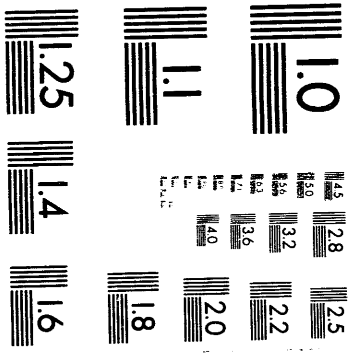
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DOE/PC/92521--T92

FINAL TECHNICAL REPORT

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Project Title: **CARBONATION AS A BINDING MECHANISM FOR COAL/CALCIUM HYDROXIDE PELLETS**

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ABSTRACT

This research was an investigation of calcium hydroxide, a sulfur-capturing sorbent, as a binder for coal fines. The reaction of carbon dioxide with calcium hydroxide, referred to as carbonation, was studied as a method for improving pellet quality. Carbonation forms a cementitious matrix of calcium carbonate.

Research has demonstrated that calcium hydroxide is a viable binder for coal fines and that a roller-and-die pellet mill is an effective method of pellet formation. From a minus 28 mesh preparation plant fine coal sample, a roller-and-die pellet mill produced strong pellets when 5 and 10% calcium hydroxide was used as a binder. The pellets containing 10% calcium hydroxide strengthened considerably when air cured. This increase in strength was attributed to carbonation via atmospheric carbon dioxide. Pellets containing 10 wt% calcium hydroxide were produced using an extruder but pellets formed in this manner were much weaker than pellets produced with the roller-and-die mill.

In tests performed using a laboratory hydraulic press, the effect of particle size and compaction pressure on pellet strength was studied. Particle distributions with mean sizes of 200, 90 and 40 microns were tested. The results indicate that pellet strength increased with decreasing particle size and increasing compaction pressure when calcium hydroxide was used as a binder. Pellets containing 10 wt% calcium hydroxide increased in strength by approximately 40% when air dried for one day. As above, this increase in strength was attributed to carbonation of the calcium hydroxide via atmospheric carbon dioxide.

"U.S. DOE Patent Clearance is NOT required prior to publication of this document."

EXECUTIVE SUMMARY

Coal fines are routinely discarded at coal cleaning plants in Illinois. Each year, 2-3 million tons, approximately 5% of the state's annual production of coal, are impounded in tailings ponds. The fines, generated during the routine mining and processing of coal, are discarded because it has been considered uneconomical to recover and process them into a form that could be marketed.

Currently, the only option available to Illinois companies for selling coal fines is to blend and ship them along with the coarse cleaned coal. In many cases, this cannot be done because of product quality considerations such as total moisture content and the allowable percentage of fines.

Pelletization represents a method to improve the marketability of these fines. The ISGS has been investigating calcium hydroxide, a sulfur capturing sorbent, as a binder/sorbent for pelletized coal fines. To improve pellet quality, the reaction of calcium hydroxide with carbon dioxide was investigated. Referred to as carbonation, the reaction results in the formation of a cementitious matrix of calcium carbonate. This research encompassed the effect of particle size on pellet quality, methods of pellet production, the study of alternate binders for relative effectiveness and laboratory combustion testing.

Particle Size Effects - The effect of particle size and compaction pressure on pellet strength was studied using IBC-106 from the Illinois Basin Coal Sample Program. Pellets were prepared using a laboratory Carver hydraulic press from samples with mean particle sizes of 200, 90 and 40 microns. Compaction pressures ranged from 6,250 to 18,750 psi. Pellets were prepared with calcium hydroxide in the amount of 0, 5, 10 and 15 wt% at all particle size distributions.

The results indicate that pellet strength increased with increasing compaction pressure and decreasing particle size. Increases in pellet strength with calcium hydroxide binder were marginal at the coarsest particle size but increased as particle size was reduced to the 40 micron mean size. Pellets containing calcium hydroxide prepared using the 40 micron mean particle sized feed that were air dried for one day were approximately 40% stronger than pellets fully dried in a vacuum drier and tested for strength. This increase in pellet strength is attributed to carbonation of calcium hydroxide via atmospheric carbon dioxide.

Pellet Production - Pellets were produced by a California Pellet Mill, a roller-and-die extrusion pellet mill using a 28x0 mesh fine coal sample collected from an Illinois preparation plant. Pellets of 1/2-inch diameter were produced containing 0, 5 and 10% calcium hydroxide. The pellets containing 5 and 10% calcium hydroxide, which are 0.8 and 1.6 Ca/S ratios for a 3% sulfur Illinois coal, met pellet strength criteria established by Battelle Columbus(1). The pellets containing 10% calcium hydroxide achieved a green strength (strength after formation) of 40.5 psi and increased in strength to 77.9 psi after air-curing for 3 days. Pellets formed with 5% calcium hydroxide had 29.7 and 32.3 psi green and cured strengths. The Battelle standards for green and cured strength, when converted to psi, are 6.3 and 25 psi. Pellets formed without binder did not meet the criteria at 5.8 and 5.5 psi respectively.

Alternate binders - Several alternate binders were studied with corn starch showing the most promise. The effectiveness of corn starch at 2 wt% increased only marginally with increased compaction pressure and pellet strength increased with increased particle size. This trend is the reverse of that determined for calcium hydroxide as a binder.

Combustion Testing - Combustion tests were conducted in a tube furnace on pellets containing 0, 5, and 10% calcium hydroxide. Combustion ashes were analyzed by neutron activation for the amount of chlorine, sodium, and arsenic retained in the ash. Feed chlorine, sodium and arsenic contents were 0.4 wt%, 0.1 wt% and 19 ppm, respectively. Tests conducted at 850°C indicated that calcium hydroxide was effective at retaining portions of the coals chlorine and arsenic in the ash. Sodium content in the ash decreased with increasing calcium hydroxide content.

Specifically, chlorine capture in the ash ranged from essentially nil at 0% calcium hydroxide to over 19% at 10% calcium hydroxide. For sodium, essentially all the sodium was retained in the ash of the pellet formed with no calcium hydroxide. For the pellets formed with 5 and 10% calcium hydroxide, only about 72% sodium was retained in the ash. Results for arsenic capture show that at 850°C, approximately 63% arsenic was retained in the ash for the 0% calcium hydroxide pellets. This amount increased to essentially 100% for pellets containing 5 and 10% calcium hydroxide.

Review - Research has indicated that strong pellets can be produced with 5 and 10% calcium hydroxide binder using a roller-and-die extrusion pellet mill. The pellets increase in strength with air curing and become weatherproofed. There is indication that finer particle sized feeds will produce stronger pellets. In addition to the well known sulfur capture potential for calcium hydroxide, tests indicate that calcium hydroxide also decreases emissions of chlorine and arsenic but increases emissions of sodium. Potential markets for pellets containing calcium hydroxide include fluidized bed combustors, stokers, pulverized coal combustors and gasification.

REFERENCE

1. Pelletizing/Reslurrying as a Means of Distributing and Firing Clean Coal, Final Report to the U.S. D.O.E., Contract No. DE-AC22-90PC90166, 1992.

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DISCLAIMER

OBJECTIVES

This research was a two-year effort with two complementary goals.

1) A Pellet Fuel from Preparation Plant Coal Fines - This work focused on production of pellets from 28x0 mesh coal fines collected from an Illinois preparation plant. Several topics were explored.

A. Pellet production using a commercially available pelletizer, a California Pellet Mill, was investigated. This mill is a roller-and-die extrusion pellet mill.

B. Cellulosic residue from the Tennessee Valley Authority's (TVA) process to produce ethanol from municipal waste (in this case, newspaper) was tested as a binder/admixture for coal fines. This material is low in sulfur and lowers the sulfur content of the composite fuel. The burning properties of the composite fuels were also evaluated by thermogravimetric analyses (TG).

C. The effectiveness of commercially available binders was studied in order to provide a frame of reference for evaluation of calcium hydroxide as a binder.

D. Calcium hydroxide is well known as a sulfur sorbent. In this work, the effect of calcium hydroxide on emissions of arsenic, chlorine and sodium was investigated.

E. The applicability of the pellets as a fuel for stokers and fluidized bed combustors was addressed.

2) A General Approach to the Production of Coal/Calcium Hydroxide Pellets - Particle size is an important factor to consider when investigating pelletization. Goal two was to determine a general approach for pelletization. For this work, IBC-106 was used. The following were investigated:

A. The effect of particle size, calcium hydroxide content and compaction pressure on pellet strength was studied. Corn starch was also tested for purposes of comparison.

B. Extrusion was evaluated as a method of pellet formation. Results were correlated with work in the particle size study.

C. Filtration tests were conducted to study the effect of particle size on filter cake moisture. This work was coordinated with work in the particle size study.

INTRODUCTION

Project Background

This research represented a continuation of two projects (2,3) co-funded by the Center for Research on Sulfur in Coal (CRSC-now the Illinois Clean Coal Institute (ICCI)),and the Army Construction Engineering Research Lab (CERL). Previous funding from the CRSC has been $77,817; CERL has contributed $40,000. The CRSC's interest in funding the previous work has been to develop a method for utilizing Illinois coal fines that, in many cases, are currently being disposed of in tailings ponds. CERL's interest has been to develop a fuel for their stoker boilers that would burn at the year 2000 compliance sulfur dioxide emission level.

The Carbonation Reaction

For calcium hydroxide, the carbonation reaction is:

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O + 19.6 \text{ kcal.}$$

The reaction is an ionic reaction with water acting as a solvent for both the carbon dioxide and calcium hydroxide. The proposed mechanism involves the dissolution of the $Ca(OH)_2$ to produce Ca++ and OH- ions. The carbon dioxide dissolves to form HCO_3-, CO_3-- and H+ ions. The Ca++ and CO_3-- ions react to form insoluble calcium carbonate (4). As shown, carbonation produces a net increase in water in the system.

Key factors influencing the rate of carbonation for pellets are the concentration of carbon dioxide in the carbonating gas and the moisture content of the pellet. If too much moisture is present in a pellet, the pore spaces are filled and the carbon dioxide must diffuse through the water to react with the calcium hydroxide. This can severely slow the reaction. The ideal situation for the reaction to proceed is when there is enough moisture to coat the calcium hydroxide but leaving an open pore structure for the rapid ingress of carbon dioxide.

EXPERIMENTAL PROCEDURES

Materials

Goal One-Minus 28 Mesh Preparation Plant Fines

For the work performed under Goal One, a 28x0 fine coal sample was collected from a southern-Illinois preparation plant. The sample had been mined from the Springfield coal seam (Illinois No. 5) and was a concentrate from spiral concentrators and flotation circuitry. The concentrates from the spirals and flotation cells were joined and dewatered in a screen bowl centrifuge. The moisture content after dewatering was approximately 22%. After collection, the sample was stored in two, sealed, 55-gallon drums equipped with plastic liners.

The sample (Table 1) was quite low in sulfur for an Illinois coal at 1.6%. The mean particle size was 227 microns with a 90% passing size of 590 microns. The coal fines are referred to as minus 28 mesh as this is the cut the plant wished to send to their spirals and flotation cells.

