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TECHNICAL REPORT
December 1, 1994 through February 28, 1995

Project Title: **DESIGN AND FABRICATION OF ADVANCED MATERIALS FROM ILLINOIS COAL WASTES**

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Principal Investigator: Vivak M. Malhotra, Professor
Southern Illinois University at Carbondale
Other Investigators: Maurice A. Wright, Director
Materials Technology Center, Southern Illinois University at Carbondale
Project Manager: Dr. Dan Banerjee, Illinois Clean Coal Institute

ABSTRACT

The main goal of this project is to develop a bench-scale procedure to design and fabricate advanced brake and structural composite materials from Illinois coal combustion residues. During the first two quarters of the project, the thrust of the work was directed towards characterizing the various coal combustion residues and FGD residue, i.e., scrubber sludge. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), differential thermal analysis (DTA), and transmission-Fourier transform infrared (FTIR) were conducted on PCC fly ash (Baldwin), FBC fly ash (ADM, unit1-6), FBC fly ash (S.I. coal), FBC spent bed ash (ADM, unit1-6), bottom ash, and scrubber sludge (CWLP) residues to characterize their geometrical shapes, mineral phases, and thermal stability. Our spectroscopic results indicate that the scrubber sludge is mainly composed of a gypsum-like phase whose lattice structure is different from the lattice structure of conventional gypsum, and sludge does not contain hannebachite ($CaSO_3.0.5H_2O$) phase. Our attempts to fabricate brake frictional shoes, in the form of 1.25 inch disks, from PCC fly ash, FBC spent bed ash, scrubber sludge, coal char, iron particles, and coal tar were successful. Based on the experience gained and microscopic analyses; we have now upscaled our procedures to fabricate 2.5 inch diameter disks from coal combustion residues. This has been achieved. The SEM and Young's modulus analyses of brake composites fabricated at 400 psi < Pressure < 2200 psi suggest pressure has a strong influence on the particle packing and the filling of interstices in our composites. Also, these results along with mechanical behavior of the fabricated disks lead us to believe that the combination of surface altered PCC fly ash and scrubber sludge particles, together with FBC spent bed ash particles are ideal for our composite materials.

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

EXECUTIVE SUMMARY

This project seeks to make use of an advanced, integrated approach for the design and fabrication of brake and structural composite materials from coal combustion residues and coal gasification by-products. The composite materials, which will use significant amounts of combustion residues (20 to 50 wt %) and coal chars (10 to 30 wt %), not only will alleviate the disposal costs and the potential environmental damage costs associated with residues but will also convert residues into high value structural composite materials.

During the first two quarters of this project, the main thrust of the work was directed towards characterizing various coal combustion residues and flue gas desulfurization residue from Illinois sources. In addition, we have demonstrated the feasibility of converting these combustion residues into brake composites and structural composites by fabricating 2.5 inch disks suitable either for frictional performance or structural composite. To characterize PCC fly ash, FBC fly ash (ADM, unit1-6), FBC spent bed ash (ADM, unit1-6), FBC fly ash (S.I. Coal), bottom ash, and scrubber sludge (CWLP), we undertook differential scanning calorimetry (DSC) measurements at $30°C < T < 600°C$ and differential thermal analysis (DTA) at $50°C < T < 1100°C$. Moreover, we subjected the residues to SEM and transmission-FTIR analyses. Based on these characterization data the following was concluded: (a) The PCC fly ash particles are spherical in shape and range from 0.2 μm to 15 μm. Because of their shape and since the particles are thermally inert up to 1100°C, the PCC fly ash is an excellent raw material for our brake and structural composite materials. The PCC fly ash is largely composed of oxides including hematite and magnetite. The presence of these two microwave lossy components makes sintering of materials containing PCC fly ash via microwave heating possible. (b) The scrubber sludge particles, in general, have a shape which is whisker-like, thus imparting it with fiber-like characteristics. Our FTIR analysis of the scrubber sludge sample revealed that CWLP sludge does not contain calcite, hannebachite ($CaSO_3.0.5H_2O$), or bassanite. Our analysis also showed that sludge is mainly composed of gypsum ($CaSO_4.2H_2O$). However, it must be cautioned that the sludge's gypsum lattice structure is different from the conventional gypsum lattice structure. Therefore, the scrubber sludge particles may not display the physical and chemical properties of conventional gypsum. Also, our DSC and DTA data suggested that before scrubber sludge particles can be used they must be heated to 200°C to evolve out the water associated with sludge. At $200°C < T < 1000°C$, our DSC and DTA data indicated the dehydrated gypsum is thermally stable, thus. very suitable for our composites. Therefore, the presence of scrubber sludge particles in our composites will provide mechanical strength to our materials. (c) The FBC fly ash and FBC spent bed bottom ash particles showed a considerable amount of fusion resulting in larger sized particles, i.e., 100 μm to 750 μm. The transmission-FTIR data on the two FBC fly ashes examined lead us to believe that the main constituents of FBC fly ash are anhydrite, lime, portlandite, calcite, hematite, magnetite, and various glass phases. The FBC spent bed ash is largely composed of anhydrite, lime, portlandite, calcite, periclase, hematite, and magnetite. The thermal stability characteristics of FBC fly ash and FBC

spent bed ash, as determined by DSC and DTA techniques, are such that they make these particles suitable raw materials for brake composite materials and structural composites. (d) The bottom ash particles contained a considerable amount of carbon and have a highly porous but glassy structure, thus, making the bottom ash particles an ideal filling material for our brake lining material and structural composites. (e) After our initial attempts to form structural composites, in the form of 1.25 inch disks, from PCC fly ash, FBC spent bed ash, scrubber sludge, coal char, and coal tar were successful, we upscaled the size of our structural composites to 2.5 inch diameter disk size. One of the disks fabricated is shown in the figure below.

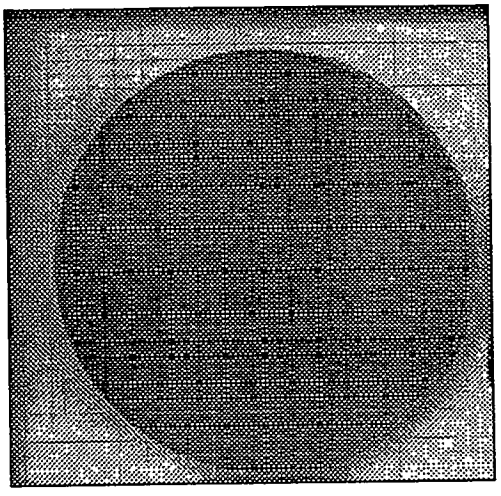

Figure showing 2.5 inch diameter disk fabricated from PCC fly ash, FBC spent bed ash, scrubber sludge, and coal char

Our microscopic results on the fabricated disks indicated that pressure had a strong influence on the pore structure of the fabricated material and pressures of 2100 psi or above should be used to control the porosity of the resultant composite. (f) The SEM and Young's modulus analyses on the brake composites fabricated from PCC fly ash, FBC spent bed ash, scrubber sludge, coal char, and iron particles as a function of pressure showed that higher pressures lead to better particle packing and better mechanical performance.

OBJECTIVES

The main goal of this project is to develop a bench-scale procedure to design and fabricate advanced brake and structural composite materials from Illinois coal waste residues by utilizing the effective capability of fly ash and FBC residues to modify coal tar's thermosetting properties. The specific objectives of our project are: (1) to characterize both structural and thermal properties of various combustion residues and gasification residues from power plants using Illinois coals, (2) to evaluate how the glass transition temperature and the subsequent thermosetting behavior of processed coal tar are altered by additives such as fly ash residue and FBC residue, (3) to optimize the thermosetting properties of processed coal tars by altering the concentration and types of residue additives used such that the desired end product, i.e., advanced brake and structural composite materials, is fabricated, (4) to identify and to optimize the engineering steps required to fabricate the high value, advanced brake composite materials, (5) to ascertain and to optimize the engineering conditions under which high value, advanced structural composite materials for the automotive industry could be fabricated from coal combustion residues, (6) to characterize the fabricated advanced brake and structural composite materials for their suitability and performance as brake and structural materials, and (7) to undertake a systematic, economic analysis of our process and to present comparisons with competitive products. In the first year of the project the thrust of the work is to be directed towards the first four listed objectives.

