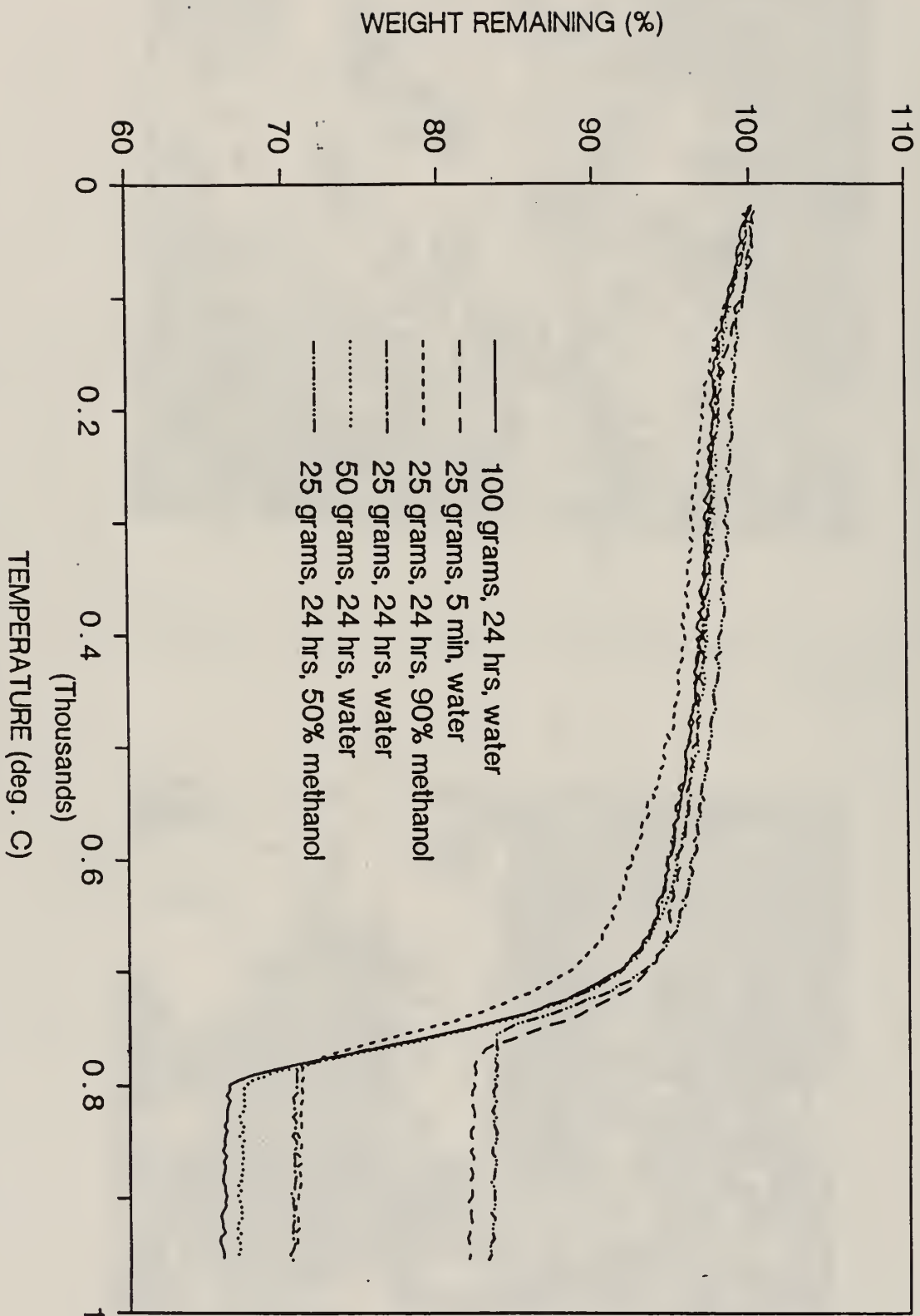


Figure 6.-TG weight loss profiles for carbonated portland cement samples.

