COMPOSITION AND PYRITE MORPHOLOGY OF MATERIALS SEPARATED FROM COAL.[1]

by

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Abstract. Flyash, scrubber sludge, gob, and slurry are materials separated during the washing and burning of coal at the Associated Electric power plant at Thomas Hill, Missouri. Each material was sampled at several time periods during summer, fall and winter of 1990. The samples were analyzed for 30 elements and X-ray diffraction patterns were run to indicate mineralogical composition. Pyrite concentration of the residues was determined by the H_2O_2 oxidation method. Pyrites were separated from the samples by size-density fractionation and evaluated by scanning electron microscopy, and energy dispersive X-ray analysis.

Flyash had high concentrations of Al and Fe together with significant percentages of B, Ca, As, Na and Mo. Quartz, Fe_3O_4 and Fe_2O_3 are the predominant minerals in flyash. Scrubber sludge had high concentrations of Ca and S as $CaSO_4 \cdot 0.5H_2O$ and $CaCO_3$ with low concentrations of Cl and Na. The major minerals of the slurry and gob are: quartz > chlorite > illite and 20 to 40 g kg^{-1} pyrite. Selenium, Sb, Sn, Ag, Bi, Cd, Tl and As (except in flyash) concentrations in the different residues are very low or below the detection limit of the inductively coupled plasma unit used in the analysis. Energy dispersive X-ray analysis and scanning electron microscopy was used to evaluate the chemical variability and morphology of the pyrites. Scrubber sludge contained trace amounts of pyrite in the form of smooth-rounded, conglomerate, and framboidal forms. Both gob and slurry contained large amounts of conglomerate and framboidal pyrite. Numerous octahedral, cubic, and pyritohedral pyrite crystals were present in slurry. X-ray microanalysis for Fe, S, Al and Si on the surface of individual pyrite crystals indicated high pyrite purity and the extent and shape of aluminium silicate inclusions within pyrite crystals.

Additional Key Words: Flyash, scrubber sludge, gob, slurry, chemical and mineral composition of wastes, and composition and morphology of pyrite.

Introduction

Coal combustion at the Associated Electric power plant at Thomas Hill, Missouri produces large amounts of flyash, scrubber sludge, gob, and slurry. The amount of waste associated with coal burning is expected to double in the next 40 years (Francis et al., 1983). Wastes associated with mining and burning of coal are classified according to the processes by which they are produced. As the coal is unloaded at the plant site it is washed with high pressure water and the sediment removed is called gob. Next the coal is crushed and again washed and the resulting suspension of fine particles called slurry. Some coal burning furnaces are equipped with electrostatic precipitators which collect a fine dust called flyash. Newer furnaces are equipped with scrubbers which inject a limestone slurry into the stack and produce a material called scrubber sludge. Flyash and scrubber sludge are mixed within the power plant and the mixture is called flyash-scrubber-sludge. Most of these wastes contain potentially hazardous materials, including pyrite, which readily oxidizes when exposed to air and water to produce sulfuric acid. A description of the chemical and physical properties of these materials and of the pyrite forms they contain is presented as an aid to those developing environmentally sound disposal techniques.

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Pyrite is the most prevalent form of iron sulfide present in U.S.A. coals and a major source of acid in mine drainage. Pyrite surface morphology is one of the important factors determining its oxidation rate. Arora et al. (1978) summarized reports of pyrite morphology and indicated that it occurred as acicular forms, coarse-grained masses, euhedral forms, framboids and polyframboids, octahedral, and pyritohedral crystals. They reported that pyrite isolated from lignite coal was composed of porous and nonporous irregular grains. Ainsworth et al. (1982) studied the morphology of pyrite isolated from Pennsylvania-age shales in Missouri and grouped them as smooth crystal surfaces, conglomerates with irregular surfaces composed of many cemented particles, and framboids in which the cemented crystals form a smooth sphere. They found that conglomerates were the predominant form. Pyrite framboids and polyframboids are of particular interest because they are more reactive than conglomerate pyrite due to higher surface area, higher porosity, and smaller size (Caruccio et al., 1977). It has been suggested that the quantity of framboidal pyrite, not the total pyrite, determines the rate of acid production in mine spoils (Caruccio et al., 1977).