Goal Two-IBC-106

For Goal two, IBC-106 from the Illinois Basin Sample Program was used. The sample is a preparation plant product and was mined from the Indiana No.5 Seam (Illinois No. 5).

For both goals, the calcium hydroxide used was a commercial product prepared from the Burlington limestone. The corn starches tested were obtained from commercial grain processing facilities.

Procedures

Pellet Formation-Hydraulic Press - To prepare coal/binder mixtures, the desired wt% of binder was added to the coal sample and blended for two minutes using a variable speed hand-held mixer. Sample sizes were 125 grams in the Binder Study and 100 grams in the Particle Size and Extrusion Studies (dry basis).

Pellets were formed using a 1/2-inch (inside diameter) stainless steel cylindrical mold and piston and a Carver hydraulic press. Pellets were approximately equal in height and diameter. The sample was placed in the mold, compacted for 10 seconds with the desired pressure, the pellet was then removed from the mold. Pellet height was a function of the amount of sample placed in the mold, which varied with each pellet, there were slight differences in pellet height.

For each mixture, a sample was removed to obtain a moisture content before pellet formation. Moisture content was determined by drying on a hot plate at 105 °C until no further weight loss due to evaporation was observed. Moisture content after pellet formation was also determined by removing three pellets and drying them on the hot plate.

Pellet Formation-California Pellet Mill - Pellet production tests were performed using a California Pellet Mill (CPM), a commercially available pelleting machine. For this work, a laboratory version (Series CL), was used. The CPM used in this work was located in Crawfordsville,Indiana, site of CPM's laboratory facilities. A CPM is a roller-and-die extrusion pelletizer (5). In brief, coal fines were fed into a cylindrical chamber with twin circular rolls rotating about the interior. Pellets were formed when the rotating rolls extruded coal fines through circular holes in the chamber. Knife-like blades cut the extrudates to length.

Pellet Formation-Extrusion - Extrusion tests were conducted at the University of Illinois Ceramic Engineering Building. The extruder was a 40-ton Loomis piston extruder with a 4-inch diameter barrel. The extrusion pressure was in the range of 2000 to 2500 psi. A circular die of approximately 0.56" in diameter was used.

Pellet Carbonation, static system - Pellets were carbonated in a desiccator reaction chamber connected to a carbon dioxide reservoir at atmospheric pressure. The carbon dioxide reservoir consisted of a weather balloon filled with commercial grade 100% carbon dioxide. The procedure followed was to fill the weather balloon with carbon dioxide, close the valve to the balloon, place the pellets in the desiccator, evacuate the desiccator using the vacuum line (pressure of 250 mm Hg absolute), then open the valve to the weather balloon to introduce the carbon dioxide into the desiccator. Carbonation times were one hour using this procedure.

Pellet Carbonation, dynamic system - Pellets were carbonated for 15 minutes using 100 vol% carbon dioxide in 10 cm diameter Buchner funnel sealed with a No.15 rubber stopper. A 0.6 cm inch hole was cut into the stopper to allow the carbonating gas to escape. Inside the funnel, a wire screen was mounted approximately 1.3 cm above the base of the funnel. The wire screen served as a platform to allow all portions of the pellets to be exposed to the carbonating gas. The rubber stopper used to seal the funnel was shortened by about 1.3 cm to provide enough room in the funnel for the pellets once the system had been sealed. The carbonating gas was introduced into the funnel through the base and exited the funnel through the hole in the rubber stopper. The exit gas was passed through a flow meter to monitor total gas flow rate to ensure that there were no leaks in the system.

Tensile Strength Test, Radial Axis - A Geotest model S2013 was used for radial axis strength testing. A pellet was positioned on its side, a force was then applied at 0.25 cm/minute and load at failure in lbf (pounds-force) was recorded.

All pellets referred to as dried pellets were dried prior to testing for one hour using a vacuum drier set at 70°C and with a vacuum of approximately 125 mm Hg pressure absolute. Thus, all cured pellets were tested on a "moisture free" basis. Pellets referred to as green were tested before drying.

The results for pellet strength are reported in psi (pounds per square inch) to failure. For pellets tested in the above mentioned manner, conversion from lbf to psi is accomplished by use of the formula below. The measurement is referred to as diametral compression.

$$\text{Strength (psi)} = \frac{2\ (\text{Load})}{3.14\ (\text{Diameter})\ (\text{Length})}$$

The diameter of each pellet was 1/2-inch (unless noted otherwise). The length of each pellet was measured by use of a digital micrometer. Because the extruded pellets had irregular ends, the ends of each extrudate were sanded to produce planer surfaces.

Combustion testing - The apparatus used for combustion testing consisted of a high-temperature furnace, a mullite combustion tube, two gas wash bottles, a LFE computerized temperature controller, a Dycor quadropole gas analyzer (QGA), and a personal computer. A second oxidation zone (filled with CuO and held at 800°C) was made in the mullite tube to assure that all the volatiles were oxidized during combustion to CO_2 and SO_2 prior to exiting to the tube. The combustion furnace temperature was 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 burned. As the combustion gases exited the mullite tube, a continuous sample was taken through a capillary tube and monitored for CO_2 by the QGA. The QGA, the LFE temperature controller, and the inside thermocouple was connected to the Compaq PC which controlled the data acquisition for each combustion experiment.

Combustion tests were performed using air with a flow rate of 560 cc/min. For each test, the furnace was brought to the desired combustion temperature and the pellet was placed in the furnace (the pellets used were 1/4" in diameter and approximately equivalent in length). Combustion and monitoring of combustion gases by the QGA commenced immediately. Each test was run until the QGA output indicated CO_2 emissions had ceased.

Thermogravimetric Analysis

Burning profiles of fuel samples 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. A sample mass of 2 to 4 mg was loaded into the platinum pan of the TGA and was heated at a constant heating rate of 20°C/min in a 10% O_2-90% N_2 gas mixture to 750°C. A gas flow rate of 200 cc/min (STP) was used. The percent weight of the unburned sample, the rate of weight loss, and the gas temperature in the vicinity of the sample pan were collected by the computer at 12 second intervals.

Filtration Testing

Filtration tests were conducted using equipment obtained from EIMCO Process Equipment Company. The apparatus was designed to simulate belt filtration. The device consisted of a 3.75 inch inside diameter cylinder measuring approximately 3.75 inches in depth. The cylinder bottom was threaded and the lower portion was tightened against a gasket seated in the upper portion to secure the filter cloth in place. The cylinder was mounted on a 500 ml vacuum flask; a globe valve was positioned between the flask and cylinder. Two other vacuum reservoirs were stationed between the vacuum flask and the vacuum pump. The second reservoir was equipped with a screw valve used to regulate the vacuum for each test.

For each test, 500 ml of a 10 wt% slurry of IBC-106 was used. This volume of slurry resulted in a cake thickness of approximately 0.4 inches for each test. If for the test an additive was used, it was added to a 500 ml volumetric flask and shaken by hand for 1 minute. The sample was then added to the cylinder. After the sample was poured in the cylinder, vacuum was initiated by opening the valve below the cylinder. For each test the initial vacuum was 20 inches of Hg. The time for surface water to disappear (form time) was noted as was the total time for filtration. The cake moisture was determined by drying a portion of the sample on a hot plate at 105 °C until weight loss due to evaporation ceased. The filtrate volume and pH was measured for each test. The volume of solid passing through the filter cloth was also determined. For each test, a polyethylene filter cloth with EIMCO media no. of PO-801HF was used.

RESULTS AND DISCUSSION

Note: The results reported cover significant findings of the two years of research and emphasize research performed in the second year. Earlier work is referenced and an appendix is attached to provide information which could not be included in the body of the report because of report length restrictions.

California Pellet Mill

A California-Pellet-Mill (CPM) was tested as a method of pellet formation. A CPM is a roller-and-die extrusion pellet mill. Pellets were formed with 0, 5 and 10% calcium hydroxide. Pellets were tested for the strength before drying, after drying for one hour in a vacuum dryer, after carbonating for one hour in a desiccator with 100% commercial grade CO_2, and after air curing for various intervals of time.

The tensile strength (Table 2) of the dried pellets formed with no binder was low at 5.5 psi but strength increased considerably with addition of calcium hydroxide. At 5% calcium hydroxide, the strength was 30.8 psi and the strength increased further for pellets containing 10% calcium hydroxide to 40.9 psi. Carbonation improved pellet strength for the pellets containing 10% calcium hydroxide to 64.3 psi but there was no strength increase due to carbonation for the pellets formed with 5% calcium hydroxide.

Drying only marginally increased the strength of the pellets. There was no increase in strength for the pellets formed without binder and the pellets formed with 5% calcium hydroxide increased in strength from 23.8 to 30.8 psi. For the pellets containing 10% calcium hydroxide, strength increased from 36.4 to 40.9 psi. For the carbonated pellets, strength for the dried and non-dried pellets was essentially equivalent at 62.9 and 64.3 psi, respectively.

The effect of air-curing on pellet strength was investigated. The results were compared to those achieved for pellets formed with no binder and pellets containing 5 and 10% calcium hydroxide which were carbonated in a desiccator reaction chamber with 100% commercial grade carbon dioxide.

The results for the pellets containing 10% calcium hydroxide show that the pellets air cured for three days (Table 3) achieved a tensile strength (77.9 psi) greater than that achieved for the pellets carbonated for one hour in the desiccator indicating that atmospheric carbon dioxide slowly carbonated the pellets as they dried. For the pellets containing 5% calcium hydroxide (Table 4), the strength after 3 days was comparable to that for the vacuum-dried pellets but at 11 days it appears that the pellets had achieved a strength superior to the pellets carbonated in the desiccator and then vacuum dried. This gradual reaction with atmospheric carbon dioxide to harden pellets has been reported in other work investigating calcium hydroxide as a binder for refuse-derived-fuels (6).

The meaning of the above results is enhanced by comparison to results recently reported by Battelle Columbus (1). The Battele study evaluated the reconstitution of coal fines using roller-and-die, disk and extrusion pelletization. The roller-and-die, in this case a CPM, was selected as the most economical. The study indicated that 2.0% corn starch was required to produce pellets of acceptable quality. The required cured pellet compressive strength was 100 lbf/in^3 (equivalent to 25 psi for the 1/2" diameter pellets in the ISGS work, the conversion varies with pellet diameter, for a 1/4" pellet, the value is 12.5 psi) and the green strength specified was 25 lbf/in^3 (6.3 psi).

For the pellets in this work, the pellets formed with both 5 and 10% calcium hydroxide met the Battelle criteria without carbonation although the strength for the pellets containing 5% calcium hydroxide was only marginally greater than the criteria for cured strength (30.8 vs. 25 psi). The strength of the 10% calcium hydroxide carbonated pellets was more than double that of the 25 psi value at 64.3 psi. The air cured pellets containing 5% and 10% calcium hydroxide both achieved strengths superior to those determined as acceptable in this study.

Also, pellets of 1/4" diameter were produced using the CPM. Pellets with no binder, 10% calcium hydroxide and 2.5% corn starch were produced. The results were similar to those for the 1/2-inch diameter pellets and are reported elsewhere (7).