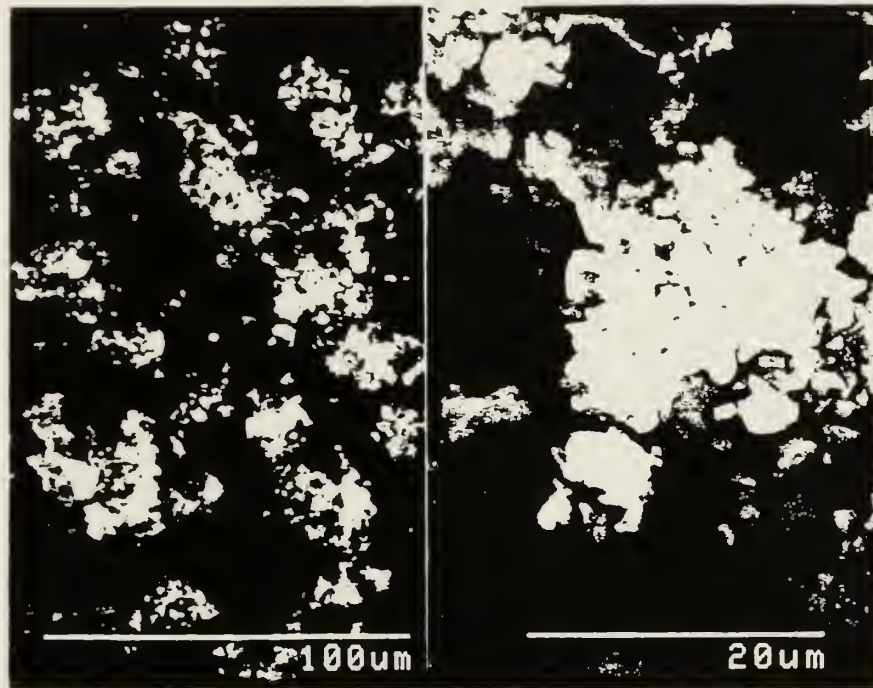


Figure 7.-SEM photomicrograph of the 100 gram,24 hr sample carbonated in water.

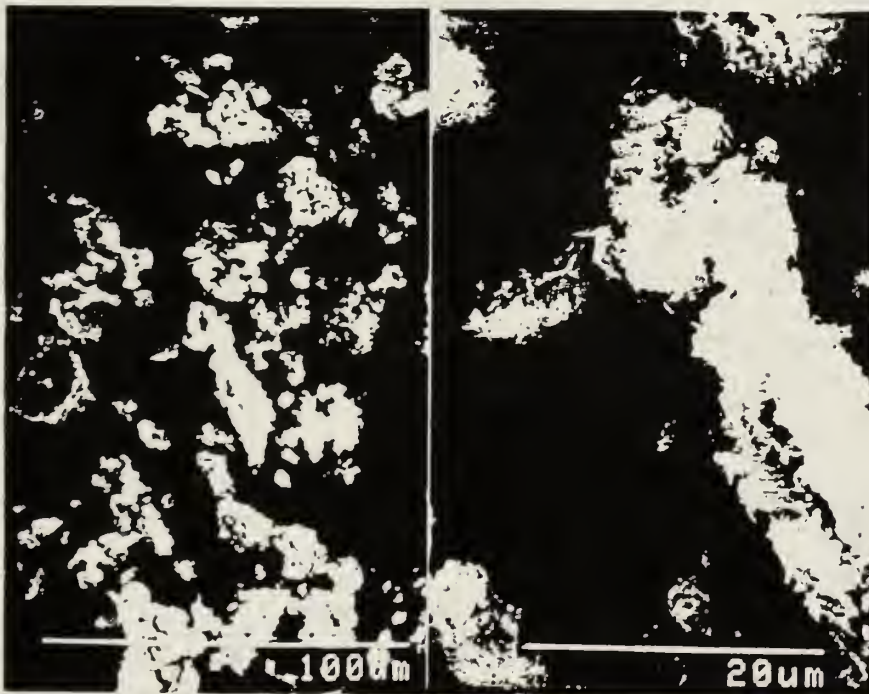


Figure 8.-SEM photomicrograph of the 25 gram,24 hr sample carbonated in methanol.