INTRODUCTION AND BACKGROUND

Massive quantities of inorganic residues are generated when coal is gasified or burned, and when flue gases are scrubbed of sulfur dioxide. According to Golden of EPRI, the electric utilities in the USA produce about 90 million tons of coal combustion ash residues annually. It is believed that a typical 800 Megawatt power plant consumes about 7500 tons of coal and generates 1000 tons of fly and bottom ash per day. The Federal Clean Air Act Amendments of 1990 mandate that sulfur emissions by coal-fired industry be significantly reduced by the year 2000. Illinois coals contain high sulfur. The sulfur is in the form of inorganic minerals (chiefly pyrite) and is also organically bound. Therefore, continuous utilization of midwest coal will require scrubbing which will further enlarge combustion residue production. It is estimated that by the turn of century about 200 million tons of coal combustion residue will be produced annually. With the current cost of residue disposal expected to rapidly escalate from $10/ton to $30/ton by the year 2000, the economic stakes for the coal utilization industry are substantial. Consequently, the technologies which can convert combustion residues into high value, but economically sound, materials are of utmost importance. Our proposed research of converting combustion residues into advanced brake and structural materials precisely does that.

EXPERIMENTAL TECHNIQUES

Transmission-Fourier Transform Infrared (Transmission-FTIR) Measurements : This quarter we continued our efforts to characterize the coal combustion residues (CCR) and flue gas desulfurization (FGD) residue obtained from the Mining Engineering (Southern Illinois University at Carbondale) Department's Combustion Residue Bank. The Transmission-FTIR data were collected on PCC fly ash (Baldwin, unit #3), FBC fly ash (ADM, unit 1-6), FBC spent bed (ADM, unit # 1-6), FBC fly ash (S.I. coal), scrubber sludge (CWLP, Springfield), and bottom ash. The KBr pellet technique was adopted to record the transmission-FTIR spectra of CCR and scrubber sludge. The spectra were obtained on a Nicolet IR-44 FTIR spectrometer equipped with a DTGS detector and interfaced with a PC computer. Typically, 100 single beam scans (interferograms) of the sample were collected. The reference interferograms were collected under identical conditions but without a sample in the beam. During this process, the spectrometer was continuously purged with dry nitrogen gas. With the use of the transformed single-beam sample and reference spectra, the spectra of the sample could be plotted as transmittance or absorbance. We used triangular apodization to transform the interferograms acquired at 4 cm^{-1} resolution. Therefore, the effective resolution of the spectra was approximately 6 cm^{-1}. The KBr pellets were dried for 24 hours in a desiccator before the pellets were subjected to transmission-FTIR measurements.

Fabrication of Structural and Brake disks : In the last three months, we continued with our attempts to fabricate both structural composite materials and brake composite materials from coal combustion residues, scrubber sludge, and coal tar. Generally, the following steps were executed for fabricating the composites: (1) As a first step, the coal tar obtained from Illinois coals was processed to enhance its ash wetting properties. (2) A dilute solution of the processed coal tar was formed with tetrahydrofuran. This product henceforth will be called "Tar-THFsolution". The PCC fly ash combustion residue particles were combined with Tar-THF solution to form a colloidal structure which ensured that the residue particles were thoroughly coated with tar. The tetrahydrofuran was recovered from the colloidal structure by rotary evaporation, and the tar coated particles were dried in air. The dried particles had the appearance of a fine powder. This powder will be classified as "MAL101" powder. (3) A similar colloidal structure, as described in step 2, was prepared with scrubber sludge particles. The powder obtained from the sludge particles will henceforth be referred to as "MAL201". (4) The tar coated particles of the combustion residue were mixed with various ingredients as shown in Table 1 to form structural composite materials. (5) The tar coated particles of scrubber sludge, FBC spent bed ash, and iron were mixed with various ingredients as shown in Table 2 to fabricate brake composite. (6) Mixtures listed in Tables 1 and 2 were accurately weighed and were ground in a mortar. The ground samples were thoroughly mixed to ensure the best achievable homogeneous distribution of the particles. A one and one quarter inch diameter pellet die was prepared by applying a thin coating of a standard release agent. The die was cured at 200°C (473 K) for one hour and cooled to room temperature. The sample mixtures were poured into

the die and hot pressed at the desired pressure and temperature to form the primary composite skeleton. (7) A procedure identical to step 6 was used to form 2.5 inch diameter composite disks except the die was of the appropriate size. It is worthwhile to remark here that the hot pressed sample must be cooled to room temperature before the sample is removed from the die. Failure to do so, our observations indicate, will result in the collapse of the composite structure.

TABLE 1
Various Mixtures Used To Fabricate Structural Composites at 200° C

Sample No.	Coated Particles (wt%)	Coal Char (wt%)	Asphaltene (wt%)	FBC Spent Bed Particles (wt%)	Phenolic Resin (wt%)	Press-ure (psi)
MAL 204	MAL201: 36 %, MAL101: 15.3 %	3 %	10.4 %	16.8 %	13.40 %	2012
MAL 205	MAL201: 36 %, MAL101: 12.6%,Fe:6%	6 %	7.5 %	18 .0 %	12.00 %	2012
MAL 206	MAL201: 33.4%, Fi-bers: 1%	16.6 %	16 %	20.0 %	13.0 %	2982
MAL 207	MAL201: 33.4%, Fibers:1.8%	16.6 %	16 %	20.0 %	13.0 %	2982
MAL 208	MAL201: 33.4%, Fibers:0.6%	16.7 %	16 %	20.0 %	13.0 %	1760

Scanning Electron Microscopic (SEM) Measurements: We collected SEM images on brake composite materials AMOL001, AMOL002, AMOL003, AMOL004, and AMOL005. These data were collected with a view to understand how pressure and particle packing affect the composite. The SEM images were obtained using a Hitachi S-570 scanning electron microscope. A thin portion of the composite was cut and was glued on a SEM high resolution stub. The composite samples were then heated at 60° C (333 K) for 24 hours. These steps were necessary to ensure that the composite would not detach from the stubs when under electron beam and also would not decompose when under electron bombardment. The composite samples were sputter coated with a 400°A thin layer of gold to reduce sample charging. Generally, the SEM micrographs were collected using an accelerating voltage of 20 kV. The working distance used was in the range of 8 mm to 12 mm.

Mechanical Tests (Young's Modulus): The hot pressed brake composite materials, i.e., AMOL002, AMOL003, AMOL004, and AMOL005, were subjected to the three point

TABLE 2
Various Mixtures Used To Fabricate Brake Composites at 180° C

SAMPLE NO.	Coated particles (grams)	Coal Char (grams)	Iron Particles (grams)	FBC Spent Bed Ash (grams)	Phenolic Resin (grams)	Pressure (psi)
AMOL001	MAL201: 6.68 , Fibers: 0.40	7.00	0.0	2.00	4.5	2100
AMOL002	MAL201: 6.68, Fibers: 1.00	6.00	2.0	2.00	4.5	2100
AMOL003	MAL201: 6.68, Fibers: 1.00	6.00	2.0	2.00	4.5	1700
AMOL004	MAL201: 6.68, Fibers: 1.00	6.00	2.0	2.00	4.5	1100
AMOL005	MAL201: 6.68, Fibers: 1.00	6.00	2.0	2.00	4.5	500

bend test to determine their mechanical performance. It is worthwhile to point out here that our brake composite material had not yet undergone sintering reactions to strengthen the chemical bonds in the material. We used a diamond circular saw to cut rectangular strips of the sample having nominal thickness of about 0.2 inch and width of 0.4 inch from 2.5 inch diameter brake composite material. Seven samples were subjected to three point bend testing to determine the Young's modulus of our hot pressed, but not sintered, brake composite material. The samples were labeled as follows:

1. AMOL002
2. AMOL003A
3. AMOL003B
4. AMOL004A
5. AMOL004B
6. AMOL005A
7. AMOL005B

The equipment used to measure the Young's modulus was the Instron Universal Testing Instrument (model 4206) located in the Mechanical Engineering Department. This system is a highly reliable precision system for evaluating the mechanical properties of materials. The system is designed to test materials under either tension or compression; and a complete range of extensometers, fixtures, and local cells is available. The equipment is controlled by a microprocessing unit which in turn is controlled by a computer for actuation and data collection. A sketch of the fixture used for three point bending measurements of our brake composites is shown in the figure below. The span length was fixed at 1.6 inch. The sample was supported by two cylinders below and one cylinder

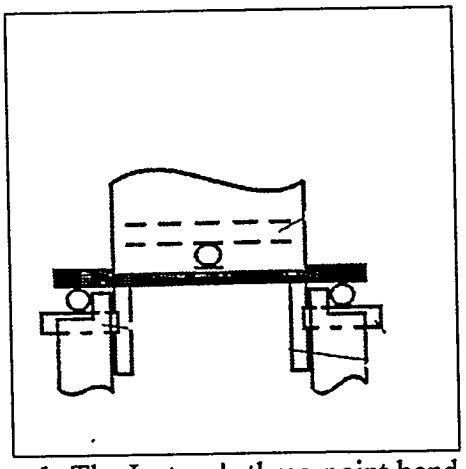

Figure 1. The Instron's three-point bend fixture.

above the center of the specimen. A force was applied directly above the center of the specimen to measure the deflection as the force was applied. The Young's modulus, E, was determined by plotting the force versus deflection. In the region of the plot before the specimen breaks, the curve was linear and the behavior was elastic. The slope, S, of that linear region was used to determine the Young's modulus of the material, i.e.,

$$E = \frac{SL^3}{4wt^3} \quad , \qquad (1)$$

where L is the span length, w is the width, and t is the thickness of the sample.

RESULTS AND DISCUSSION

FTIR Characterization Results: The spectroscopic studies of various combustion residues were undertaken to characterize the mineral and glass phases of the PCC fly ash, FBC fly ash, FBC spent bed ash, bottom ash, and scrubber sludge. These data are important for our composites because they will help us in predicting the thermal and mechanical stability of the fabricated material. Our transmission-FTIR results on various residues are summarized below. **Scrubber Sludge**: In Fig. 2 we have reproduced the transmission-FTIR spectrum of scrubber sludge particles which were air dried prior to recording their spectrum. Three very strong bands were observed at 1154, 1126, and 1105 cm^{-1}. In addition, a doublet having frequencies 662 and 602 cm^{-1} was observed. In the water's stretching region, two distinct vibrational modes can be seen in Fig. 2 at 3617 and 3559 cm^{-1}. In the water's bending region only a single oscillator is observed at 1620 cm^{-1}. It is generally believed that the FGD residue, e.g., scrubber sludge, contains calcite ($CaCO_3$), hannebachite ($CaSO_3.0.5H_2O$), gypsum ($CaSO_4.2H_2O$), quartz (SiO_2), and troilite (FeS). The absence of any vibrational bands below 450 cm^{-1} lead us to discount the presence of troilite. Since we did not observe any band in the FTIR spectrum of the scrubber sludge at around 1430 cm^{-1}, we can also rule out the presence of calcite particles in our sludge sample. The argument that quartz may be present in our sample

was discarded because the diagnostic bands for it at around 1050 and 472 cm^{-1} were not observed in our FTIR spectrum. However, our transmission-FTIR data do suggest the presence of gypsum in our sample. The vibrational bands at 1154, 1126, and 1105 cm^{-1} can be assigned to ν_3 of sulfate of gypsum, while the oscillators at 662 and 602 cm^{-1} can be attributed to ν_4 of sulfate ions. The presence of two vibrational modes in the water's stretching region implies the presence of two types of hydrates in our scrubber sludge. A comparison of a commercially available gypsum's FTIR spectrum, see Fig. 2, with our scrubber sludge spectrum indicates that gypsum formed in the FGD residue has a lattice structure which is different from that of commercial gypsum. It is worth pointing out that the FTIR spectrum of bassanite ($CaSO_4.0.5H_2O$) shows a vibrational mode at about 3615 cm^{-1} and we observe a band at 3617 cm^{-1}. However, we cannot assign 3617 cm^{-1} band to bassanite because the accompanying water band at 3465 cm^{-1} is absent in our spectrum. We also rule out the presence of hannebachite because of two reasons, i.e., (a) we did not observe the expected strong bands at 975 and 940 cm^{-1} of SO_3 ion in our FTIR spectrum of the scrubber sludge, and (b) we did not see any rectangular crystals, which can be associated with hannebachite, in our SEM images of the sludge. In view of the discussion presented above we argue that scrubber sludge is mainly composed of gypsum. However, its lattice structure is not identical to the lattice structure of conventional gypsum.

PCC Fly Ash (Bladwin) : The PCC fly ash sample was magnetically separated into two parts, i.e., non-magnetic PCC fraction and magnetic PCC fraction. The two fractions' transmission-FTIR spectra along with the spectrum of whole PCC fly ash were recorded. The observed infrared frequencies of PCC fly ash along with their assignments are listed in Table 3. Based on the data presented Table 3, it is argued that PCC fly ash is largely composed of various oxides. The strongest bands in our transmission-FTIR spectrum of PCC fly ash originated from quartz. The results are consistent with those reported by other researchers. **FBC Fly Ash (ADM, unit 1-6):** The transmission-FTIR spectrum of as-received FBC fly ash along with its non-magnetic and magnetic components' FTIR spectrum are displayed in Fig. 3. The observed infrared frequencies are listed in Table 3. Also given in Table 3 are the assignments of observed frequencies. It has been argued that FBC fly ash contains quartz, anhydrite ($CaSO_4$), gypsum, lime (CaO), portlandite ($Ca(OH)_2$), calcite, periclase (MgO), hematite (Fe_2O_3), magnetite (Fe_3O_4), feldspar, illite, and glass phases. Our transmission-FTIR results confirm the presence of portlandite, anhydrite, lime, hematite, magnetite, and calcite in our FBC fly ash samples. **FBC Spent Bed Ash (ADM, unit 1-6)** : In Fig. 4 we have reproduced our FTIR spectrum of FBC spent bed ash. Also shown in this figure is the FTIR spectrum of non-magnetic and magnetic fraction of spent bed ash. From the observed infrared frequencies, which are listed in Table 3, the following minerals have been identified, i.e., anhydrite, lime, portlandite, calcite, periclase, hematite, and magnetite. It is also generally reported that spent bed ash contains CaS. The formation of CaS is believed to occur for circulating fluidized bed combustion (FBC) via the following reaction, i.e., $CaO + H_2S \rightarrow CaS + H_2O$. However, it is difficult for us to confirm the presence of CaS in our FBC spent bed ash as CaS produces no infrared bands.

The Structural Composites : This quarter we continued our efforts to optimize the procedures for hot pressing the structural composite materials. In addition, to establish the steps required to achieve maximum packing of the particles, we tested different combinations of MAL101 (PCC fly ash tar coated particles) and MAL201 (scrubber sludge tar coated particles). Our SEM measurements on FBC spent bed ash have shown these ash particles to be irregular in shape and size. Therefore, when spent bed ash particles are mixed with MAL101 particles, the spherical MAL101 particles are expected to fill the interstices formed by large FBC spent bed particles when pressed. It is well known that the porosity of structural materials directly affects their mechanical strength. Therefore, it is imperative that we minimize the porosity in our structural composites. Our results show that on hot pressing the ingredients listed in Table 1 at 200°C we do form good quality composite materials. The composite MAL207 in the form of a 1.25 inch disk, fabricated from scrubber sludge, FBC spent bed ash, coal char, asphaltene, phenolic resin, and low grade carbon fibers, is shown in Fig. 5. Encouraged by our success to form 1.25 inch structural composite disks, we have now upscaled the disk size to 2.5 inch diameter. Figure 6 reproduces the 2.5 inch and 1.25 inch diameter structural composites fabricated from PCC fly ash, FBC spent bed ash, scrubber sludge, and coal char. Presently, we are systematically varying the pressure, time of hot pressing, and the relative concentration of PCC fly ash, FBC spent bed ash, and scrubber sludge particles in our composites whose mechanical properties will be gauged.