Additionally, an attempt was made to correlate results achieved using the CPM with results achieved using a laboratory hydraulic press and it was determined that the hydraulic press could not produce pellets of equal quality to the CPM, even at high compaction pressures (8). The CPM likely produces better pellets because the shearing force produced in pellet formation (5) produces better particle packing than for pellets formed with the hydraulic press. Pellets produced using the hydraulic press at high compaction pressure had horizontal cracks which likely were produced as the compaction pressure was reduced after pellet formation. These cracks weakened the pellets.

TVA Cellulosic Residue as a Binder

In many portions of the country, including Illinois, there is an increasing concern over the amount of municipal waste reporting to landfills and over the future availability of sufficient landfill capacity to dispose of municipal waste. Recycling can play a role in addressing the problem but it is no panacea. The TVA is investigating acid hydrolysis of municipal waste to produce ethanol and small amounts of furfural and acetic acid. The TVA was interested in finding a use for the residue from this process that would improve the economics of their operation. The residue supplied the ISGS was from the processing of newsprint and was low in sulfur at 0.3% and low in ash at 0.7% (Table 5).

The cellulosic residue could be a desirous addition to coal pellets for two reasons. Namely, the material could serve as a binder, and because of the low sulfur content, would lower the concentration of sulfur in the pellets.

The results for pelletization testing are discussed in greater detail elsewhere (9,appendix) and indicated that the residue can function as a binder but greater amounts are required to produce compressive strengths equivalent to that attained when using a conventional binder such as corn starch. Approximately 17 wt% TVA residue was required to produce a pellet with strength equivalent to a pellet with 1.7 corn starch. However, if the TVA process becomes a viable method of producing ethanol from municipal waste products such as newspaper, the material may be advantageously blended with coal for its binding properties and as a low sulfur fuel. To determine potential advantages of burning the mixtures of coal, TVA residue and calcium hydroxide, the following samples were tested by Thermogravimetric Analyses (TG).

1. 100% coal;
2. 100% TVA material;
3. coal, 5% TVA material
4. coal, 10% TVA material;
5. coal, 20% TVA material;
6. coal, 10% calcium hydroxide;
7. coal, 20% TVA material, 5% calcium hydroxide
8. coal, 20% TVA material, 10% calcium hydroxide

Burning profiles refer to a plot of the TGA rate of weight loss against temperature as a sample is burned in air at a constant heating rate. A typical burning profile and weight loss curve of the feed coal burning in 10% O_2-90% N_2 are shown in Figure 1. The weight loss curve shows a slight gain in weight between 200 and 320°C due to the tendency of coal to adsorb oxygen in this temperature range. A major weight loss begins at 395°C (T_I, the temperature corresponding to a rate of weight loss of 1%/min) and peaks at about 559°C (T_P). The rate of burning then decreases until sample oxidation is complete at a burnout temperature (T_B) of about 624°C, where the rate of weight loss is again 1%/min. The weight remaining at 700°C is the ash content of the sample, which is about 12%. Under the conditions used, characteristic temperatures (T_I, T_P, and T_B) were reproducible within 2%.

Weight loss curves of selected samples are shown in Figure 2. The TVA material exhibits three distinct regions of weight loss. Rapid weight loss occurs below 340°C, a gradual weight loss occurs between 340 and 450°C, and a more rapid weight loss occurs from about 450°C to 575°C, where the sample has been completely burned. Pyrolysis of the TVA material in N_2 suggests the weight loss below 340°C shown by the burning profiles is due mainly to devolatilization of gases and light oils present in the sample, although some oxidation seems to occur. The weight loss between 340 and 450°C is due to a combination of devolatilization of higher molecular weight materials and the onset of oxidation. The weight loss above 450°C is due mainly to the oxidation of the carbonaceous matrix remaining after the initial devolatilization. The sample containing 10% $Ca(OH)_2$ exhibits weight loss similar to the coal sample, but above 480°C appears to burn more rapidly than the coal. This suggests the $Ca(OH)_2$ has a slight catalytic effect under the conditions tested. The samples containing varying amounts of TVA material exhibit weight loss curves which are a combination of the TVA and coal weight loss curves.

Burning profiles of the samples are shown in Figure 3. All samples except the coal exhibit several distinct peaks, depending on the composition of the sample. The TVA material gives two peaks at 330 and 520°C, corresponding to the regions of rapid weight loss in Figure 2. The samples containing 20% and 10% TVA have a major peak below 380°C due to the devolatilization of the TVA material present in the samples, and a second, larger peak from about 450 to 620°C, due to the devolatilization and subsequent oxidation of the coal portion of the sample. The smaller peaks occur at about 355°C and 320°C for the samples containing 20% and 10% TVA material, respectively. Both samples exhibit a small peak from about 400 to 440°C which is due to continuing devolatilization of the TVA portion and the onset of devolatilization of the coal portion of the sample. The samples containing $Ca(OH)_2$ exhibit a very small peak from 445 to 485°C which could be due to residual $Ca(OH)_2$ which was not completely carbonated. These samples also exhibit a peak from 625 to 680°C due to the decomposition of $CaCO_3$.

Burning profiles are useful for determining the relative combustion characteristics of a fuel. According to published reports (10), fuels which give similar burning profiles exhibit similar combustion reactivities in larger furnaces. More reactive fuels exhibit lower characteristic temperatures. Characteristic temperatures of the fuels were obtained from the burning profiles and are listed in Table 6. Samples that have two or more burning profile peaks were assigned a temperature for each of the peaks. The TVA material exhibits the lowest characteristic temperatures as expected. The other samples which contain TVA material all exhibit about the same T_I which is much lower than that of the coal. This suggests the volatile matter would be released from the TVA material prior to the volatile matter from the coal, and could help with ignition and flame stability in a larger furnace. The lower T_p values for all the samples containing 20% TVA are about the same (345-355°C), while T_p for the samples containing 10% and 5% TVA material are significantly lower. The higher peak temperature (T_p) for samples containing coal are all the same (548-564°C) within experimental error, as expected. The samples containing coal all exhibit about the same burnout temperature (T_B) as the raw coal, except for the sample which contains jut 10% $Ca(OH)_2$ and coal. This sample has a slightly lower burnout temperature, which suggests a possible catalytic effect from Ca under the conditions of the test. It is questionable whether this catalytic effect would be observed under conditions found in larger furnaces, although the sample containing $Ca(OH)_2$ would be expected to burn at least as well as the parent coal.

Binder Study

Several binders were tested for effectiveness using the Illinois No. 5 seam preparation plant coal fines. The laboratory hydraulic press was used to prepare the pellets. Two corn starches were tested; one a lower quality, lower priced starch, the other a higher quality, higher priced starch. Also tested were calcium lignosulfonate and a petroleum water emulsion, SHUR BOND. These binders were tested to evaluate the relative effectiveness of calcium hydroxide and the carbonate binding system under the conditions tested.

The binders were tested using the fines at the "as received" moisture content which was approximately 22 wt%. Pellets were tested for the green strength, the strength immediately after formation, and the dried strength, the strength after the pellets were dried in a vacuum drier for approximately 1 hour. Both were tensile strengths. Pellets were formed at three compaction pressures.

The results (Table 7) show that higher priced corn starch (corn starch 1) produced pellets of the highest strength per the amount of binder added. The pellets bound using corn starch 1 showed no improvement in pellet quality with increased compaction pressure as did the pellets bound using calcium lignosulfonate. The lower priced starch did not impart any binding action at the compaction pressures tested showing results similar to those for no binder. The green strengths for these binders were quite low.

The binder SHUR BOND did not impart significant pellet strength under the conditions tested. Pellet strength did not increase with addition of increased amounts of binder, in fact it decreased as the amount of SHUR BOND was increased above 2.5 wt%. For SHUR BOND, even 2.5 wt% may have been more binder than was necessary to get the most strength for the least cost. Although the pellets containing SHUR BOND exhibit strengths similar to those for pellets without binder, the pellets by inspection were better than pellets without binder with regards to fines production and weatherability. For this test series though, these characteristics were not quantified.

For the pellets bound with calcium hydroxide, strength increased with compaction pressure and carbonation increased the strength of pellets by approximately a factor of 4. In another test shown in Table 3, pellets containing 10 wt% calcium hydroxide, formed with 18,750 psi, were air cured to determine how much strength developed due to exposure to atmospheric carbon dioxide. The pellets in this example did not achieve a strength equivalent to those pellets carbonated with 100% carbon dioxide. The pellets did increase in strength though and attained a strength in one day of the same order of magnitude as did pellets formed with 1 wt% corn starch 1 and 2.5 wt % calcium lignosulfonate.

Combustion Testing

Combustion tests were conducted on pellets containing 0, 5, and 10% calcium hydroxide. Pellets were analyzed for the amount of chlorine, sodium, and arsenic retained in the ash. Tests were conducted at 850°C and 1100°C. It was intended to test for chlorine, sodium and arsenic at 1350°C but the combustion residues fused in the combustion boat and formed a glassy deposit that was impossible to remove to obtain a sample for analysis. For the pellets formed with calcium hydroxide, carbonated pellets were tested; for the pellets formed without calcium hydroxide, corn starch was used as a binder. The results are expressed in terms of the percentage of the element in the feed pellet to that in the combustion residue.

The tests (Table 9) indicate that calcium hydroxide was effective at retaining portions of the coals chlorine and arsenic in the ash. Sodium content in the ash decreased with increasing calcium hydroxide content.

Specifically, chlorine capture for tests conducted at 850°C ranged from essentially nil at 0% calcium hydroxide to over 19% at 10% calcium hydroxide. Results for tests at 1100°C were nearly identical to those attained at 850°C.

For sodium, in tests conducted at 850°C, essentially all the sodium was retained in the ash for the pellet formed with no calcium hydroxide. For the pellets formed with 5 and 10% calcium hydroxide, only about 72% sodium was retained in the ash. At 1100°C, this effect was more pronounced, with 91.7% sodium retained in the ash for the pellet formed without calcium hydroxide, while the pellet formed with 10% calcium hydroxide retained only 20% sodium in the ash.

The decrease of sodium in the ash is possibly due to calcium replacing sodium in silicate minerals and forming calcium silicate minerals, which are more stable at higher temperatures than the sodium minerals. X-ray diffraction of the ash material would help determine the actual mineralogy involved in such reactions.

Results for arsenic capture show that at 850°C approximately 63% arsenic was retained in the ash for the 0% calcium hydroxide pellets. This amount increased to essentially 100% for pellets containing 5 and 10% calcium hydroxide. For tests conducted at 1100°C, only 10% arsenic was retained in the ash for the pellets formed with 0% calcium hydroxide but about 86% arsenic was retained in the ash for the pellets formed with 10% calcium hydroxide.

Evaluation as a Fuel for Fluidized Bed Combustion

A fluidized bed is capable of achieving the high level of sulfur capture necessary for cleanly burning a high-sulfur fuel such as Illinois coal. In a fluidized bed, limestone can be used as bed material for reacting with and capturing the sulfur gas released as the coal is burned. Combustion temperatures when burning coal are generally around 850 °C, a temperature favorable for capturing sulfur. At this temperature, the limestone calcines to form calcium oxide (lime) which in turn reacts with sulfur dioxide in the presence of oxygen to form calcium sulfate.