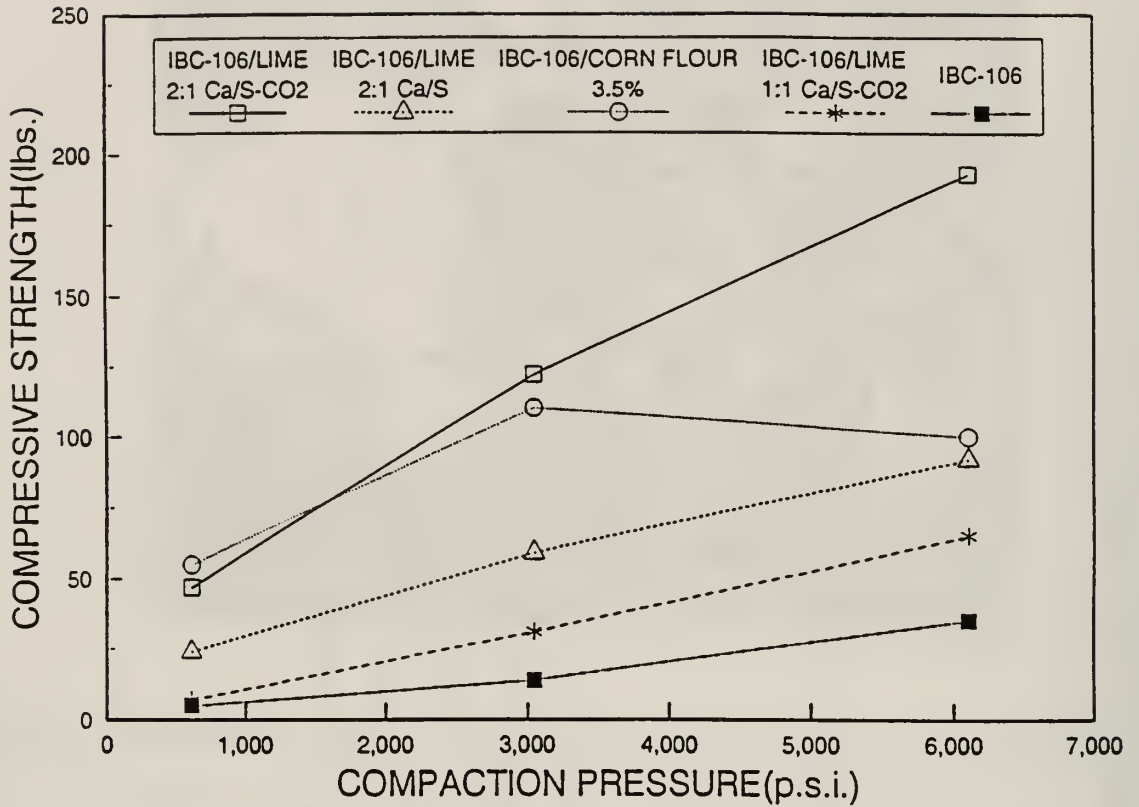


Figure 9.-Compaction pressure vs. compressive strength for IBC-106 pelletized with and without binder (CO2 indicates carbonated pellet).

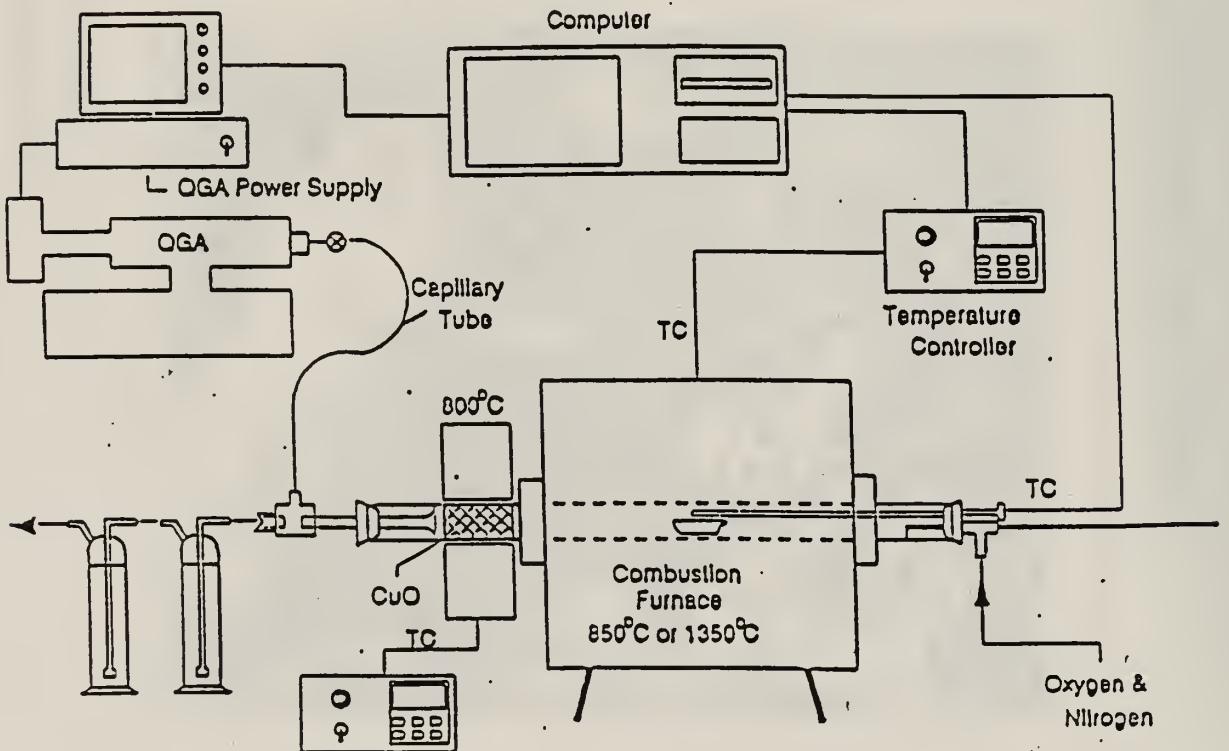


Figure 10.- Schematic of combustion testing equipment.