The chemical and mineralogical composition of coal residues depends on the geologic and geographic aspects of the coal deposit and the processing and combustion conditions. Flyash is a major solid residue from coal burning and has been studied extensively. Page et al. (1979) and Adriano et al. (1980) reviewed chemical and physical properties of flyash and indicated that although the elemental composition of fly ashes could vary widely, ashes usually contain higher concentrations of essential plant nutrients, except N, than do common cropland soils. The major matrix elements in flyash are Si, Al, and Fe together with significant percentages of Ca, K, Na, and Ti. Several studies showed that boron contained in flyash is of special concern in agriculture because of its toxicity to plants (Page et al., 1979; Keren and Bingham, 1985; Hollis et al., 1988). The variability in chemical properties of the flyash scrubber sludge produced by the Thomas Hill power plant was evaluated by Wendell et al. (1992). They found that the material varied significantly with time of sampling and concluded that analysis was required of each batch prior to use. Zhang et al. (1992) measured the effect of flyash scrubber sludge added to soil on the growth and chemical composition of plants. They found salt and boron added with the flyash scrubber sludge limited the amount that could be added to soil to 5% (w/w). The material used by Zhang et al. (1992) had sufficient excess $CaCO_3$ to increase the soil pH. However, in many instances the amount of $CaCO_3$ in the materials may not be sufficient of neutralize soil acidity and acid produced by the oxidation of pyrite.

The objective here is to determine pyrite concentration, mineralogy, and morphological form in gob, flyash, scrubber sludge, and slurry. Chemical composition measured by ICP, mineralogy using X-ray diffraction and morphological form by scanning electron microscopy and energy dispersive X-ray analysis were used to achieve the objective.

Materials and Methods

Sampling and preparation

At various times during the summer, fall, and winter of 1990, personnel at the Associated Electric power plant took 2 kg samples of flyash and scrubber sludge before they were mixed as a part of the standard plant operation. Flyash samples were taken from each of the three furnaces with electrostatic precipitators. Grab samples of gob and slurry were also collected at various times. The gob, scrubber sludge, and slurry were separated into solid and liquid by sedimentation. The solid portions of all samples were air dried. A subsample of 200 to 300 g was ground, passed through a 150 µm sieve, and used throughout the study. The soil used in this study was collected from the scraper piles and is a silty clay loam mixture of the A horizons of Aquic Argiudolls, Aquic Hapludalfs, Typic Dystrochrepts, Typic Fluvaquents, and Typic Udipsamments.

Digestion of sample for ICP analysis

Samples were placed in polyethylene bottles, HNO_3 and H_2O_2 added, and heated in a microwave oven (White and Douthit, 1985). The University of Missouri Trace Substances Laboratory analyzed the solutions for 30 elements by inductively coupled plasma emission spectroscopy (ICP). A portion of the digest was analyzed for Cl^- by the Cl^- sensitive electrode (Gaines et al., 1984), total S by the turbidimetric method (Blanchar et al., 1965), and total B by azomethine-H method (Bingham, 1982). Pyrite was determined by the H_2O_2 titration method as described by O'Shay et al. (1990).

X-ray diffraction analysis

One hundred gram of each material was passed through a 250 µm screen and used to separate the heavier than carbon tetrachloride fraction as described (Paulson et al., 1971). About 40 g of sample and 160 mL of carbon tetrachloride were added to a 250 mL wide mouth plastic bottle and thoroughly shaken. When the materials had separated the heavy fraction was removed and suspended in fresh carbon tetrachloride and the process repeated. The sample was dried and then placed into a 2 cm diameter and 3 mm deep sample holder. The sample holder was attached to the X-ray machine. X-ray diffraction patterns were obtained using a Scintag PADV Model (1988), with a Cu target, operated at 30 mA and 40 KV. Diffracted X-rays were detected by a Geiger detector and the counts processed through a Micro VAX 2000 computer. Diffraction profiles were analyzed using Siemens software and (JCPDS, 1986) files stored on disk.

Scanning electron microscopy(SEM) and energy-dispersive X-ray analysis(EDS)

Pyrite was removed from samples by density fractionation with bromoform (density = 2.8 to 2.85 g cm^{-3}) and tetrabromoethane (density = 2.95 to 3.00 g/cm^{-3}) as described by Ainsworth et al. (1982). The pyrite was mounted with double tape on aluminum stubs, carbon coated, and examined in an AMRAY 1600 SEM at an accelerating voltage of 15 kV, and a beam current of 2 nA.