Brake Composite Materials: As mentioned in the experimental section, we examined the microscopic structure of our brake composite by conducting SEM measurements on AMOL002, AMOL003, AMOL004, and AMOL005. In Figs. 7 and 8, we reproduce the brake composites AMOL005 and AMOL002's SEM microphotographs, respectively. It should be noted that AMOL005 was hot pressed at 500 psi pressure, while sample AMOL002 was hot pressed at 2100 psi. It is clear from Figs. 7 and 8 that composite AMOL005 has much larger porosity than AMOL002 composite. Therefore, it appears that higher pressures result in reduced porosity in the hot pressed samples. As pointed out earlier reduced porosity should increase the mechanical strength of our materials. In view of this we propose to limit the lower pressure under which our brake composites are fabricated to 2100 psi. It also appears from Figs. 7 and 8 that fibers tended to bunch in our composite. To achieve better dispersion we will pre-wet and shear mix our fibers before the brake composites are hot pressed. In Table 4, we have listed the Young's modulus (E) values for various brake composites hot pressed at 180°C. Since the brake materials have not yet undergone sintering, we expect dramatic changes in its E values after sintering.

CONCLUSIONS AND RECOMMENDATIONS

During the first two quarters of this project, the main thrust of the work was directed towards characterizing various coal combustion residues and flue gas desulfurization residue from Illinois sources. In addition, we have demonstrated the feasibility of

TABLE 3
The observed FTIR frequencies from PCC fly ash, FBC fly ash, and FBC spent bed ash.

PCC Fly Ash (cm^{-1})	FBC Fly Ash (cm^{-1})	FBC Spent Bed Ash (cm^{-1})	Intensity*	Assignment
3,642	3,642	3,642	sp,m	O-H stretch of $Ca(OH)_2$
3,448	3,462	3,448	vb,m	O-H stretch of H-O-H
1,631	-	1,624	b,w	H-O-H bend of H_2O
-	1,449	1,448	b.m	$CaCO_3$
-	1,144	1,154	b,vs	$CaSO_4$
-	1,111	1,122	b,vs	$CaSO_4$
1,072	-	-	b,vs	Si-O-Si stretch of quartz (SiO_2)
-	1,011	-	sp,w	$CaSO_4$
-	-	945	b,m	$Ca(OH)_2$
-	-	920	b,m	$Ca(OH)_2$
-	885	-	sp,m	$CaCO_3$
794	795	-	sp,m	quartz (SiO_2)
778	-	-	sp,m	quartz (SiO_2)
694	-	-	w	quartz (SiO_2)
	681	680	sp,m	$CaSO_4$
613	616	615	sp,w	$CaSO_4$, Al_2O_3, Fe_2O_3
-	602	605	sp,w	
-	-	595	sh,w	$CaSO_4$
560	-	560	b,w	CaO, MgO
-	515	-	sp,w	Fe_2O_3
462	462	462	sp,s	CaO, MgO,quartz (SiO_2)

* sp: sharp, sh: shoulder, vs: very strong, s: strong, m: medium, w: weak, b: broad, vb: very broad

converting these combustion residues into brake composites and structural composites by fabricating 2.5 inch disks suitable either for frictional performance or structural composite. To characterize PCC fly ash, FBC fly ash (ADM, unit1-6), FBC spent bed ash (ADM, unit1-6), FBC fly ash (S.I. Coal), bottom ash, and scrubber sludge (CWLP), we undertook differential scanning calorimetry (DSC) measurements at $30°C < T < 600°C$ and differential thermal analysis (DTA) at $50°C < T < 1100°C$. Moreover, we subjected the residues to SEM and transmission-FTIR analyses. Based on these characterization data the following was concluded: (a) The PCC fly ash particles are spherical in shape and range from 0.2 μm to 15 μm. Because of their shape and since the particles are thermally

inert up to 1100°C, the PCC fly ash is an excellent raw material for our brake and structural composite materials. The PCC fly ash is largely composed of oxides including hematite and magnetite. The presence of these two microwave lossy components makes sintering of materials containing PCC fly ash via microwave heating possible. (b) The

TABLE 4
The Young's Modulus of Brake Material Hot Pressed at 180°C

SAMPLE I.D.	FABRICATION PRESSURE (psi)	THICKNESS (inch)	WIDTH (inch)	YOUNG'S MODULUS, E, (GPa)
AMOL002	2100	0.185	0.41	7.63
AMOL003A	1700	0.193	0.391	4.02
AMOL003B	1700	0.193	0.367	2.15
AMOL004A	1100	0.193	0.378	5.29
AMOL004B	1100	0.193	0.396	5.13
AMOL005A	500	0.201	0.381	5.93
AMOL005B	500	0.199	0.376	5.19

scrubber sludge particles, in general, have a shape which is whisker-like, thus imparting it with fiber-like characteristics. Our FTIR analysis of the scrubber sludge sample revealed that CWLP sludge does not contain calcite, hannebachite ($CaSO_3.0.5H_2O$), or bassanite. Our analysis also showed that sludge is mainly composed of gypsum ($CaSO_4.2H_2O$). However, it must be cautioned that the sludge's gypsum lattice structure is different from the conventional gypsum lattice structure. Therefore, the scrubber sludge particles may not display the physical and chemical properties of conventional gypsum. Also, our DSC and DTA data suggested that before scrubber sludge particles can be used they must be heated to 200°C to evolve out the water associated with sludge. At $200°C < T < 1000°C$, our DSC and DTA data indicated the dehydrated gypsum is thermally stable, thus. very suitable for our composites. Therefore, the presence of scrubber sludge particles in our composites will provide mechanical strength to our materials. (c) The FBC fly ash and FBC spent bed bottom ash particles showed a considerable amount of fusion resulting in larger sized particles, i.e., 100 μm to 750 μm. The transmission-FTIR data on the two FBC fly ashes examined lead us to believe that the main constituents of FBC fly ash are anhydrite, lime, portlandite, calcite, hematite, magnetite, and various glass phases. The FBC spent bed ash is largely composed of anhydrite, lime, portlandite, calcite, periclase, hematite, and magnetite. The thermal stability characteristics of FBC fly ash and FBC spent bed ash, as determined by DSC and DTA techniques, are such that they make these particles suitable raw materials for brake composite materials and structural composites.

(d) The bottom ash particles contained a considerable amount of carbon and have a highly porous but glassy structure, thus, making the bottom ash particles an ideal filling material for our brake lining material and structural composites. (e) After our initial attempts to form structural composites, in the form of 1.25 inch disks, from PCC fly ash, FBC spent bed ash, scrubber sludge, coal char, and coal tar were successful, we upscaled the size of our structural composites to 2.5 inch diameter disk size. Our microscopic results on the fabricated disks indicated that pressure had a strong influence on the pore structure of the fabricated material and pressures of 2100 psi or above should be used to control the porosity of the resultant composite. (f) The SEM and Young's modulus analyses on the brake composites fabricated from PCC fly ash, FBC spent bed ash, scrubber sludge, coal char, and iron particles as a function of pressure showed that higher pressures lead to better particle packing and better mechanical performance.