## COMBUSTION OF PELLETS (Untreated Coal)

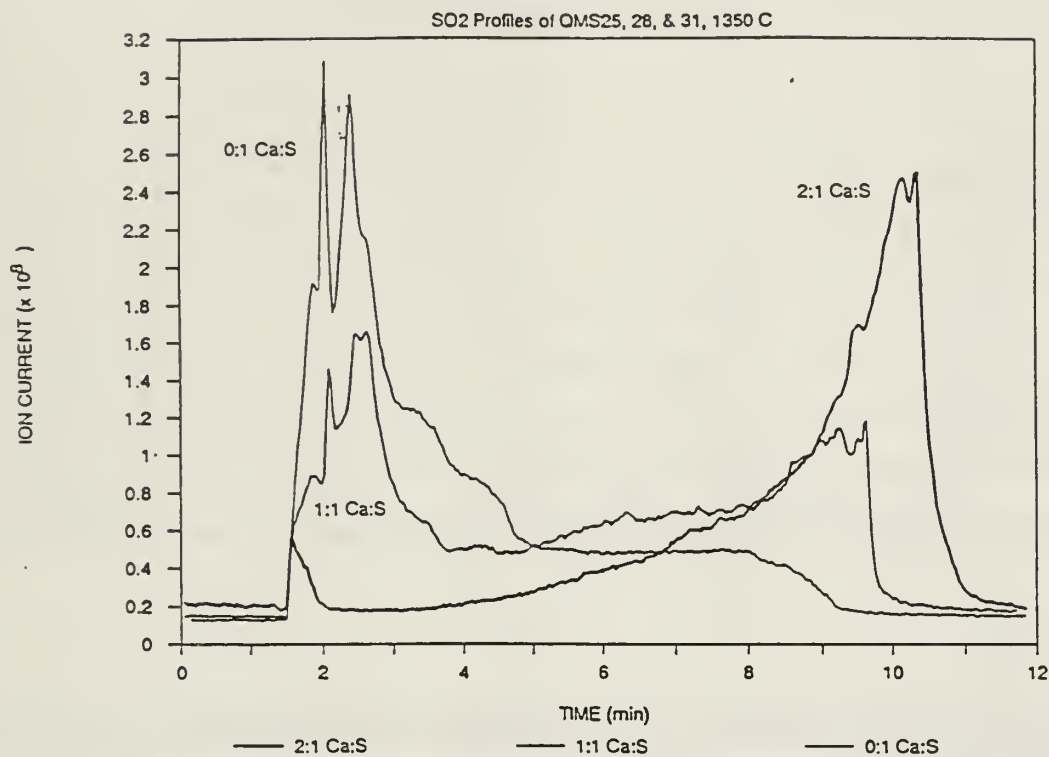


Figure 11.-QGA plot of time vs. ion current (proportional to partial pressure) for sulfur emissions resulting from combustion of 0,1 and 2:1 Ca/S ratio coal lime pellets.