Samples were prepared for EDS by selecting, with the aid of a light microscope, 8 to 10 pyrite particles with diameters less than 150 µm. The particles were set in epoxy, dried, then samples were ground with 240 grit followed by 600 grit powder, and polished with 3 and 0.3 µm Al_2O_3. When the surfaces were smooth, flat, and bright as viewed by light microscopy, they were mounted on aluminum stubs and carbon coated. EDS was performed by Si(Li) detector with standard Be window and analyzed by a KEVEX 7000 multi-channel analyzer. Polished standard pyrites with certified pyrite concentration of 99.992% from multi-element standard no. 203-52 from C. M. Taylor Corp. Sunnyville, CA were used as standards for quantitative analysis. The electron beam was focused on selected particles and a total of 400,000 counts taken by the SEM/EDS unit. A John Colby software package was used for data processing. A PC computer with a digital acquisition board was used to display back scattering and secondary electron images, and to give elemental X-ray maps. The images and maps were printed from a Macintosh Computer.

Result and Discussion

Chemical composition of wastes

Data presented in Table 1 shows that B is concentrated in the flyash and Cl^- and SO_4^{2-} are concentrated in the scrubber sludge. Wendell et al. (1992) found B, Cl^- and SO_4^{2-} concentrations in flyash scrubber sludge to be highly variable and at much higher concentrations than in soil. Concentrations of B and Cl^- in gob and slurry are similar to soil concentrations. Zhang et al. (1992) showed that concentrations of B limited the amount of flyash scrubber sludge that could be applied to soil. The consistency of the data in Table 1 clearly show that the variability in composition of the combined material "flyash scrubber sludge" is a function of the amounts of each component in the mixture.

A gob sample, six flyash, two scrubber sludge, and six slurry samples were analyzed for 30 elements by ICP. The means are shown in Table 2. Calcium and sulfate are major components of scrubber sludge with concentrations orders of magnitude higher than in gob, slurry or soil. The S associated with scrubber sludge is primarily SO_4^{2-}. Pyrite is the major form of S in gob and slurry which contain 2 to 5% S as pyrite.

Table 1. Boron, chloride, sulfur, and pyrite concentrations in gob, flyash, scrubber sludge and slurry with time and different electrical units.

Date	B	Cl	S	FeS_2
	mg kg^{-1}		--- %	---
Flyash (unit 1)				
12/12/90	1238	<1	0.15	0.0
12/19/90	1249	<1	0.06	0.0
12/26/90	1101	<1	2.05	0.0
1/2/91	1138	<1	2.25	0.0
Flyash (unit 2)				
12/26/90	1345	<1	0.37	0.0
1/2/91	1138	<1	1.14	0.0
Flyash (unit 3)				
12/12/90	1479	<1	0.20	0.0
12/19/90	1262	<1	0.20	0.0
12/26/90	1344	<1	0.20	0.0
1/2/91	1172	<1	0.23	0.0
Scrubber Sludge (Unit 3)				
12/19/90	125	617	35.6	tr
12/26/90	116	605	32.2	tr
1/2/91	52	882	32.2	tr
Gob				
20/5/90	--	5	2.75	4.6
Slurry				
7/2/90	78	12	1.91	2.7
7/23/90	72	12	1.54	2.6
7/27/90	61	7	2.10	3.3
8/3/90	69	9	1.87	2.8
8/9/90	67	5	1.67	2.6
8/14/90	59	7	2.37	3.8

Aluminum and Fe concentrations in flyash, gob, slurry, and soil were much higher than in scrubber sludge. The concentration of Al or Fe in the flyash scrubber sludge mixture is a convenient way to estimate the relative proportions of flyash to scrubber sludge in any particular sample.

The elemental concentrations of the wastes vary widely, and many are of the same orders of magnitude as those in soils (Table 2). Concentrations of Ca, Fe and B in flyash, Ca, S and Cl in scrubber sludge and pyritic S in gob and slurry are higher than in soils. Concentrations of B, Ba, Co, Cr, Cu, Ni, Pb, Ti, V, Zn, Be, Cd, Mo, As, and Tl were higher in flyash than in other wastes or soils. Of the elements present in flyash only B was at high enough concentrations to limit the use of the material as a soil amendment. Zhang et al. (1992) showed that the concentrations of

Table 2. Element concentrations in flyash, scrubber sludge, gob, slurry and soil.