DISCLAIMER STATEMENT

This report was prepared by Vivak M. Malhotra of Southern Illinois University at Carbondale with support, impart by grants made possible by the U. S. Department of Energy Cooperative Agreement Number DE-FC22-92PC92521 and the Illinois Department of Energy through the Illinois Coal Development Board and the Illinois Clean Coal Institute. Neither Vivak M. Malhotra of Southern Illinois University at Carbondale nor the U. S. Department of Energy, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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Figure 2

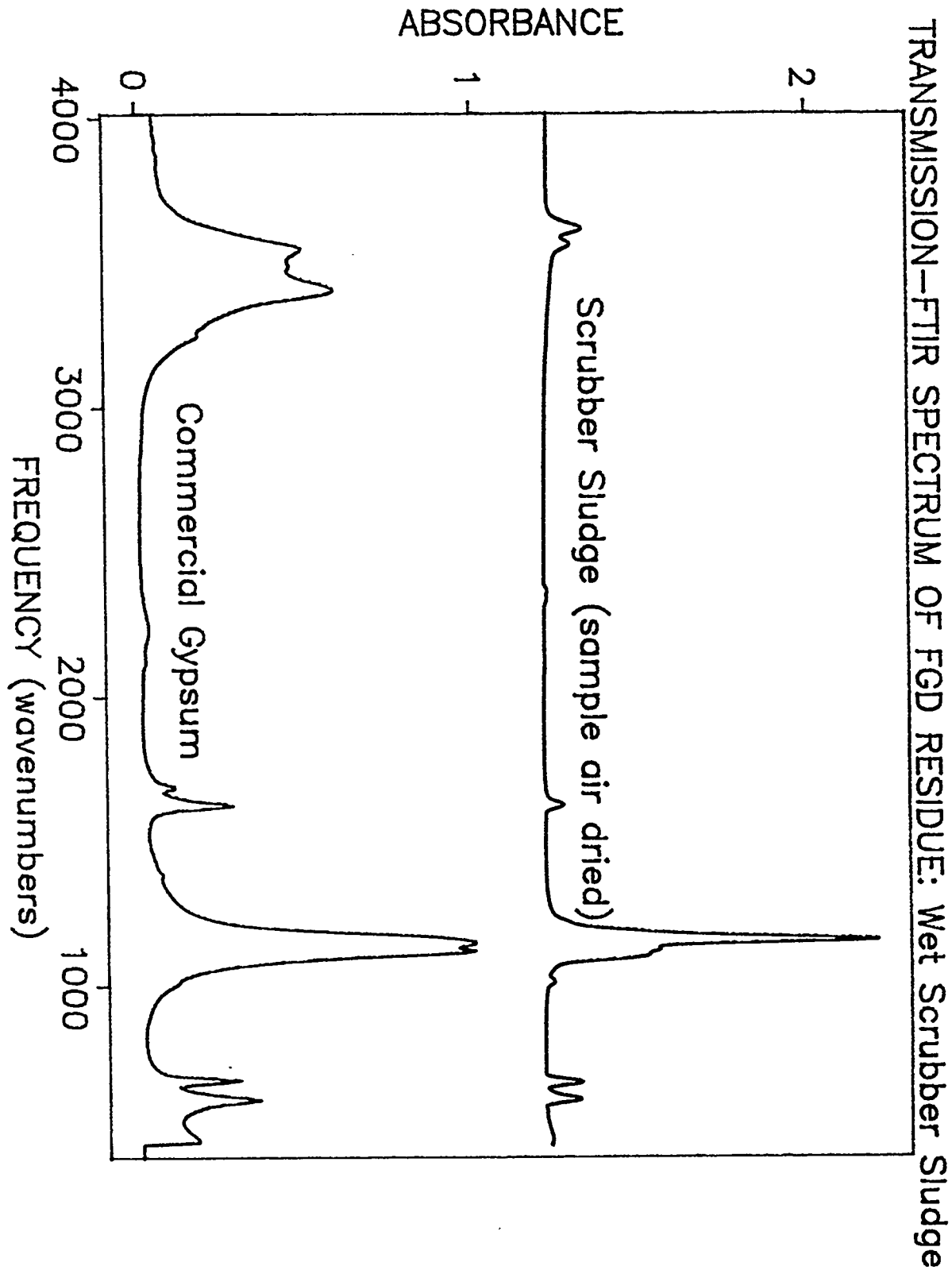

TRANSMISSION–FTIR SPECTRUM OF FGD RESIDUE: Wet Scrubber Sludge
ABSORBANCE
0
1
2
4000
3000
2000
1000
FREQUENCY (wavenumbers)
Scrubber Sludge (sample air dried)
Commercial Gypsum

Figure 3

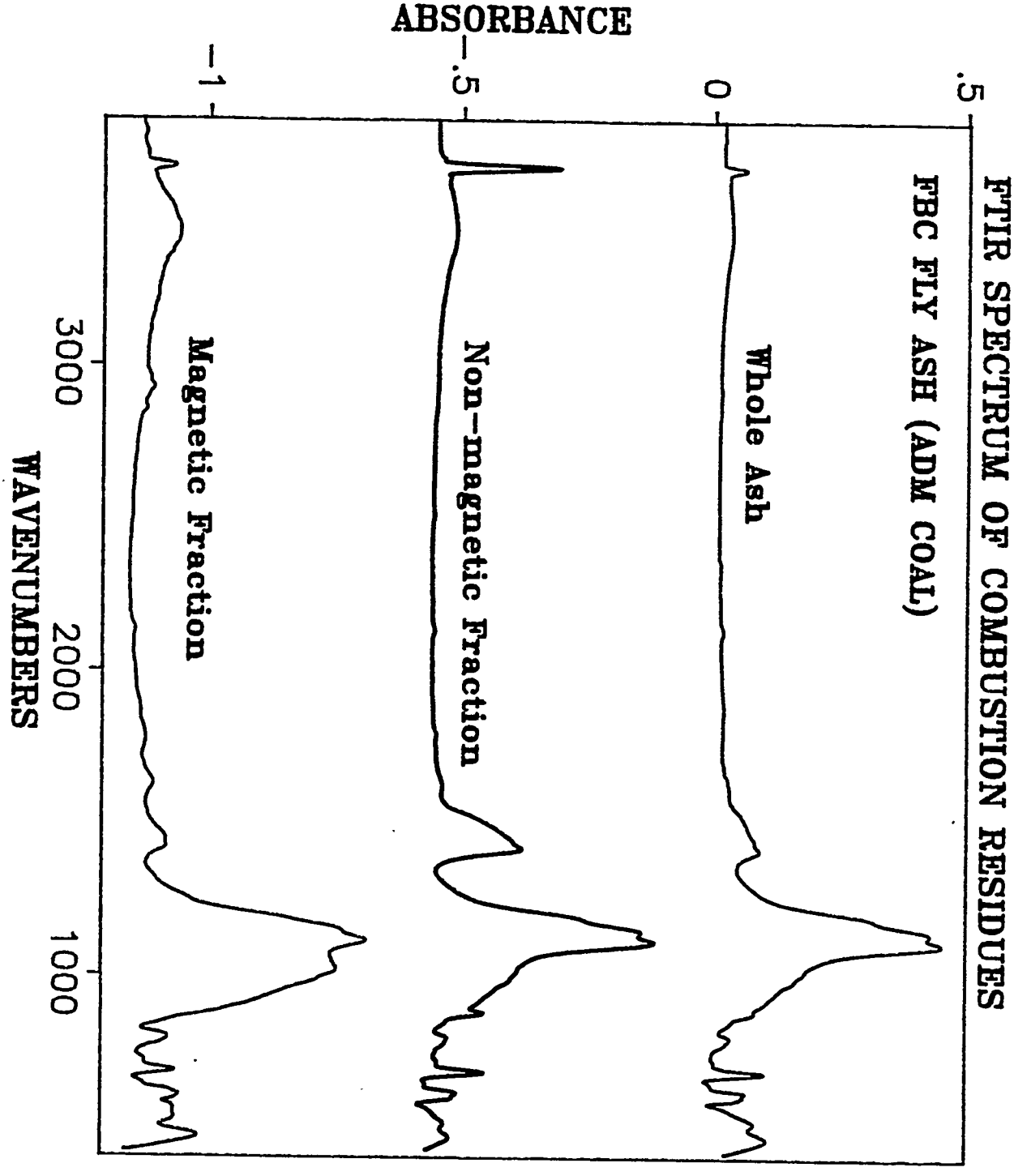

FTIR SPECTRUM OF COMBUSTION RESIDUES
FBC FLY ASH (ADM COAL)
Whole Ash
Non-magnetic Fraction
Magnetic Fraction
ABSORBANCE
.5
0
-.5
-1
3000
2000
1000
WAVENUMBERS