## COMBUSTION OF PELLET

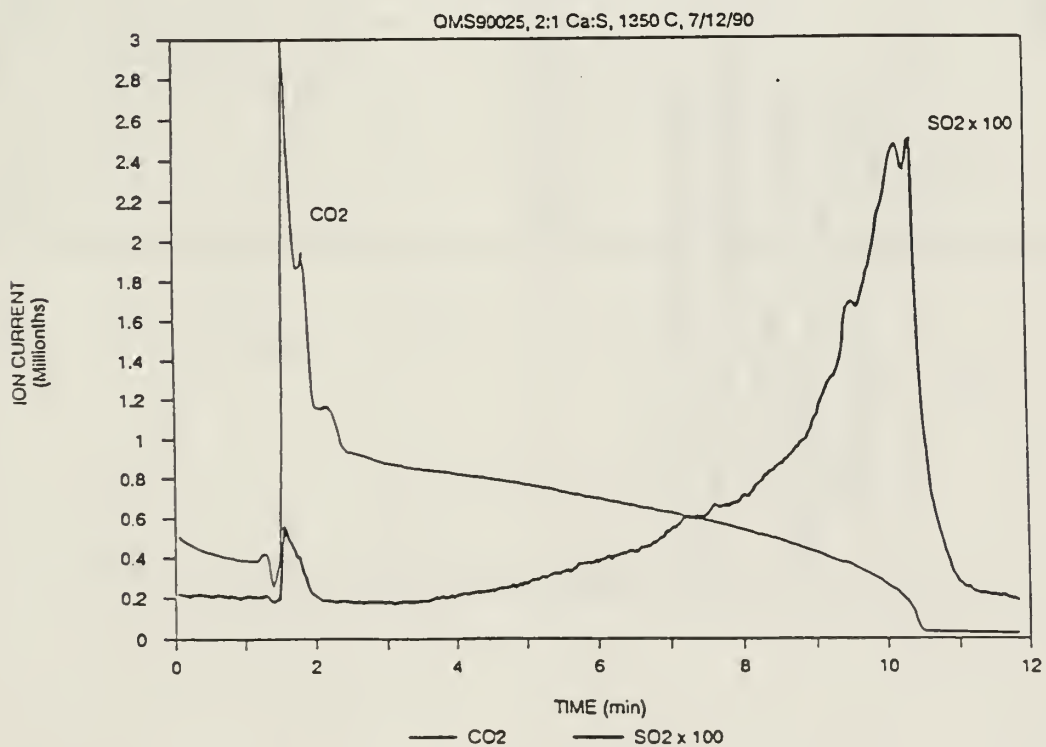


Figure 12.-QGA plot of time vs. ion current (proportional to partial pressure) for sulfur and carbon dioxide emissions resulting from combustion of a 2:1 Ca/S pellet.