	Fly ash	SS	Gob	Solid Slurry	Soil
			----------%	------------	
Ca	2.1	25.4	0.98	0.93	0.29
S	0.68	33.4	2.74	1.91	0.13
Al	1.24	0.04	2.53	2.45	3.24
Fe	10.0	0.14	4.96	3.41	2.48
K	0.31	0.01	0.93	0.09	0.26
Mg	0.10	0.27	0.40	0.36	0.30
Na	0.07	0.12	0.15	0.05	0.01
	---------	mg/Kg	---------		
B	1247	98	--	68	56
Cl	<1	701	5	8	--
Ba	238	66	118	119	193
Co	49	<2	4	11	11
Cr	68	7	31	31	31
Cu	102	57	60	47	16
Li	20	<1	30	32	21
Mn	165	97	227	137	553
Ni	96	4	59	47	16
P	443	145	1875	1216	540
Pb	206	<7	71	42	28
Sr	74	100	160	108	29
Ti	769	18	39	65	296
V	101	1	25	26	66
Zn	654	28	190	37	52
Be	8	2	2	2	1
Cd	6	1	2	<1	<1
Mo	75	bd	5	4	1
As	98	bd	25	bd	bd
Tl	14	bd	bd	bd	bd
Sb	bd	bd	bd	bd	bd
Bi	bd	bd	bd	bd	bd
Se	bd	bd	bd	bd	bd
Sn	bd	bd	bd	bd	bd
Ag	bd	bd	bd	bd	bd

*bd below the detection limit. Detection limits for Pb, Mo, As, Tl, Sb, Bi, Se, Sn, and Ag are 7, 1, 20, 5, 5, 5, 20, 5, 1, respectively.

most of these elements, except B and Mo, in tissues of plants grown on soil amended with 5%(w/w) flyash scrubber sludge were reduced. Lower metal concentrations in plants were attributed to increased pH of the soil mixture due to unreacted $CaCO_3$ in the scrubber sludge. Antimony, Bi, Se, Sn, and Ag concentrations were below the detection limits of the ICP unit.

Mineral composition

Figs. 1 to 4 are X-ray diffractograms for each waste. The X-ray pattern for flyash in Fig. 1 shows the predominant peaks for hematite and magnetite with the quartz peak clearly identified. Pyrite was not identified in flyash which confirms the results of chemical analyses. X-ray diffraction of gob, scrubber sludge, and slurry (Figs. 2, 3, and 4) confirm the presence of pyrite, which is consistent with chemical analysis in Table 2. Calcium sulfate and carbonate are indicated as components of scrubber sludge (Fig. 2) which is consistent with the concentrations of Ca and S reported in Table 2.

The mineral compositions of gob and slurry are similar and are a mixture of clays, quartz and pyrite (Figs. 3 and 4).

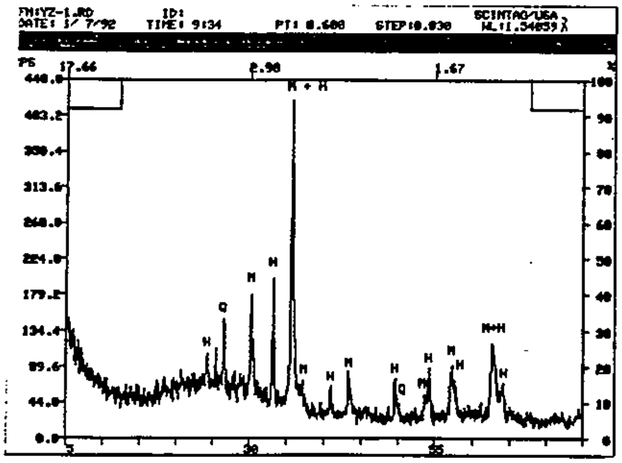


Figure 1. X-ray diffractogram of flyash. (H = hematite, M = magnetite, and Q = quartz)

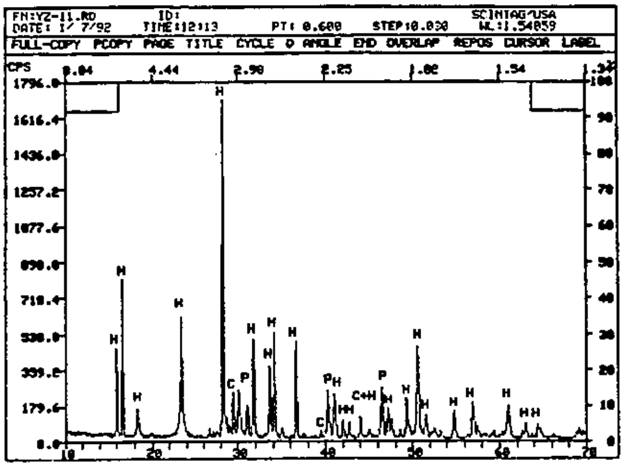


Figure 2. X-ray diffractogram of scrubber sludge. (C = Calcium carbonate, H= Calcium sulfate hydrate, P = Pyrite)