Sorbent utilization and sulfur capture can vary considerably among different limestones. A variety of factors have been cited as responsible for these differences. An important factor is the porosity of the limestone (11). For the reaction to occur, the sulfur dioxide has to be exposed to unreacted calcium oxide. The molar volume of calcium sulfate is greater than the molar volume of the calcium oxide, and, as calcium sulfate reaction products accumulate in the porous structure of the lime, a diffusional barrier is created which prevents utilization of the remaining lime for sulfur capture.

It has been found that use of limestones with impurity content, such as dolomitic limestone with magnesium replacing calcium in the calcium carbonate lattice, can achieve improved sorbent utilization because the non-reactive impurities delay closure of the pores, and, hence, increase the amount of lime exposed to the sulfur gas (12). To achieve high sulfur captures, Ca/S ratios ranging from 2.5 to 3.5 are common.

In a fluidized bed with limestone bed material, nearly all the sulfur capture is achieved after the sulfur gas is released from individual particles of coal (The exception would be sulfur capture achieved by calcium inherently present in the coal as mineral matter). Because of the nature of the pellets in this work, with the finely grained crystals of calcium hydroxide used as a binder and because of the nature of how the pellets burn, each pellet could function as an unique and effective sorbent for capturing sulfur. Scanning Electron photomicrographs of the pellets have shown the calcium hydroxide particles are micron and sub-micron in size (7) which indicates these pellets are ideally suited for fluidized bed combustion.

Evaluation as a Stoker Fuel

An objective of this research was to evaluate the potential for producing a stoker fuel from relatively low-sulfur coal fines which would burn at 1.2 lbs $SO_2/10^6$ Btu. The coal fines used in this work would burn with 2.45 lbs $SO_2/10^6$ Btu. To achieve the year 2000 compliance emission standard of 1.2 lbs $SO_2/10^6$ Btu requires that sulfur emissions be reduced by just over 50%.

Plant-scale tests conducted using coal/sorbent pellets in stoker boilers have reported sulfur captures of 25-45% (13,14 and 15). In earlier work performed in this research, using a laboratory tube furnace coupled with a quadropole gas analyzer, it was shown that when pellets containing calcium hydroxide are burned at 1350 °C, initial sulfur captures are appreciable, but sulfur is released as the pellets burn and are exposed to high temperature (3).

This finding concurs with results reported by researchers in the United Kingdom for plant-scale stoker tests and fixed grate stoker simulator studies (15). In this work, a sulfur capture of 31% was reported for commercial scale stoker tests using coal/calcium carbonate pellets formed at a 2/1 Ca/S ratio. In fixed grate simulator tests also reported in this research, it was shown that a significant portion of the coals sulfur was captured initially as CaS but this sulfur was released as the CaS oxidized to form $CaSO_4$ which in turn decomposed. Based on test run at the commercial scale and using the fixed-grate simulator, it was postulated that sulfur capture could be improved by cooling the latter portions of the grate with a water spray. The drawback to this approach is the ash may have a significant fraction of CaS which could present disposal problems.

Limestone particle size and coal/sorbent contact were also cited as a potentially important factors in sulfur capture with increased sulfur capture experienced with finer limestone and better coal/sorbent contact. For the pellets in this work, with calcium hydroxide as the binder/sorbent, there is potential for improved sulfur capture with the intimately mixed crystals of micron and sub micron calcium hydroxide and carbonate. Another method to improve the chances of achieving compliance sulfur emissions would be to blend the coal fines with the low-sulfur TVA residue previously mentioned.

IBC-106 Particle Size Study

The following test matrix has been completed on IBC-106. The coarsest particle size distribution approximates a 28x0 preparation plant clean coal concentrate such as would be produced by blending a 28x100 gravity concentrate with a minus 100 mesh flotation concentrate. The finest particle size approximates a flotation concentrate.

Mean Particle Size (um)	Wt% Calcium Hydroxide	Compaction Pressure (psi)
200,90,40	0,5,10,15	6,250;12,500;18,750

The results for calcium hydroxide were reported earlier (16) and to save space the data is reported in the Appendix of this work. Figures derived from data collected in this effort are presented though. In addition to the above matrix, tests were run at the finest particle size using 1 and 2 wt% corn starch. Pellets were tested for tensile strength immediately after formation (green), after drying in a vacuum drier for one hour at 70 °C with a vacuum of approximately 125 mm Hg absolute and after air curing for one day.

Significant findings of the study are:

1. For binderless pellets and pellets formed with calcium hydroxide, pellet strength increased as particle size was decreased (Figure 4) and compaction pressure was increased (Figures 5).

2. Calcium hydroxide improved pellet strength (Figure 6). Pellets containing calcium hydroxide formed at the finest particle distribution (mean size of 40 microns) when air cured for one day were approximately 40% stronger than pellets that were vacuum dried (Figure 7). The increased strength is attributed to the calcium hydroxide in the pellets reacting with atmospheric carbon dioxide to form a cementitious matrix of calcium carbonate. The increase in strength with air curing was less pronounced at the coarser particle size distributions.

3. The effectiveness of corn starch increased only marginally with increased compaction pressure and pellet strength increased with increasing particle size (Tables 10,11, Figure 8). The trend of increased strength with increased particle size is the opposite of that determined for calcium hydroxide as a binder.

Extrusion

Extrusion tests were conducted using an extruder located at the University of Illinois Ceramic Engineering Building. Used as binders were corn starch (number 1 in the Binder Study) in the amount of 2 wt%, and 10 wt% calcium hydroxide. The results (Table 12) indicate that, for extrusion, corn starch is significantly better as a binder than calcium hydroxide. The strength attained using corn starch was 84.7 psi. The strength for the pellets formed with calcium hydroxide was 15.7 psi. This finding is in accordance with findings from the particle size study where corn starch was determined to be effective at producing strong pellets at lower compaction pressures such as would be expected from extrusion. The feed to the extrusion tests was also relatively coarse which favors the starch binder.

The feed to the extrusion tests was 25.7 wt% moisture and the extrudate moisture was essentially unchanged at 25.2 wt% moisture. This feed moisture content was in the same range as that used in the particle size study so results from the extrusion tests can be compared to the particle size study for potential correlations.

The results show that the extrusion products corresponded well with the results in the Particle Size Study for both calcium hydroxide and corn starch. For calcium hydroxide, the average strength of the extrudates was 15.7 psi. This value is intermediate to the value achieved at the 12,500 psi compaction pressure for the 200 mean particle size sample with 10 wt% calcium hydroxide (11.6 psi) and the 90 micron mean particle size sample (19.1 psi). As mentioned, the mean particle size of the extrusion feed was 150 microns. For corn starch as a binder the greatest pellet strength was for the 200 micron sample at 12,500 psi.

This information, along with the information determined for the pellets containing corn starch, indicate that the extruder can be roughly simulated in the lab using a 12,500 psi compaction pressure on a 1/2-inch diameter cylindrical mold.

Filtration Study-IBC-106

Filtration tests were conducted on IBC-106 samples ground to mean particle sizes of 200, 90 and 40 microns, the particle size distributions investigated in the Particle Size Study. The objective was to acquire information to determine how effectively the filtration and pelletization unit operations could be integrated. The results are listed in Tables 13-15.

For each particle size, the sample was tested with 0,5 and 10% calcium hydroxide. At the finest particle size, which most closely resembles a minus 100 mesh flotation concentrate, an anionic flocculent, ACCOAL-Floc 1206, was also tested.

The tests indicate that addition of calcium hydroxide increased the time required to allow all the visible water drain from the filter cake (form time) and with equivalent drying times resulted in increased cake moisture content. The pH of the slurry samples without calcium hydroxide were, in most cases, in the range of 4.4-4.9. The results indicate the increase in pH with addition of calcium hydroxide resulted in the sample being farther from the point of zero charge, the point where coagulation would occur.

At the finest particle size, the addition of flocculents was tested and found to increase the filtration rate considerably. At 0.5 lbs/ton the form time was cut to 14 second from 34.8 second (average of 4). Even at 0.1 lbs/ton, the form time was only 19 seconds. Filter cake moisture with 45 seconds of total filtration time was 33.4 wt%.

Importantly, by observation, it was determined that at this moisture content, the cake would be easily handled and fed to a pelletizer. As cake moisture approaches 40 wt%, materials handling problems would likely increase. A workable flowsheet would be to blend the lime or calcium hydroxide with the filter cake and feed it to a CPM. There is every indication that a high quality pellet could be produced in this manner.

California Pellet Mill

A California Pellet Mill (CPM) was ordered and received in the last quarter of the research. The mill has been installed at the Applied Research Lab of the ISGS in preparation for next year's research.

SUMMARY

This research was an investigation of calcium hydroxide as a binder/sorbent for coal fines. A flowsheet is proposed where coal fines would be recovered by column flotation, dewatered using vacuum filtration or a centrifuge, lime (CaO) or calcium hydroxide is then added to the filter cake and pelletized using a CPM and the resultant pellets air cured to increase in strength and become weatherproofed. This research will continue next year (1993-94) in the ICCI funded project "Production and Combustion Testing of Coal/Sorbent Pellets".

ACKNOWLEDGEMENTS

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Table 1 - Chemical analysis of 28x0 Illinois No. 5 coal (Wt% on a dry basis).

	Wt%		Wt%		Wt%
Ash	9.7	Sulfatic Sulfur	0.11	Carbon	74.9
Total Sulfur	1.6	Total Chlorine	0.4	Hydrogen	4.7
Pyritic Sulfur	0.75	Sodium	0.1	Nitrogen	1.5
Organic Sulfur	0.74	Arsenic	19 (ppm)	Heating Value (Btu/lb)	13,141

Table 2 - Tensile strength of 1/2-inch diameter CPM pellets.

	Compressive Strength (psi)			
	Non-Carbonated		Carbonated	
Binder	Pre-dried	Dried	Pre-dried	Dried
No Binder	5.8	5.5		
5% $Ca(OH)_2$	23.8	30.8	19.2	27.5
10% $Ca(OH)_2$	36.4	40.9	62.9	64.3

Table 3 - Tensile strength of air cured 1/2-inch diameter CPM pellets containing 10% calcium hydroxide as binder.

Days air-cured	Compressive Strength (psi)	Moisture %
0	40.5	18.7
1	45.5	12.8
3	77.9	5.0
7	71.7	5.3

Table 4 - Tensile strength of 1/2-inch diameter air cured CPM pellets containing 5% calcium hydroxide as binder.

Days air-cured	Compressive Strength (psi)	Moisture %
0	29.7	23.2
1	32.6	5.7
3	32.3	2.3
11	45.7	2.4

Table 5 - Chemical analysis of TVA cellulosic residue (% on a dry basis).

	Wt%		Wt%
Ash	0.3	Nitrogen	0.2
Total Sulfur	nil	Oxygen	39.8
Carbon	53.5	Heating Value (Btu/lb)	9436
Hydrogen	6.2		

Table 6 - Characteristic temperatures[*] for samples (°C).