# LIME ADDITION TO IBC-106 PELLETS

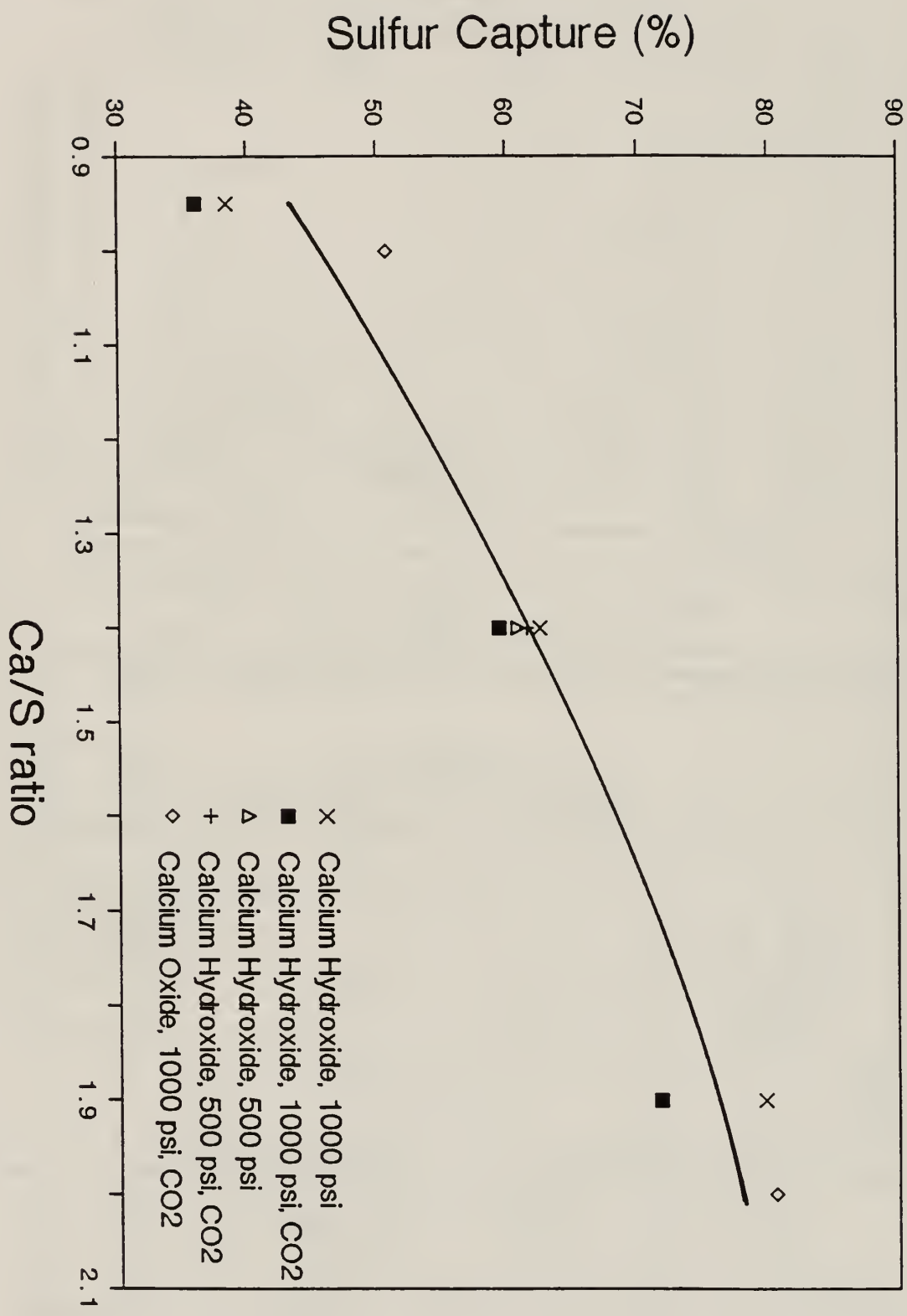


Figure 13.-Sulfur capture as a function of Ca/S ratio for carbonated and non-carbonated coal/sorbent pellets.



Table 1. Results from sulfation capacity testing of carbonated lime.

Sample	% Sulfated	% Carbonated
Lime	56	0
6.8g, 5 min H <sub>2</sub> O	91	100
6.8g, 24 hrs H <sub>2</sub> O	92	100
13.7g, 24 hrs H <sub>2</sub> O	97	100
27.4g, 24 hrs H <sub>2</sub> O	97	100
54.7g, 5 min H <sub>2</sub> O	65	14.7
54.7g, 20 min H <sub>2</sub> O	74	25.7
54.7g, 80 min H <sub>2</sub> O	84	75.3
54.7g, 24 hrs H <sub>2</sub> O	93	100
Calcium Hydroxide	83	0

Table 2. Results from sulfation capacity testing of carbonated portland cement.

Sample	% Sulfated	% Calcium Carbonated
Feed Cement	45	0
25 g, 24 hrs H <sub>2</sub> O	63	74
25 g, 24 hrs 50% MeOH	63	67
25 g, 24 hrs 50% MeOH	52	31
25 g, 5 min H <sub>2</sub> O	45	36
50 g, 24 hrs H <sub>2</sub> O	81	91
100 g, 24 hrs H <sub>2</sub> O	86	92

Table 3. Effect of moisture on strength development for 2:1 Ca/S (14% lime) pellets compacted with 3050 psi.

Sample	Compressive strength (lbs crushing force)
35% moisture, (32)*	26
35% moisture, CO <sub>2</sub> **	86
30% moisture, (28)*	38
30% moisture, CO <sub>2</sub>	97
25% moisture, (22)*	45
25% moisture CO <sub>2</sub>	41

\* moisture after pelletization

\*\* indicates carbonated pellet

Table 4. Compressive strength (lbs crushing force) of 30% moisture, IBC-106/lime pellets as a function of carbonation time and compaction pressure (14% lime or a 2:1 Ca/S ratio).

Carbonation Time (hrs)	Compaction Pressure (psi)		
	610	3050	6100
0	24	59	92
1	47	122	193
2	57	119	165

Table 5. Effects of compaction pressure on strength development.

Sample	Compaction Pressure (psi)		
	610	3050	6100
IBC-106 (25, 26.5, 25)*	5	14	35
1:1 Ca/S Lime (28, 26.5, 25)*	11	44	70
1:1 Ca/S Lime (CO <sub>2</sub> )**	7	31	65
2:1 Ca/S Lime (not determined)	24	59	92
2:1 Ca/S Lime (CO <sub>2</sub> )**	47	122	193
1:1 Ca/S Cement (28.5, 25.5, 24)	12	35	73
1:1 Ca/S Cement (CO <sub>2</sub> )**	8	40	84
2:1 Ca/S Cement (26.5, 25, 23.5)	10	35	75
2:1 Ca/S Cement (CO <sub>2</sub> )**	8	38	76
3.5% Corn Flour (29, 31.5, 27.5)	55	110	100

\* Values in parenthesis are moisture contents after formation. Respective values correspond to moisture levels at 610, 3050 and 6100 compaction pressures.

\*\* indicates carbonated pellet

Table 6. Compressive strengths (lbs crushing force) of IBC-106 pellets as a function of moisture content and compaction pressure.

% moisture*	Compaction pressure (psi)		
	610	3050	6100
10		13	39
20		19	42
30	5	14	35

\* moisture content before formation

Table 7. Analysis of Burlington Lime.