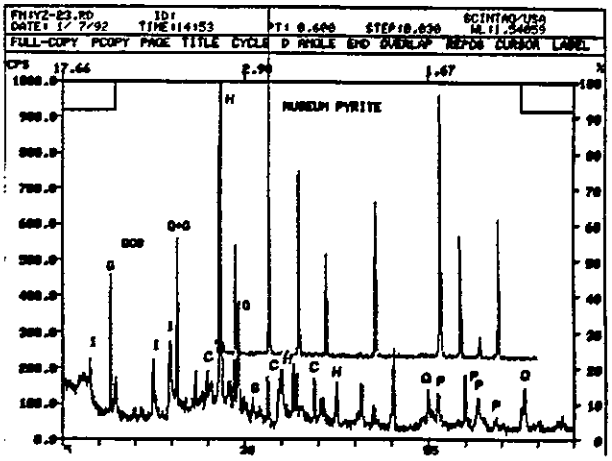


Figure 3. X-ray diffractogram of gob. (C = chlorite, G = gypsum, I = illite, P = pyrite, and Q = quartz)

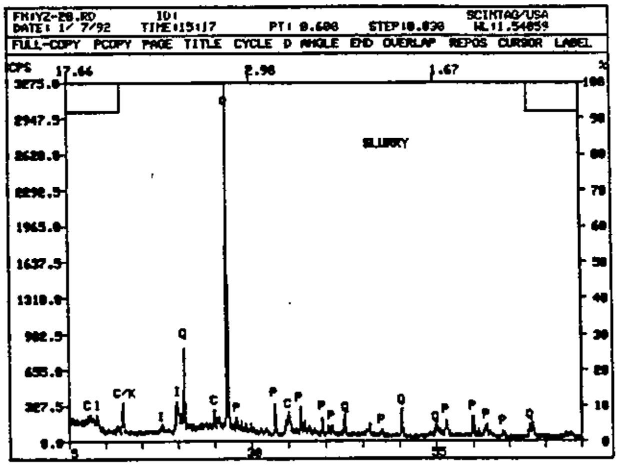


Figure 4. X-ray diffractogram of slurry. (C = chlorite, K = kaolinite, I = illite, P = pyrite, Q = quartz)

The minerals identified by X-ray diffraction for each waste are listed in descending order in Table 3.

Table 3. Mineral composition of waste materials indicated by X-ray diffraction analysis.

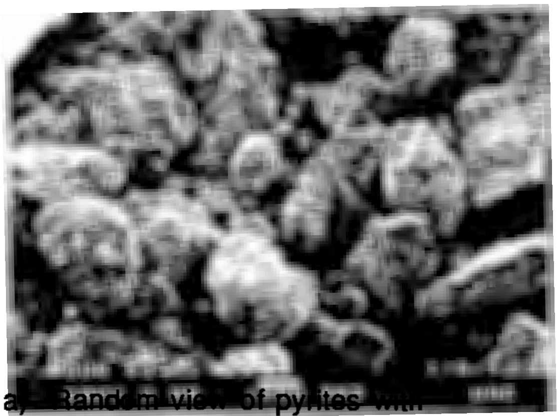
Types of wastes	Mineral composition in descending order
Flyash	Magnetite > hematite > quartz
Scrubber sludge	Calcium sulfate hydrate > calcium carbonate > pyrite
Gob	Quartz > chlorite + illite > pyrite> calcium sulfate hydrate > gypsum
Slurry	Quartz > chlorite + illite > pyrite

Flyash is composed of magnetite, hematite and quartz. The scrubber sludge is primarily calcium sulfate and calcium carbonate. Gob and slurry are quite different from either flyash or scrubber sludge and are mixtures of various clays and pyrite.

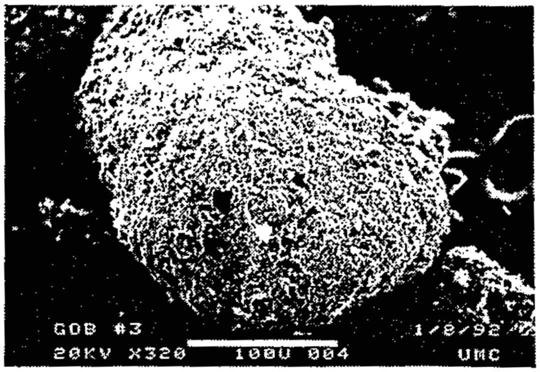
Pyrite forms

Random SEM fields of approximately 100 μm^2 of the pyrites separated from gob, scrubber sludge, and slurry are shown in Figs. 5a, 6a, and 7a. Pyrite forms observed include cubes, pyritohedrons, octahedrons, conglomerates, framboids, and polyframboids. These forms have been reported to exist (Dana, 1966), and have been observed in Pennsylvanian age shales (Ainsworth et al., 1982) and in lignite coal (Arora et al., 1978). The twinned pyrite crystal shown in Fig. 6a is a rare form.