Sample	T_1	T_P	T_B
100% TVA	263	331	570
20% TVA	311	345, 560	618
10% TVA	297	318, 548	611
5% TVA	304, 370	312, 553	617
20% TVA, 5% $Ca(OH)_2$	307	350, 564	618, 654
20% TVA, 10% $Ca(OH)_2$	302	355, 559	611, 669
10% $Ca(OH)_2$	389	555	606, 659
Coal	395	559	624

[*] All values are average of two or more runs.

Table 7 - Results from binder study on 28x0 mesh Illinois No. 5 seam coal fines. Values listed are tensile strengths.

		Compaction Pressure (psi)			
Binder		3,125	6,250	12,500	18,750
No Binder	green	0	0	0.6	1.2
	dried	6.0	8.0	7.1	5.7
1% corn starch 1,(13.5 cents/lb.)	green	0	0	0.3	0.8
	dried	26.0	31.9	26.8	27.8
2% corn starch 1	green	0	0	0	0
	dried	60.3	68.0	62.8	60.2
2% corn starch 2,(7.5 cents/lb.)	green	0	0.1	0.1	1.1
	dried	1.4	3.8	5.1	5.8
5% corn starch 2	green	0	0	0.3	0
	dried	2.7	4.4	6.8	6.0
1% calcium lignosulfonate (4 cents/lb.)	green	0	0	0.4	1.0
	dried	6.0	7.0	7.3	8.0
2.5 calcium lignosulfonate	green	0	0	0.6	1.2
	dried	28.9	29.1	29.5	29.1
2.5% SHUR BOND (25 cents/lb.)	green	0	0	0.7	0.6
	dried	3.5	3.4	3.6	4.5
5.0% SHUR BOND	green	0	0.1	1.4	1.9
	dried	0	0	0.7	1.6
10% SHUR BOND	green	0	0	0	0
	dried	0.1	0	0.3	0.3
10% calcium hydroxide (2.5 cents/lb)	green	0	.8	3.4	4.9
	dried	4.3	7.2	10.7	11.4
10% calcium hydroxide carbonated	green	7.1	12.8	23.5	21.7
	dried	23.6	30.9	44.3	47.8

Table 8 - Comparison of tensile strength for pellets dried in a vacuum drier to pellets air dried. Pellets formed with 18,750 psi using 28 x0 Illinois No. 5 seam coal fines.

10% calcium hydroxide	green	dried	1 day	1 month
	4.5	16.6	23.9	26.0

Table 9 - Results from combustion testing.

% $Ca(OH)_2$	Combustion Temp. °C	% Chlorine Capture	% Sodium Capture	% Arsenic Capture
0	850	nil	97.9	62.7
5	850	5.5	72.6	99.4
10	850	19.3	72.2	100.0
0	1100	nil	91.7	10.3
10	1100	22.9	20.5	86.2

Table 10 - Results from Particle Size Study for pellets formed with 1% corn starch.

Compaction Pressure	Mean Particle Size (microns)	1% Corn Starch	
		Green	Dried
6,250 psi	200	0.5	16.8
	90	3.0	13.1
	40	15.0	26.1
12,500 psi	200	1.8	20.8
	90	6.8	23.7
	40	10.6	24.3
18,750 psi vacuum dried	200	2.5	21.8
	90	7.7	24.6
	40	15.0	26.1
18,750 psi air dried	200	16.7	
	90	27.6	
	40	27.8	

Table 11 - Results from Particle Size Study for pellets formed with 2% corn starch.

Compaction Pressure	Mean Particle Size (microns)	2% Corn Starch	
		Green	Dried
6,250 psi	200	1.3	39.7
	90	2.3	31.4
	40	8.1	34.2
12,500 psi	200	1.8	54.0
	90	2.4	36.6
	40	7.6	32.4
18,750 psi vacuum dried	200	2.6	47.6
	90	4.6	39.2
	40	8.1	34.2
18,750 psi air dried	200	37.9	
	90	35.1	
	40	38.2	

Table 12 - Results from extrusion testing with 150 micron mean particle size feed. Result from test using the hydraulic press included for purposes of comparison.

	Compressive Strength in psi, (wt% moisture)		
Binder	green	dried	air cured 1 day
2% corn starch	6.6, (25.2)	94.9	80.6, (11.6)
10% calcium hydroxide	0.6, (27.0)	17.6	20.1, (9.13)
2% corn starch, hydraulic press		69.5	61.7, (5.2)

Table 13 - Filtration results for tests conducted on IBC-106 at a mean size of 200 microns

Sample	Form Time (sec)	Drying Time (sec)	Total Time (sec)	Cake Moisture wt%	Ph	ml Filtrate	Filtrate Solids (g)
0% $Ca(OH)_2$	28	17	45	40.6	4.7	425	0.3
0% $Ca(OH)_2$	22	38	60	32.1	4.8	435	0.1
0% $Ca(OH)_2$	25	50	75	37.1	4.4	410	0.1
0.25% $Ca(OH)_2$	18	42	60	38.4	7.2	440	0.1
0.5% $Ca(OH)_2$	53	7	60	39.4	8.7	430	0.1
0.75% $Ca(OH)_2$	40	20	60	40.6	10.7	445	0.1
1.% $Ca(OH)_2$	37	23	60	39.4	11.1	450	0.1
2.5% $Ca(OH)_2$	22	38	60	38.0	11.5	430	0.1
5.% $Ca(OH)_2$	36	24	60	42.3	11.2	430	0.1
10% $Ca(OH)_2$	56	4	60	44.6	11.4	405	0.1

Table 14 - Filtration results for tests conducted on IBC-106 at a mean size of 90 microns

Sample	Form Time (sec)	Drying Time (sec)	Total Time (sec)	Cake Moisture wt%	Ph	ml Filtrate	Filtrate Solids (g)
0% $Ca(OH)_2$	24	21	45	33.2	4.2	420	0.6
0% $Ca(OH)_2$	22	38	60	29.8	4.1	435	0.4
0% $Ca(OH)_2$	21	54	75	29.2	5.5	435	0.1
5% $Ca(OH)_2$	26	34	60	36.8	11.1	435	0.05
10% $Ca(OH)_2$	46	14	60	41.2	11.4	455	0.05

Table 15 - Filtration results for tests conducted on IBC-106 at a mean size of 40 microns

Sample	Form Time (sec)	Drying Time (sec)	Total Time (sec)	Cake Moisture wt%	Ph	ml Filtrate	Filtrate Solids (g)
0% $Ca(OH)_2$	38	22	60	38.1	5.9	450	0.6
0% $Ca(OH)_2$	32	28	60	34.8	5.5	445	1.9
0% $Ca(OH)_2$	39	51	90	33.0	4.9	437	0.05
0% $Ca(OH)_2$	34	26	60	33.5	4.6	430	0.02
0% $Ca(OH)_2$	40	80	120	33.4	4.9	420	0.1
0% $Ca(OH)_2$	35	25	60	34.7	5.5	420	0.05
0% $Ca(OH)_2$	20	40	60	33.1	6.2	430	0.05
0% $Ca(OH)_2$	23	37	60	33.9	6.1	415	0.05
0% $Ca(OH)_2$	26	34	60	34.2	7.5	435	0.05
0% $Ca(OH)_2$	33	27	60	36.5	10.0	425	0.05
0% $Ca(OH)_2$	40	20	60	39.5	10.9	450	0.05
0% $Ca(OH)_2$	35	25	60	42.4	11.4	410	0.1
0% $Ca(OH)_2$	53	7	60	48.8	11.3	400	0.05
0.005 lbs/ton floc	25	35	60	32.6	4.4	435	0.1
0.02 lbs/ton floc	27	33	60	33.5	4.6	430	0.5
0.1 lbs/ton floc	19	26	45	33.4	4.7	440	0.1
0.1 lbs/ton floc	19	41	60	31.9	4.8	435	0.1
0.2 lbs/ton floc	16	44	60	31.2	4.9	435	0.1
0.5 lbs/ton floc	14	46	60	31.5	5.3	445	0.05
1.0 lbs/ton floc	20	40	60	36.9	5.4	440	0.1

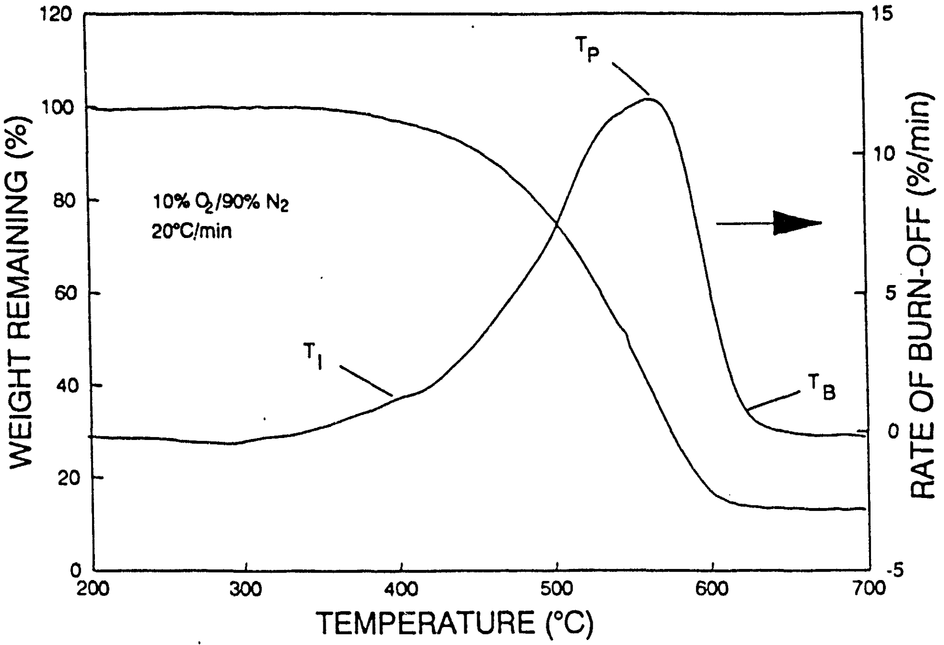


Figure 1. Typical burning profile and weight loss curve for coal burning in 10% O2, 90% N2.