Chemical Analysis	Weight Percent
CaO	96.1
SiO <sub>2</sub>	< 0.1
Fe <sub>2</sub> O <sub>3</sub>	0.08
Al <sub>2</sub> O <sub>3</sub>	0.31
MgO	0.52
SO <sub>3</sub>	<0.1
Loss on Ignition	3.2
CO <sub>2</sub>	0.81

Table 8. Analysis of Portland Cement.

Chemical Analysis	Weight Percent
CaO	64.3
SiO <sub>2</sub>	19.7
Fe <sub>2</sub> O <sub>3</sub>	2.14
Al <sub>2</sub> O <sub>3</sub>	4.84
MgO	1.31
SO <sub>3</sub>	3.67
Loss on Ignition	2.18

Table 9. Analysis of Calcium Hydroxide.

Chemical Analysis	Weight Percent
CaO	69.8
SiO <sub>2</sub>	<0.1
Fe <sub>2</sub> O <sub>3</sub>	0.06
Al <sub>2</sub> O <sub>3</sub>	0.18
MgO	0.04
SO <sub>3</sub>	<0.1
Loss on ignition	28.41
CO <sub>2</sub>	9.86

Table 10. Binder costs for systems tested.

Sample	Cost*	% Addition**
IBC-106	0	0
1:1 Ca/S Lime (7.0%)	4.70	7.5
2:1 Ca/S Lime (14.0%)	9.41	15.0
1:1 Ca/S Lime, 1% corn starch	7.20	0
1:1 Ca/S Calcium Hydroxide (8.7%)	5.29	8.7
1.5:1 Ca/S Calcium Hydroxide (13.1%)	7.96	13.1
2:1 Ca/S Calcium Hydroxide (17.4%)	10.58	17.4
3.5% Corn Flour	8.75	0

\* Binder costs are per ton of IBC-106 feed coal

\*\* Percentage compared to total coal

Lime: \$67.25/ton FOB  
 Calcium Hydroxide: \$60.75/ton FOB  
 Corn Flour: \$.125/lb FOB

Table 11. Results from compressive strength testing from characterization program.

Sample	lbs compression to failure**
IBC-106 only (26.0)*	19
1:1 Ca/S Lime (29.2)	27
1:1 Ca/S Lime (carbonated)	24
2:1 Ca/S Lime (27.5)	27
2:1 Ca/S Lime (carbonated)	52
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour (27.5)	27
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour (carbonated)	45
1:1 Ca/S Calcium Hydroxide (24.9)	41
1:1 Ca/S Calcium Hydroxide (carbonated)	44
1.5:1 Ca/S Calcium Hydroxide (26.5)	44
1.5:1 Ca/S Calcium Hydroxide (carbonated)	94
2:1 Ca/S Calcium Hydroxide (26.2)	49
2:1 Ca/S Calcium Hydroxide (carbonated)	151
3.5% Corn Flour (29%)	118

Values in parenthesis are pellet moisture content after formation

\*\* Average of three results

Table 13. Results for drop testing\* from characterization test program.

Sample	Drop Height (inches)	# of Drops to Failure
IBC-106 only	18	3
1:1 Ca/S Lime	18	6.3
1:1 Ca/S Lime (carbonated)	18	5.7
2:1 Ca/S Lime	18	5.7
2:1 Ca/S Lime (carbonated)	36	11.7
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour	18	5.7
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour (carbonated)	18	12.3
1:1 Ca/S Calcium Hydroxide	18	5.7
1:1 Ca/S Calcium Hydroxide (carbonated)	18	19
1.5:1 Ca/S Calcium Hydroxide	18	15.3
1.5:1 Ca/S Calcium Hydroxide (carbonated)	36	15
2:1 Ca/S Calcium Hydroxide	18	20
2:1 Ca/S Calcium Hydroxide (carbonated)	72	7
3.5% Corn Flour	72	13.7

\* average of three results

Table 12. Results from attrition testing from characterization test program (% material minus 20 mesh after 20 minutes on Ro-Tap).

Sample	% minus 20 mesh
IBC-106 only	100
1:1 Ca/S Lime	91
1:1 Ca/S Lime (carbonated)	89
2:1 Ca/S Lime	93
2:1 Ca/S Lime (carbonated)	26
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour	77
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour (carbonated)	49
1:1 Ca/S Calcium Hydroxide	78
1:1 Ca/S Calcium Hydroxide (carbonated)	62
1.5:1 Ca/S Calcium Hydroxide	64
1.5:1 Ca/S Calcium Hydroxide (carbonated)	26
2:1 Ca/S Calcium Hydroxide	50
2:1 Ca/S Calcium Hydroxide (carbonated)	13
3.5% Corn Flour	6

Table 14. Results from weatherability testing from characterization test program.