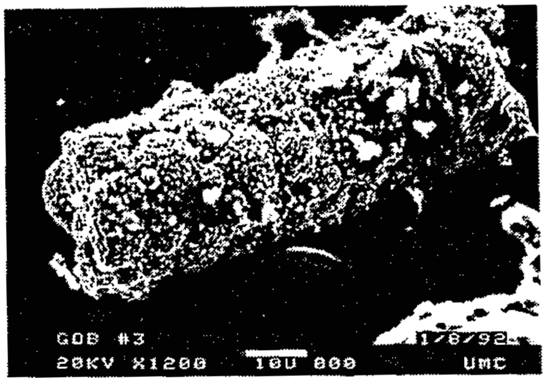
Gob and slurry contained conglomerate, framdoidal and polyframboidal forms (Figs. 5a,b,,c,d and 7a,b,d). Well-formed octahedrons were found in scrubber sludge and slurry (Figs. 6a,c and 7c). All of the forms were found in scrubber sludge even though the chemical analysis indicates that it contains small amounts of pyrite.



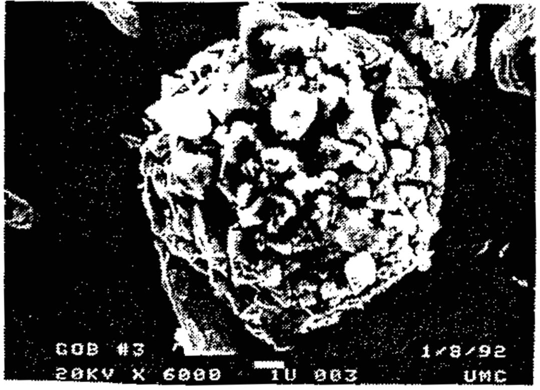
a) Random view of pyrites with conglomerate as a major form.



b) Conglomerate pyrite

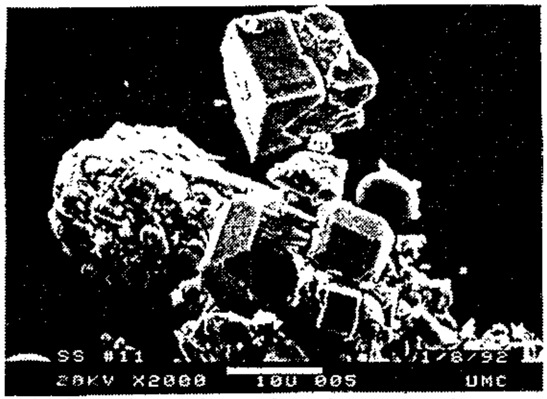


c) Polyframboidal pyrite

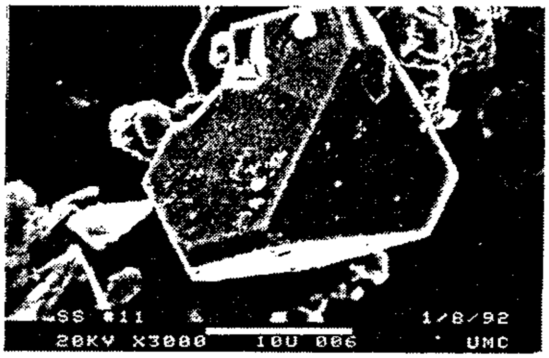


d) Framboidal pyrite

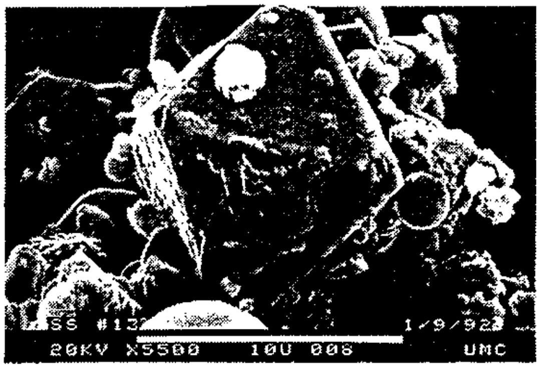
Figure 5. SEM of pyrites isolated from gob.