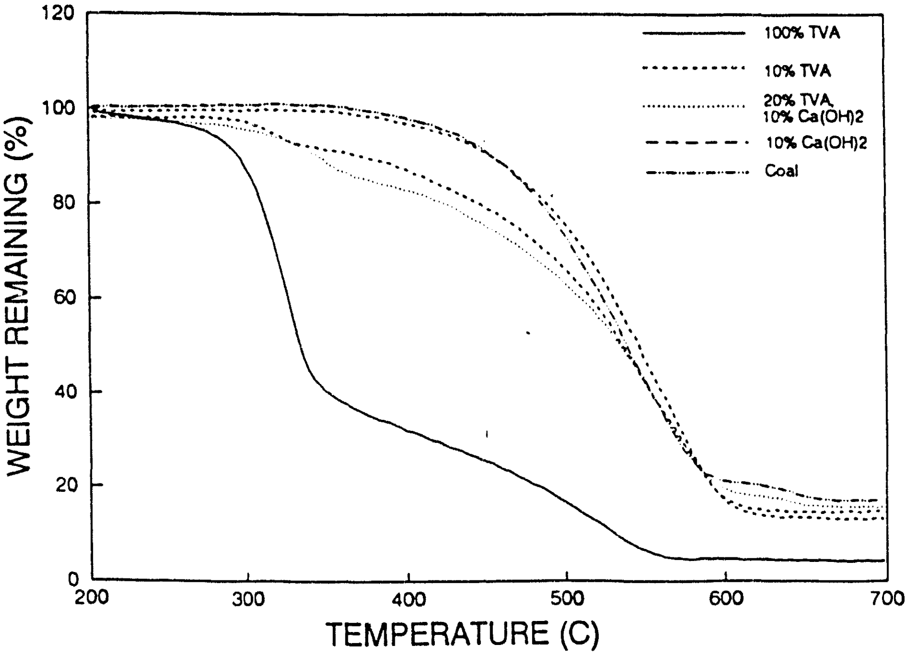


Figure 2. Weight loss curves from samples in TVA test series.

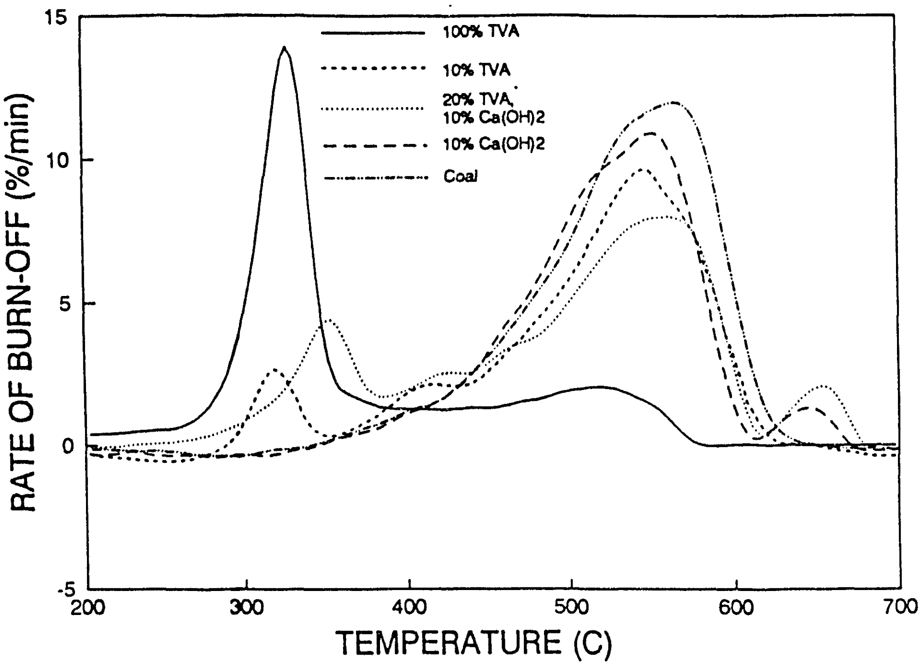


Figure 3. Burning profiles from samples in TVA test series.

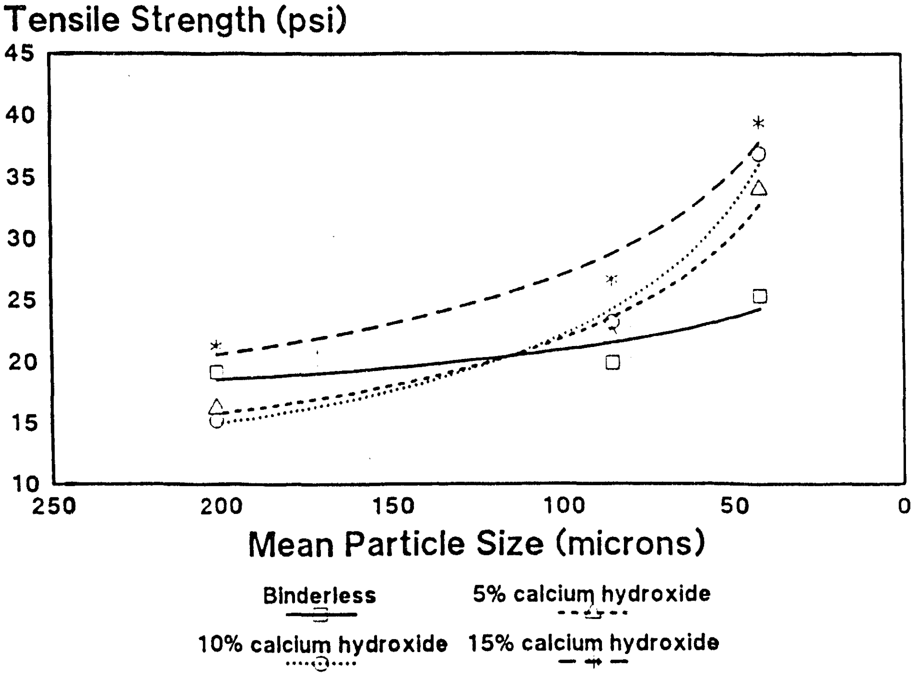


Figure 4. Effect of particle size on pellet strength with varied amounts of Ca(OH)2

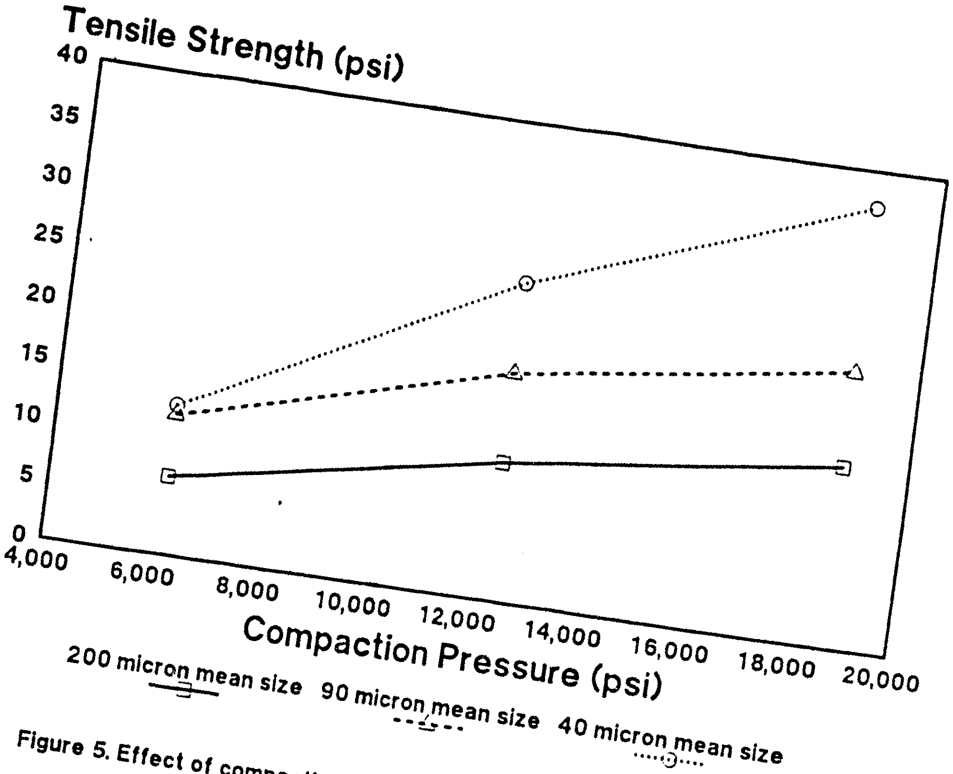


Figure 5. Effect of compaction pressure on pellet strength for pellets containing 10% $Ca(OH)_2$.

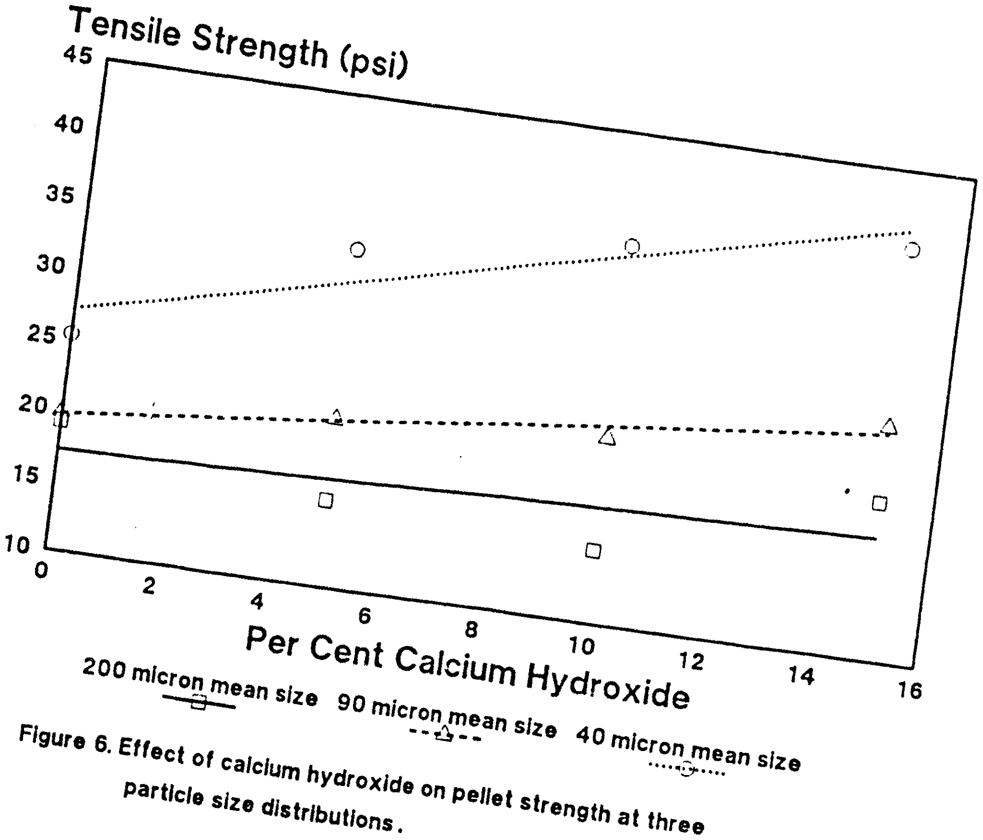


Figure 6. Effect of calcium hydroxide on pellet strength at three particle size distributions.