Figure 4

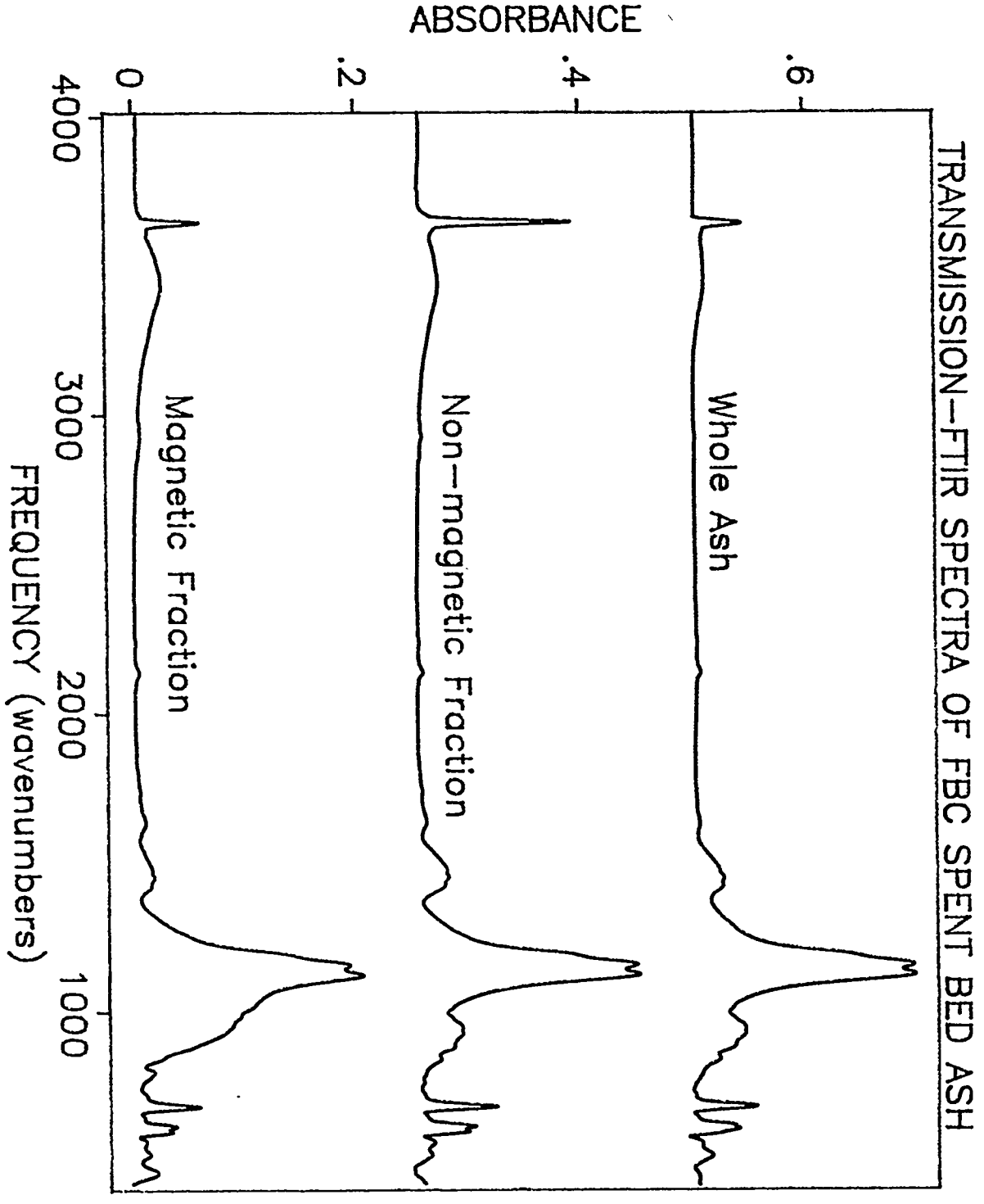
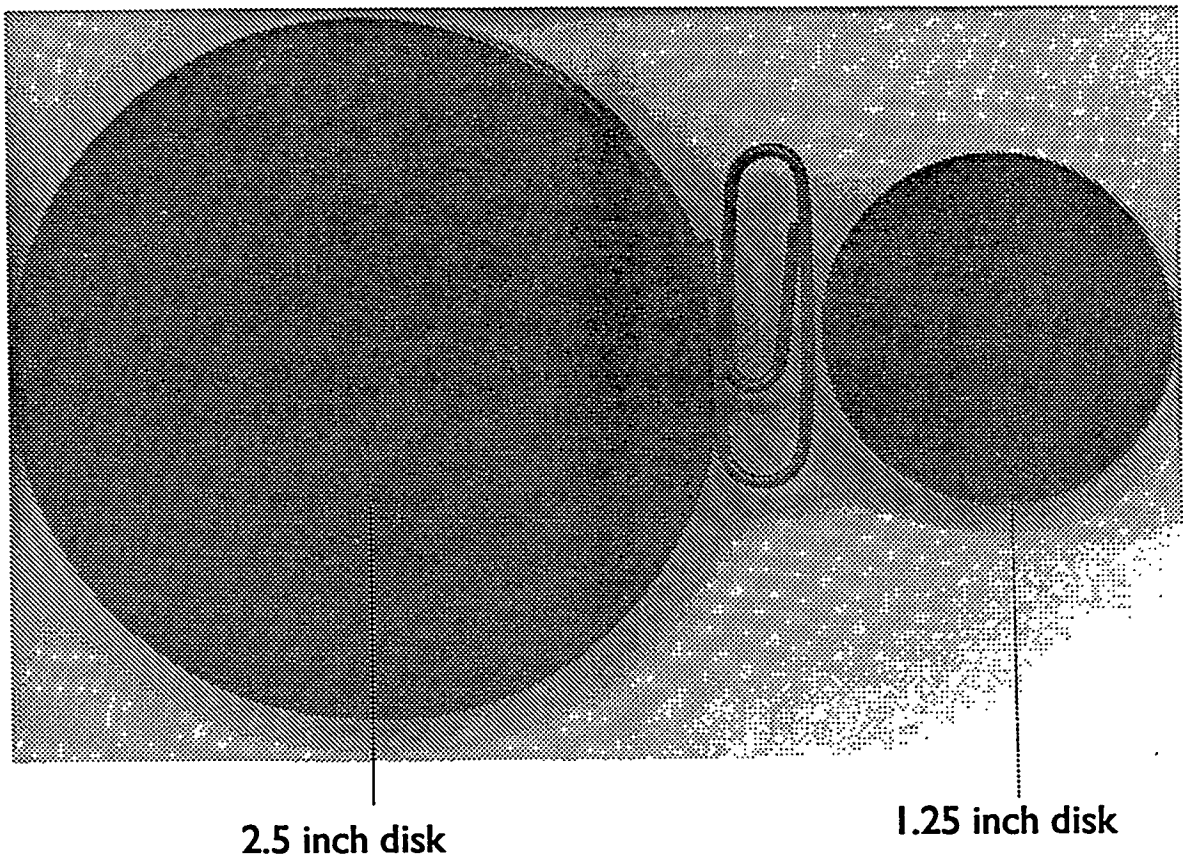

ABSORBANCE
.6
.4
.2
0
4000
3000
2000
1000
FREQUENCY (wavenumbers)
TRANSMISSION-FTIR SPECTRA OF FBC SPENT BED ASH
Whole Ash
Non-magnetic Fraction
Magnetic Fraction