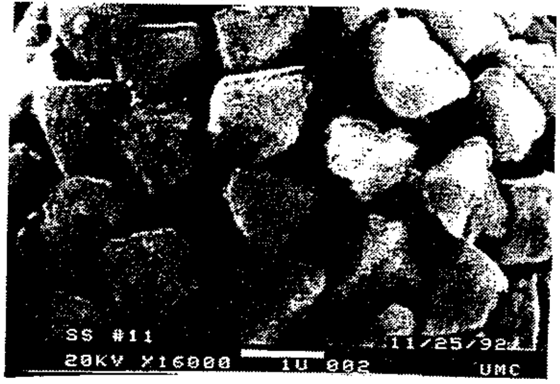
a) Random view of pyrite: conglomerate, cubic, pyritohedral, and twinned forms.



b) Pyritohedral pyrite

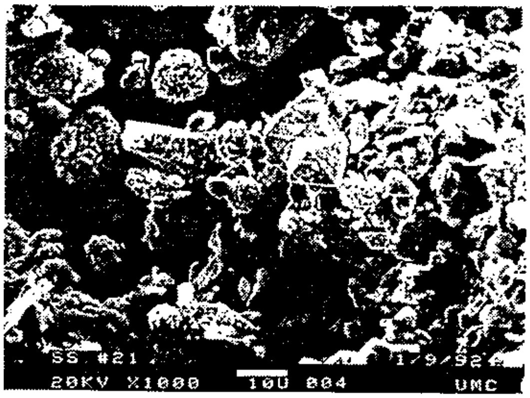


c) Octahedral pyrite

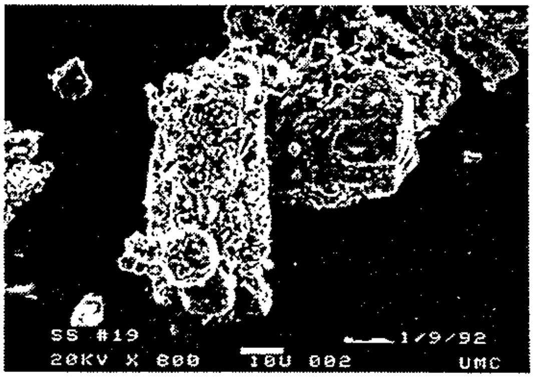


d) Framboidal pyrite

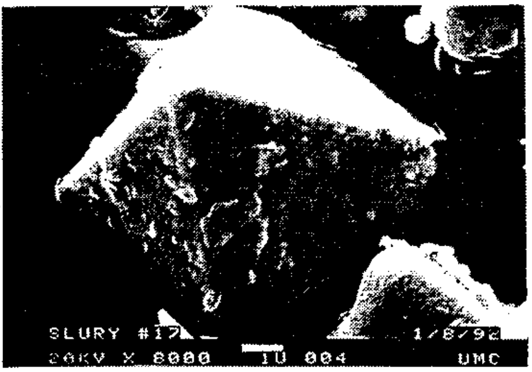
Figure 6. SEM of pyrites isolated from scrubber sludge.



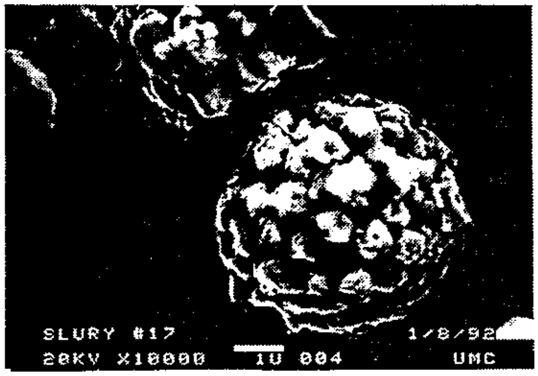
a) Random view of pyrites: conglomerate, framboidal, and octahedral forms.



b) Conglomerate/polyframboidal pyrite



c) Octahedral pyrite



d) Framboidal pyrite

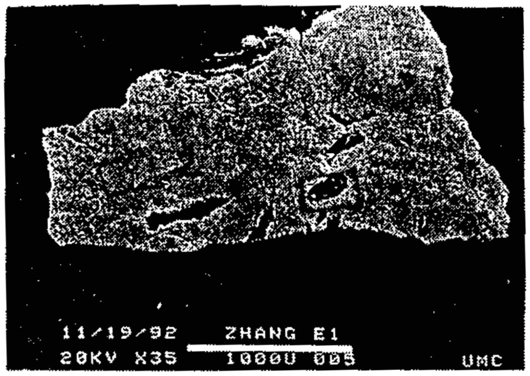
Figure 7. SEM of pyrites isolated from slurry.