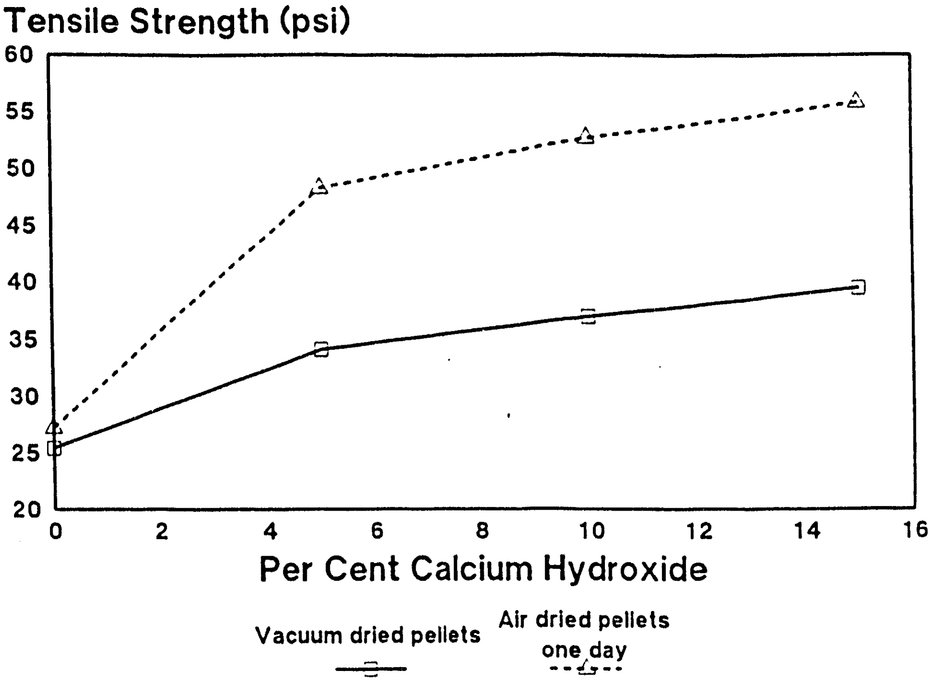


Figure 7. Effect of air-curing on pellet strength.

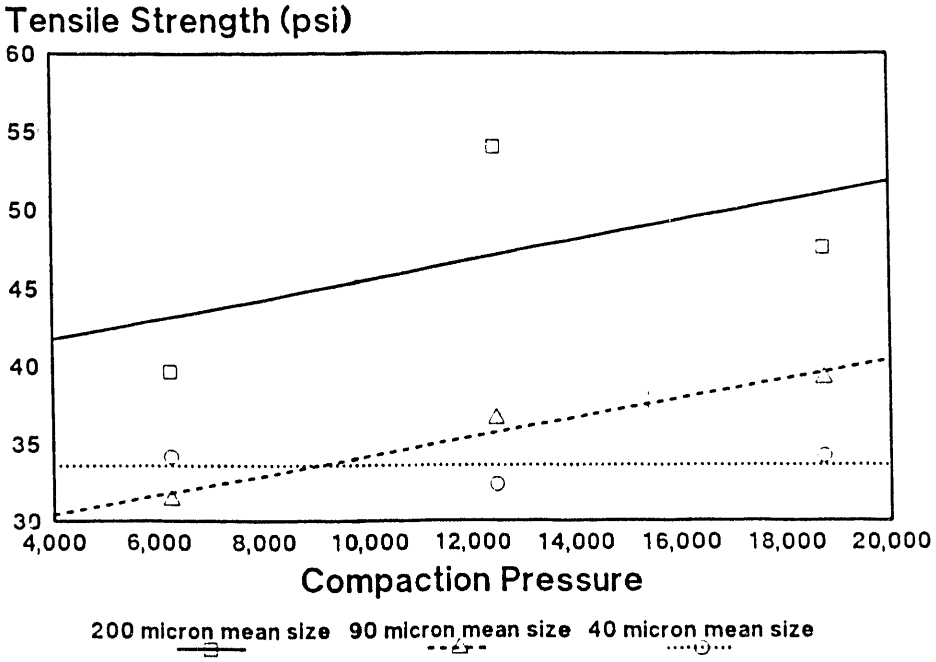


Figure 8. Effect of compaction pressure on pellet strength for pellets containing 2% corn starch.

APPENDIX

TVA Residue as a Binder

The sample of residue the ISGS received from the TVA was rather lumpy and was only 30% solids. As such, the sample was difficult to mix with the coal fines and initial attempts at forming pellets resulted in pellets that had small horizontal cracks immediately visible upon removal from the pellet mold. A small food processor was used to reduce the sample to a size that could be more evenly distributed through the coal fines.

The residue was tested for effectiveness at two moisture contents. One was at the "as received" moisture and the other was after the residue had been fully dried in a vacuum drier and sieved to remove all particles greater than 20 mesh. The two extremes in moisture were chosen to determine if additional processing (i.e. drying and sieving) would make the residue more competitive with a higher cost binder such as corn starch (13.5¢/lb).

After size reduction in the food processor, the wet material was dried and a sieve analysis was performed which indicated the product at this stage was approximately 70% minus 20 mesh. For the dried material, the screened out +20 mesh material was further ground in the food processor and re-sieved until nearly all the material was less than 20 mesh. A sieve analysis of this product indicated the particle size was approximately 80% minus 28 mesh. The two materials are referred to as the wet and dry TVA material.

For this work, the TVA material was compared to a commercially available binder, corn starch, and to the carbonate binding system. The results (Table 1A and Figure 1A) show that wet TVA material has superior binding properties to the dry material, and that the dry TVA material and calcium hydroxide function with similar effectiveness as binders. The carbonated pellets containing 10% calcium hydroxide have similar binding properties to the pellets formed with about 17% wet TVA material and with the pellets formed with about 1.7% corn starch.

Although it appears that the TVA material is significantly less effective than corn starch, the actual relative effectiveness depends on the value assigned to the TVA material. If assigned the value of $27/ton which is in the range of cost for Illinois coal, it would cost 1.35¢/pound, or 1/10th the cost of the starch. As may be observed on the graph, the binding effectiveness to achieve 400 psi strength is about 1/10th of that of corn starch. For a discussion of the effectiveness of mixtures of the material including calcium hydroxide, see the report referenced in the text.

Note: For all the work in the main body of the report, the pellets were tested for strength along the radial axis and are reported as tensile strength. For the work in this task, the pellets were tested for strength along the vertical axis and are compressive strengths. The compressive strength of a pellet is considerably higher than the tensile strength. The pellets for this work were tested in this manner because the work was performed before the ISGS purchased a strength testing machine capable of measuring lower pellet strength. The results in this work were performed using equipment in the University of Illinois Civil Engineering Department utilized to test the strength of cement materials and was not accurate at low loadings required for measurement of the tensile strength of pellets.

Compressive Strength Test, Vertical Axis - A Tinius-Olsen strength testing machine was used for this measurement. The planar ends of cylindrical pellets were placed between two parallel plates, a load was applied at 0.5 cm/minute and load at failure was recorded. The results for this measurement are reported in psi.

Table 1A - Compressive strength measured along the vertical axis for pellets in TVA test series. Pellets were 1/2" in diameter and were formed with a compaction pressure of 3000 psi. Results reported are for the average of 4 tests.

% TVA Residue*	% $Ca(OH)_2$	Carbonated **	Compressive Strength (psi)
0	0	x	5
0	5	n	85
0	5	y	180
0	10	n	110
0	10	y	390
5w	0	x	165
5d	0	x	80
5w	5	n	205
25w	5	y	240
5d	5	n	91
5d	5	y	186
5w	10	n	175
5w	10	y	355
5d	10	n	180
5d	10	y	480
10w	0	x	230
10d	0	x	105
10w	5	n	270
10w	5	y	255
10d	5	n	187

10d	5	y	300
10w	10	n	270
10w	10	y	355
10d	10	n	240
10d	10	y	540
20w	0	x	480
20d	0	x	210
20w	5	n	450
20w	5	y	460
20d	5	n	245
20d	5	y	490
20w	10	n	495
20w	10	y	545
20d	10	n	370
20d	10	y	675

* w = wet TVA residue, d = Dry TVA residue

** y = carbonated, n = noncarbonated, x = not applicable

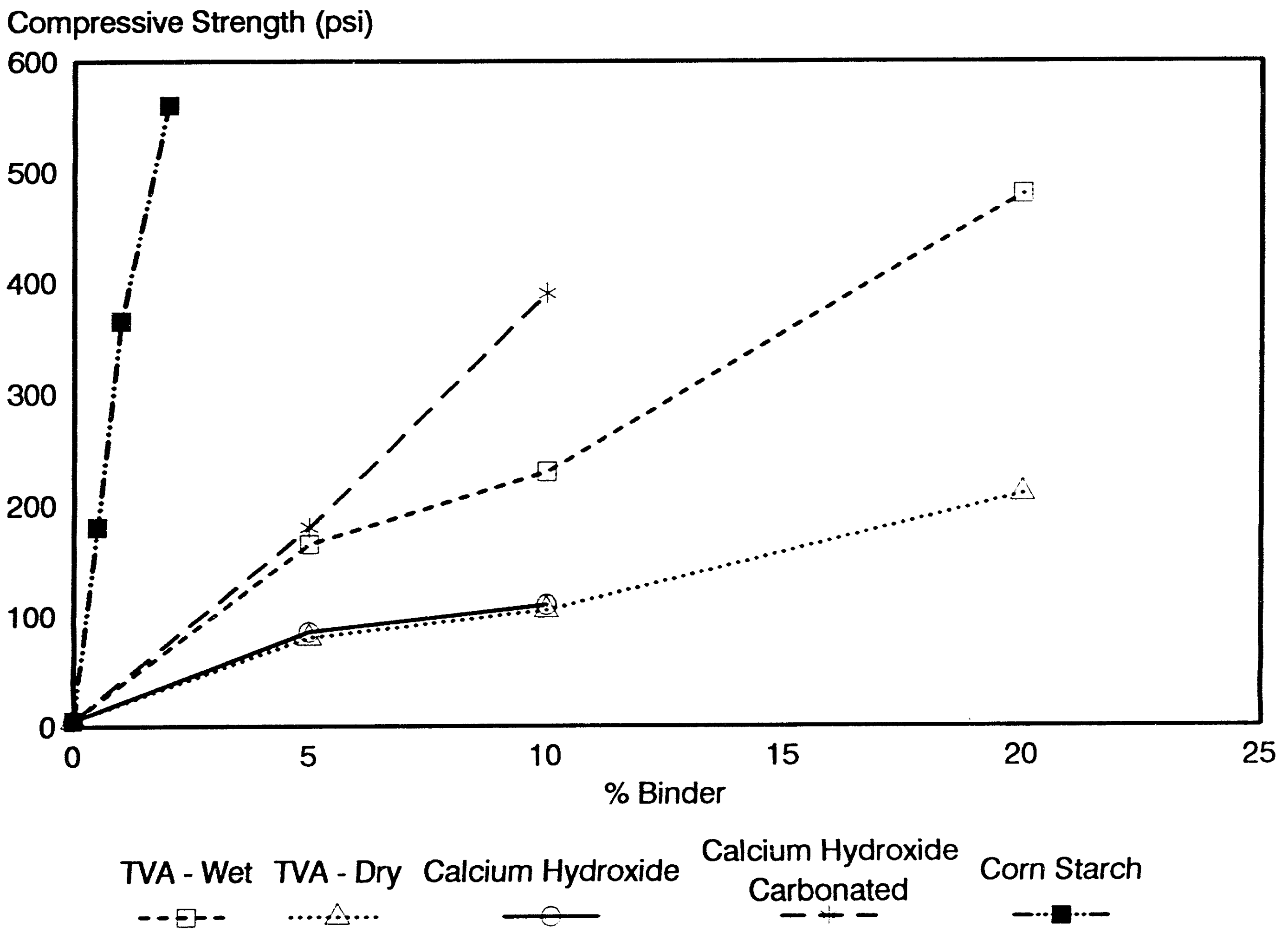


Figure 1A. Comparison of TVA residue to calcium hydroxide and the carbonate binding system and also to corn starch as binders.