Figure 5

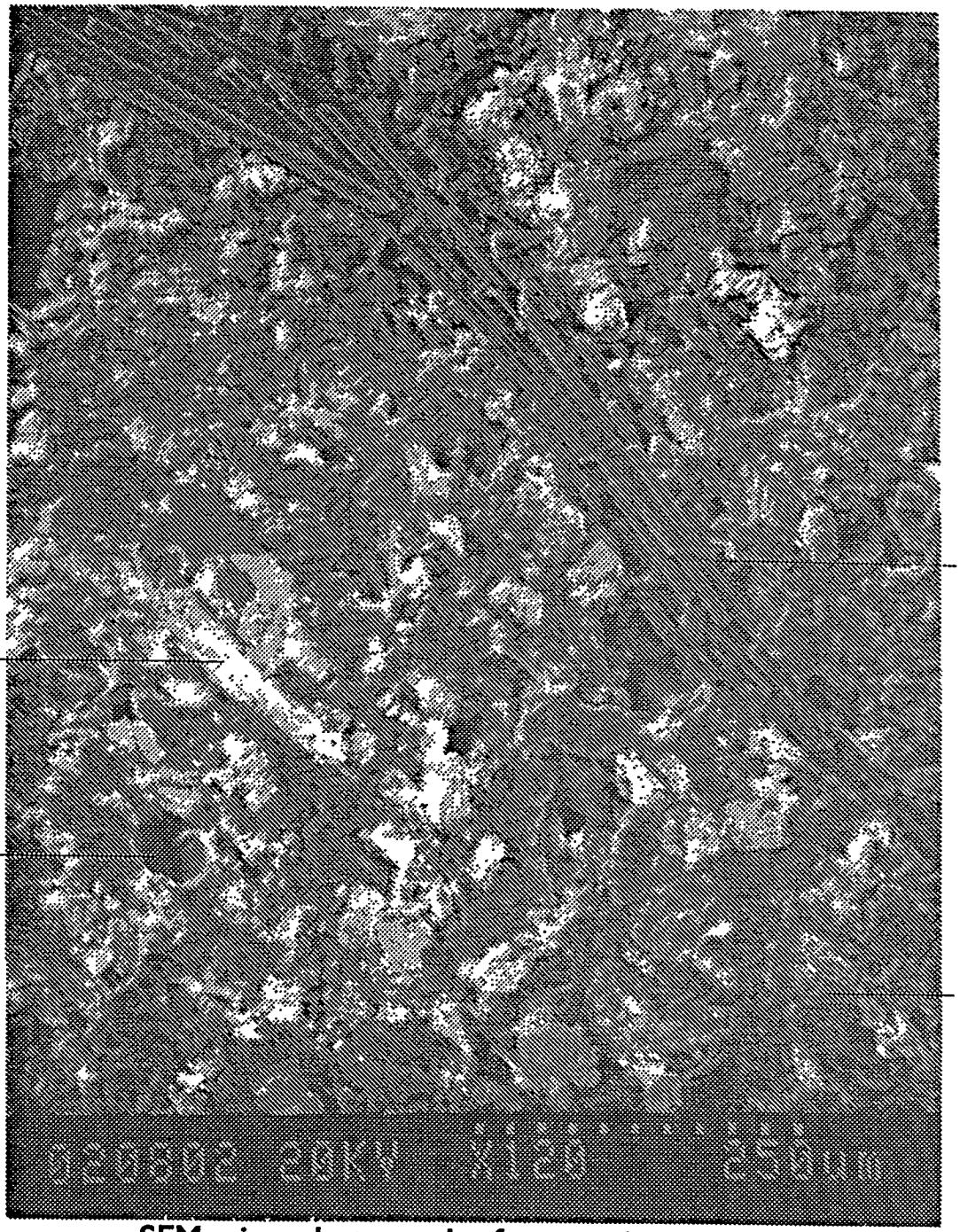
COMPOSITE MATERIAL FABRICATED FROM COAL COMBUSTION RESIDUES. [disk diameter = 1.25 inch]

Figure 6



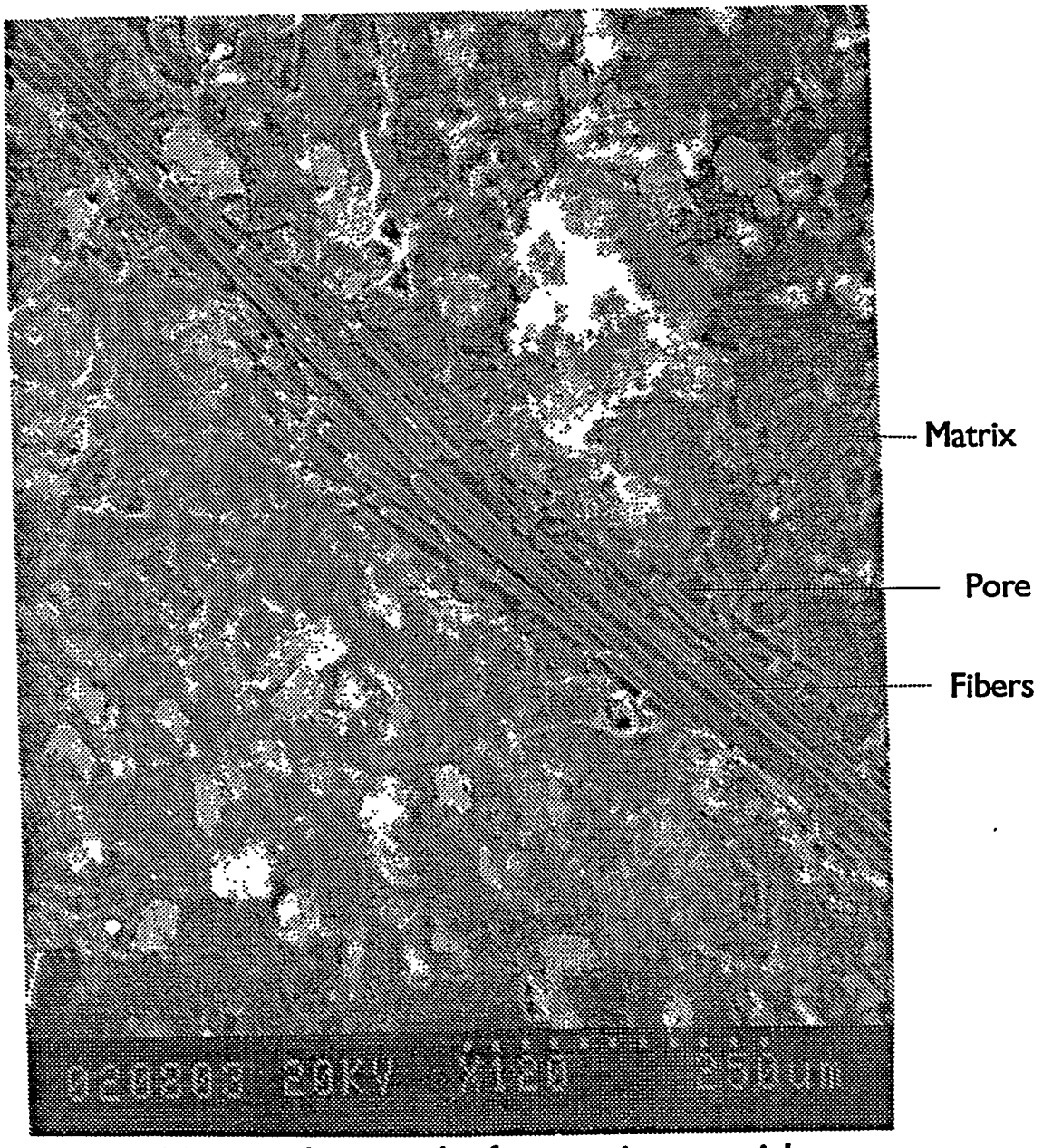
COMPOSITE MATERIAL FABRICATED FROM
PCC FLY ASH, FBC SPENT BED ASH, SCRUBBER SLUDGE, AND COAL CHAR

Figure 7



SEM microphotograph of composite material fabricated from scrubber sludge, FBC spent bed ash, coal char, and iron particles. T = 180 C and P = 500 psi

Figure 8



SEM microphotograph of composite material fabricated from scrubber sludge, FBC spent bed ash, coal char, and iron particles. T = 180 C and P = 2100 psi