Scanning electron micrographs (Figs. 5 to 7) show not only the kinds of pyrite, but reveal different grain and surface features and the ways they are associated. The relative ranges in size of framboids, the small round balls and the larger distinguishable forms, in respect to other forms can be seen in Figs. 5a,c, 6a, and 7a,b. Figs. 5d, 6d, and 7d show typical round porous single framboids composed of octahedral and pyritohedral microcrystals. The effective surface areas of framboids are evident when viewed at the higher magnification in Fig. 6d. Microcrystals in framboids appear to be randomly packed and to be about 1 µm in length. Conglomerates also are composed of many microcrystals, but cementation in conglomerates is such that they appear much less porous than framboids. Greater reactivity of framboidal pyrite in respect to similar sized conglomerates has been attributed to higher effective surface and porosity of the microcrystal structure in framboids (Caruccio et al., 1977).

Two or more framboids can be cemented together to form a polyframboid (Fig. 5c and 7b). The polyframboids shown here are cemented more than those previously reported by Ainsworth et al. (1982) and Arora et al. (1978). Arora et al. (1978) suggested that the cementing agents binding framboids are materials containing sulfur and iron. EDS analysis indicated high concentrations of Fe and S, indicating the cementing agent is most likely pyrite. Polyframboid shapes vary from globular to elongated forms and in some cases they are joined by pyrite crystals (Fig. 7b). Conglomerates may also occur in larger structures similar to polyframboids and in some cases they are difficult to differentiate (Figs. 5a and 7d). Rounded form and porosity are the usual criteria used to distinguish framboids from conglomerates.

Pyrite composition and inclusions

Individual pyrite particles from coal, gob, scrubber sludge, and slurry were mounted in epoxy, identified by SEM and analyzed for major components with EDS. The surface of a pyrite particle isolated from coal is shown in Fig. 8a. The inclusion (black spot) in Fig. 8a was examined more closely at a higher magnification and shown in Fig. 8b. The light shaded portion is pyrite and the dark shaded area composed of Al and Si. Randomly selected points within the dark area were analyzed for Al, Fe, S, and Si using EDS. Iron and S were not found. The major components were Al (19.3%) and Si (29.7%). When expressed as SiO_2 and Al_2O_3 these two components accounted for almost 100% of the mass. Similar inclusions composed of Al and Si appeared in pyrites from gob.



a) Particle isolated from coal,


b) Dark shades are inclusions of Al and Si
Light shades are pyrite surfaces:
Figure 8. SEM of polished pyrites used for EDS analysis.

The lighter shaded areas observed by SEM were analyzed for Fe and S (Table 4). The percentage by weight of total S and Fe from each sample is very close to the composition of pyrite, which is 53.45 and 46.55%. The K-values, listed in Table 4, defined here as S/Fe of the sample divided by that from pure pyrite, are all almost equal to 1. SEM, X-ray, and composition

Table 4. Composition of pyrites separated from wastes and coal.

	S	Fe	FeS_2	K-ratio
	----	%(w/w)	----	
Coal				
	52.5	45.4	97.8	1.007
	52.8	45.6	98.4	1.008
Gob				
	52.7	46.2	98.9	0.994
	52.8	46.0	98.8	1.000
	52.8	45.6	98.3	1.009
Scrubber Sludge				
	53.7	46.7	100.3	1.002
	53.6	46.5	100.1	1.004
Slurry				
	52.6	45.4	97.1	1.003
	52.0	45.1	97.1	1.003
	53.2	46.3	99.5	1.000
	52.1	45.2	97.3	1.004
	52.2	45.1	97.3	1.008

* K-ratio equals S/Fe of the sample divided by 1.148, the ratio in pyrite.

data indicate that the pyrites isolated from these coals and coal wastes have crystal structures, forms, and compositions similar to those commonly described for pyrites. There were trace amounts of pyrite in scrubber sludge and none in flyash indicating that pyrites in coal had been oxidized during burning. In the burning unit equipped with scrubbers, the S was found in the sludge as calcium sulfate hydrate. Gob and slurry contained a mixture of reactive framboidal and less reactive conglomerate and crystalline pyrites.

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Links are at the end of this paper and are numbered

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