IBC-106 Particle Size Study Data

Table 2A - Results from Particle Size Study for pellets formed without binder.

Compaction Pressure	Mean Particle Size (microns)	Binderless Pellets	
		Green	Dried
6,250 psi	200	9.0	2.4
	90	2.6	3.7
	40	7.8	5.6
12,500 psi	200	6.0	10.3
	90	9.0	10.8
	40	12.3	13.9
18,750 psi vacuum dried	200	1.7	19.2
	90	13.4	19.9
	40	18.9	25.4
18,750 psi air dried	200	18.2	
	90	18.4	
	40	27.2	

Table 3A - Results from Particle Size Study for pellets formed with 5% calcium hydroxide.

Compaction Pressure	Mean Particle Size (microns)	5% Calcium Hydroxide	
		Green	Dried
6,250 psi	200	1.4	7.4
	90	4.9	9.5
	40	6.3	10.1
12,500 psi	200	3.8	11.9
	90	8.6	19.1
	40	13.3	16.8
18,750 psi vacuum dried	200	5.8	16.2
	90	11.7	22.0
	40	20.8	34.1
18,750 psi carbonated vacuum dried	200	11.7	16.4
	90	20.7	26.5
	40	27.4	32.0
18,750 psi air dried	200	18.7	
	90	28.6	
	40	48.3	

Table 4A - Results from Particle Size Study for pellets formed with 10% calcium hydroxide.

Compaction Pressure	Mean Particle Size (microns)	10% Calcium Hydroxide	
		Green	Dried
6,250 psi	200	3.7	6.5
	90	3.7	11.7
	40	7.2	12.5
12,500 psi	200	6.0	11.6
	90	5.4	19.1
	40	13.4	26.7
18,750 psi vacuum dried	200	7.0	15.2
	90	10.3	23.2
	40	20.2	37.0
18,750 psi carbonated vacuum dried	200	24.2	56.4
	90	29.2	45.9
	40	43.4	51.8
18,750 psi air dried	200	20.8	
	90	23.6	
	40	52.7	

Table 5A - Results from Particle Size Study for pellets formed with 15% calcium hydroxide.

Compaction Pressure	Mean Particle Size (microns)	15% Calcium Hydroxide	
		Green	Dried
6,250 psi	200	3.3	13.7
	90	3.2	11.4
	40	5.9	14
12,500 psi	200	5.1	17.6
	90	6.5	17.6
	40	13.3	21.7
18,750 psi vacuum dried	200	7.8	21.3
	90	10.6	26.7
	40	19.1	39.5
18,750 psi carbonated vacuum dried	200	46.0	87.3
	90	57.5	96.9
	40	74.3	74.3
18,750 psi air dried	200	28.5	
	90	30.8	
	40	55.8	

PROJECT MANAGEMENT REPORT
June 1, 1993 through August 31, 1993

Project Title: **CARBONATION AS A BINDING MECHANISM FOR COAL/CALCIUM HYDROXIDE PELLETS**

Principal Investigator:	David Rapp, ISGS
Other Investigators:	John Lytle, ISGS
	Keith Hackley, ISGS
	Marianne Dagamac, ISGS
	Richard Berger, UI-UC
	Gary Schanche, CERL
Project Manager:	Ken Ho, ICCI

COMMENTS

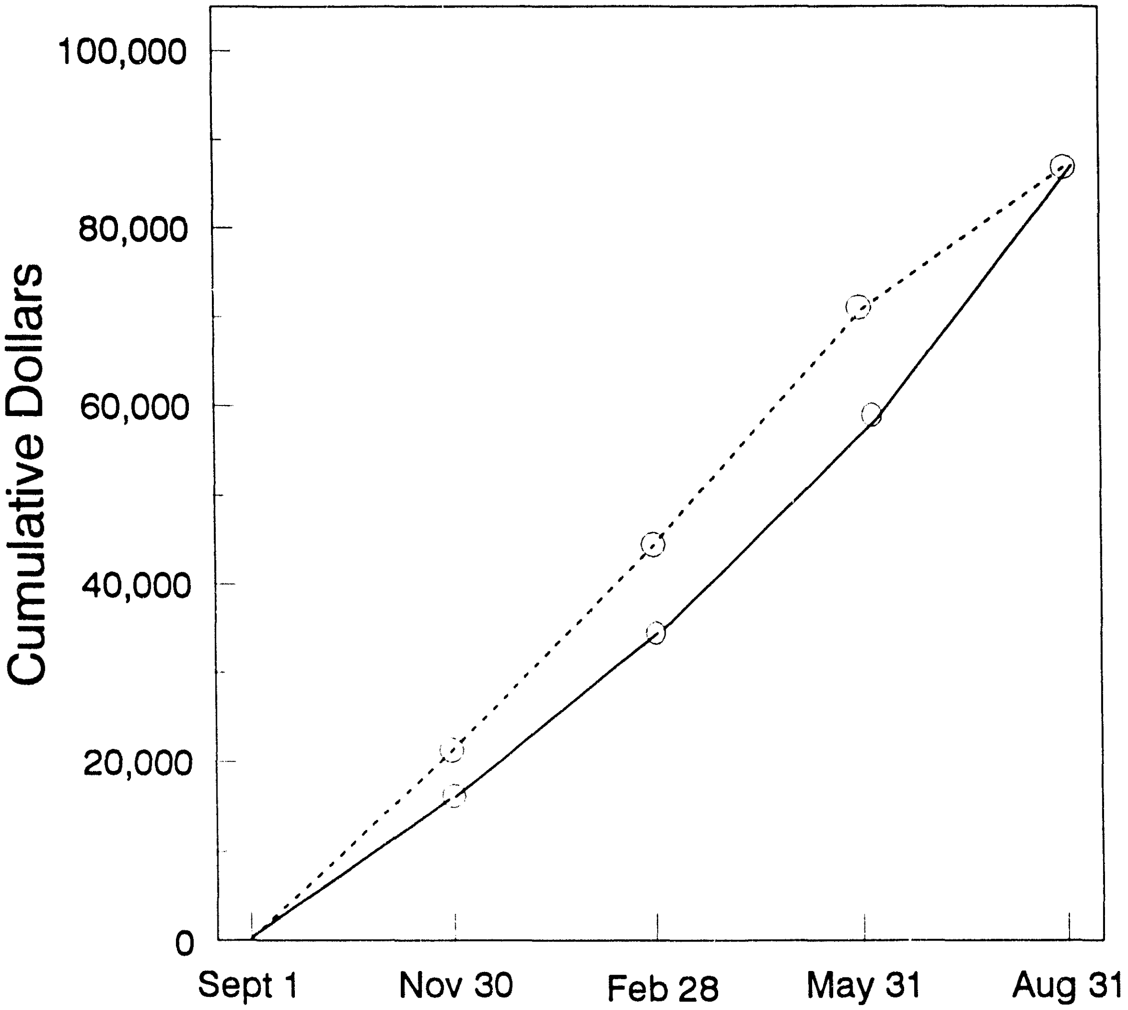
EXPENDITURES - EXHIBIT B

Projected and Estimated Actual Expenditures by Quarter

Quarter (cumulative by quarter)	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, to Nov. 30, 1992	Projected	14,526	225	0	500	3,925	1,918	21,094
	Est. Actual	14,525	607	0	0	2,001	1,713	18,846
Sept. 1, 1992 to Feb. 28, 1993	Projected	29,051	450	0	750	8,200	3,845	42,296
	Est. Actual	29,051	998	0	0	3,364	3,341	36,754
Sept. 1, 1992 to May 31, 1993	Projected	43,577	675	0	1,000	12,272	5,752	63,276
	Est. Actual	43,577	998	0	0	6,980	5,155	56,709
Sept. 1, 1992 to Aug. 31, 1993	Projected	55,392	910	50	3,710	16,196	7,626	83,884
		54,864	998	0	3,710	16,686	7,626	83,884

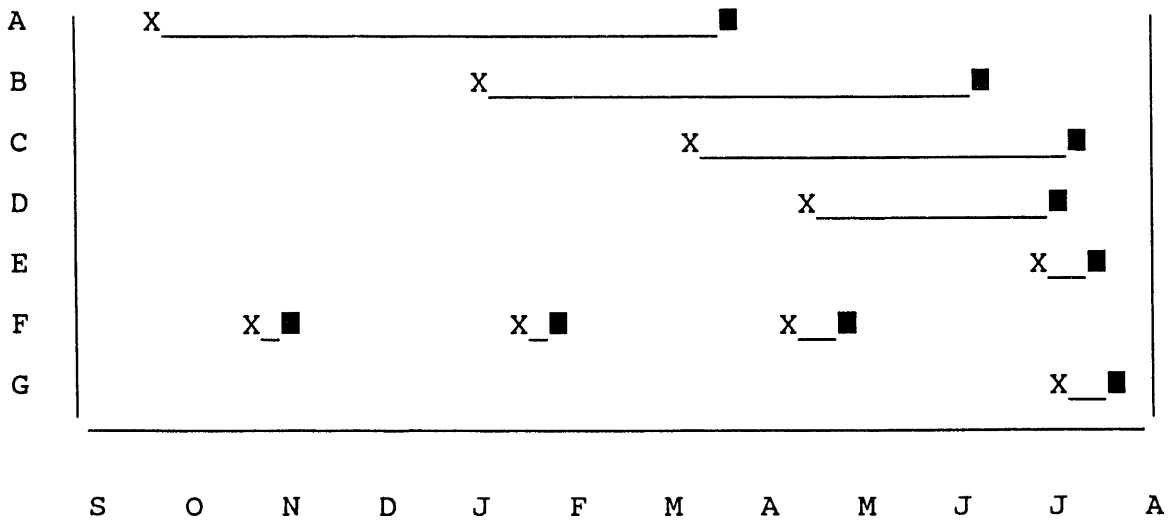
COSTS BY QUARTER - EXHIBIT C

CARBONATION AS A BINDING MECHANISM FOR COAL/CALCIUM HYDROXIDE PELLETS



Projected Expenditures - - - - - -	83,884
Actual Expenditures ———	83,884
Total ICCI Award $	83,884

SCHEDULE OF PROJECT MILESTONES



Milestone

A. Particle Size, Moisture, Binder Study
B. Binder Study
C. TVA TGA Study
D. Filtration Study
E. CPM Installation
F. Quarterly Reports
G. Final Report

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