PROJECT MANAGEMENT REPORT
December 1, 1994 to February 28, 1995

Project Title: **DESIGN AND FABRICATION OF ADVANCED MATERIALS FROM ILLINOIS COAL WASTES**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 3)
ICCI Project Number:	94-1/3.1A-3M
Principal Investigator:	Vivak M. Malhotra, Professor, Southern Illinois University at Carbondale
Other Investigators:	Maurice A. Wright, Director, Materials Technology Center, Southern Illinois University at Carbondale
Project Manager:	Dr. Dan Banerjee, Illinois Clean Coal Institute

COMMENTS

The Project is progressing as expected. The equipment required for the project has been received or will be received shortly. We have completed the modification of a microwave system so that the materials could be sintered under inert gases

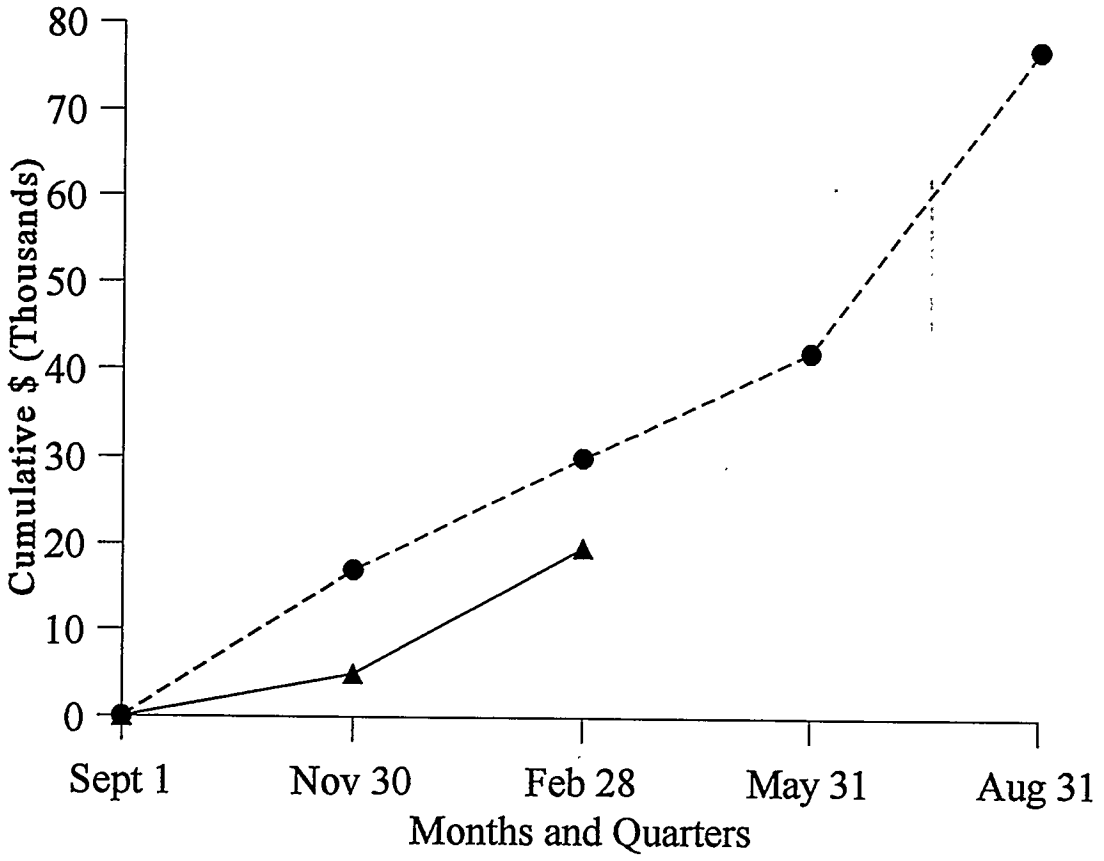
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1994 to Nov. 30,1994	Projected	6,204	1,921	1,250	0	4,500	1,750	1,563	17,188
	Estimated	3,120	700	723	0	0	372	492	5,407
Sept. 1, 1994 to Feb. 28, 1995	Projected	12,408	3,842	2,500	300	4,500	3,500	2,705	29,755
	Estimated	8,856	1,685	1,539	0	4,500	1,224	1,780	19,585
Sept. 1, 1994 to May 31, 1995	Projected	18,612	5,764	3,750	600	4,500	5,250	3,848	42,324
	Estimated								
Sept. 1, 1994 to Aug. 31, 1995	Projected	42,385	10,397	5,000	1,000	4,500	7,000	7,028	77,310
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER

Design and Fabrication of Advanced Materials from Illinois Coal Wastes

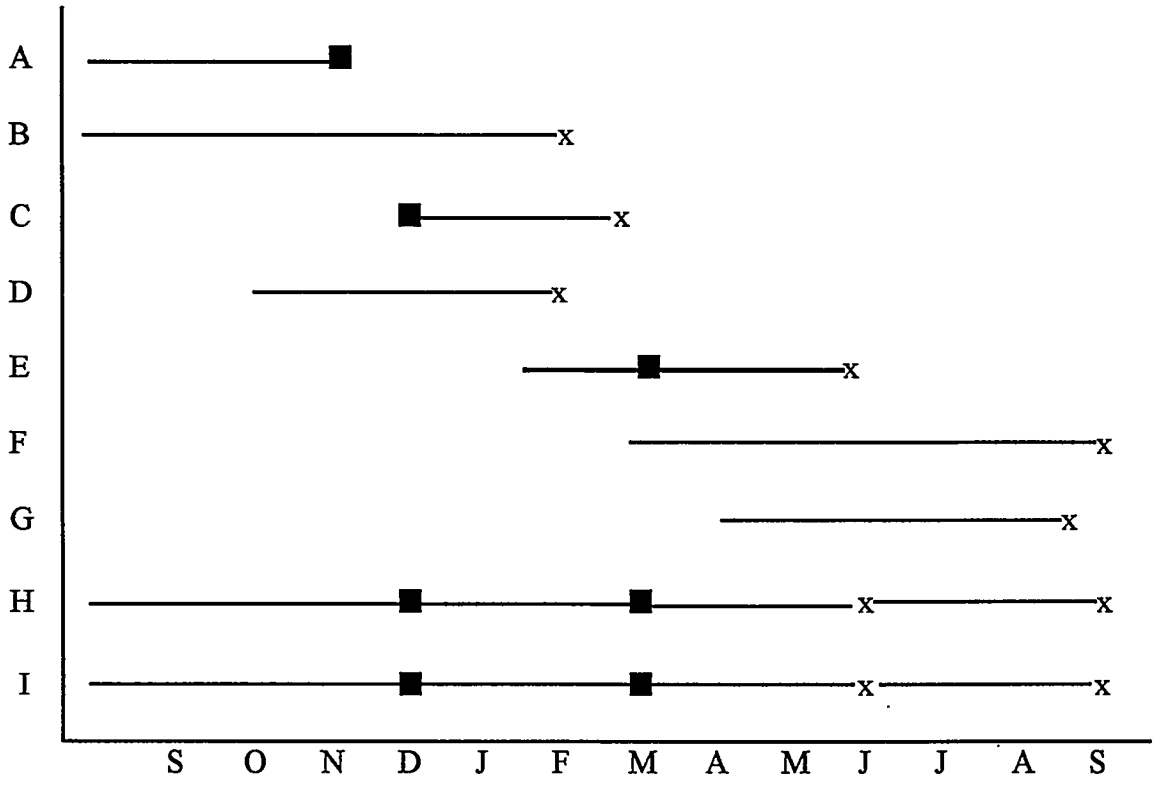


● = Projected Expenditures - - - - - - -
▲ = Actual Expenditures _____

Total Illinois Clean Coal Instutute Award $77,310

DISCLAIMER

SCHEDULE OF PROJECT MILESTONES



Begin
Sept. 1
1994

Hypothetical Milestones:

A: Order Equipment
B: Mineral Analyses of Residues
C: Thermal Stability of Residues
D: Altering Thermal Properties of Tar
E. Change Thermosetting Characteristics
F. Fabricate Brake Material
G. Fabricate Structural Material
H. Quarterly Technical Progress Reports
I. Quarterly Project Management Reports