Sample	Compressive strength (lbs original/after 24 hr immersion in water)
IBC-106 only	dissolved < 5 min.
1:1 Ca/S Lime	dissolved < 5 min.
1:1 Ca/S Lime (carbonated)	dissolved < 5 min.
2:1 Ca/S Lime	dissolved < 5 min.
2:1 Ca/S Lime (carbonated)	(52/15)
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour	dissolved < 5 min.
1:1 Ca/S Lime, 1 $\frac{1}{2}$ Corn Flour (carbonated)	*
1:1 Ca/S Calcium Hydroxide	dissolved < 5 min.
1:1 Ca/S Calcium Hydroxide (carbonated)	dissolved < 5 min.
1.5:1 Ca/S Calcium Hydroxide	dissolved < 5 min.
1.5:1 Ca/S Calcium Hydroxide (carbonated)	(94/24)
2:1 Ca/S Calcium Hydroxide	dissolved < 5 min.
2:1 Ca/S Calcium Hydroxide (carbonated)	(151/48)
3.5% Corn Flour	dissolved < 5 min.

\* maintained some integrity for 24 hours but not enough to test

Table 15. Results of Lime Filtration Test

Volume filtrate	1050 ml
pH filtrate	11.4
Calcium concentration	945 ppm
Weigh filter cake	79.5 g
% moisture in filter cake (by TG)	2.5%
Weight loss to solubility	1.05 g
% weight loss to solubility	6.5%

Table 16. Filtration Data for Coal and Coal/Lime Mixture.

Filtrate volume (ml)	Filtration Times (min)	
	Coal Only	Coal/Lime
300	3:00	1:30
350	3:40	1:50
400	4:25	2:15
450	5:15	2:35
500	6:05	3:00
550	6:55	3:20
600	7:45	3:45
650	8:35	4:05
700	9:25	4:30
750	10:15	5:00
800	11:10	6:00

Table 17. Sulfur capture at 850°C as a function of sorbent level\* and compaction force for carbonated and non-carbonated IBC-106/calcium hydroxide pellets.

Sample	Compaction pressure	Sulfur capture
1:1 Ca/S	1000 psi	38.5
1:1 Ca/S, carbonated	1000 psi	36.0
1.5:1 Ca/S	1000 psi	61.6
1.5:1 Ca/S, carbonated	1000 psi	59.4
1.5:1, carbonated	1000 psi	62.9
2:1 Ca/S	1000 psi	79.8
2:1 Ca/S, carbonated	1000 psi	71.7
1.5:1 Ca/S	500 psi	61.4
1.5:1 Ca/S, carbonated	500 psi	63.7
1.5:1 Ca/S carbonated	500 psi	59.9

\* Ca/S ratios for calcium hydroxide are actually slightly lower due to solubility loss during mixing. Estimated loss due to solubility is 6% based on work with lime.

Table 18. Sulfur capture as a function of temperature and sorbent level for IBC-106/lime pellets. All pellets are carbonated and compacted using 1000 psi.

Sample	Temperature, °C	Sulfur Capture
0:1 Ca/S	850	---*
1:1 Ca/S	850	50.8
2:1 Ca/S	850	80.4
0:1 Ca/S	1100	---*
1:1 Ca/S	1100	12.5
2:1 Ca/S	1100	57.9
0:1 Ca/S	1350	---*
1:1 Ca/S	1350	1.5
2:1 Ca/S	1350	1.4

\* indicates sulfur capture of essentially zero

Table 19. Sulfur capture as a function of temperature and sorbent level for physically cleaned IBC-106/lime pellets. Values for carbonated and non-carbonated pellets are listed, pressure of 1000 psi used to form pellets.

Sample	Temperature, °C	Sulfur Capture
0:1 Ca/S	850	4.5
1.2:1 Ca/S	850	55.2
1.2:1 Ca/S	850	54.5
1.2:1 Ca/S, not carbonated	850	60.6
2.4:1 Ca/S	850	71.6
2.4:1 Ca/S	850	80.7
2.4:1 Ca/S	850	78.0
2.4:1 Ca/S, not carbonated	850	86.8
2.4:1 Ca/S, not carbonated	850	85.0
0:1 Ca/S	1100	1.7
1.2:1 Ca/S	1100	32.7
2.4:1 Ca/S	1100	70.6
0:1 Ca/S	1350	1.8
1.2:1 Ca/S	1350	1.2
2.4:1 Ca/S	1350	15.1
2.4:1 Ca/S	1350	22.8



