

REACTIONS AND TRANSFORMATIONS OF COAL MINERAL
MATTER AT ELEVATED TEMPERATURES

G. P. Huffman and F. E. Huggins

U. S. Steel Corporation Technical Center
Monroeville, PA

Introduction

Coal contains a variety of inorganic constituents that exhibit deleterious behavior in most processes that attempt to convert the energy in coal to a useful form. As coal is heated, the inorganic phases undergo transformations and reactions that yield a complex mixture of solid, molten, and volatile species. These species give rise to slagging and fouling deposits, corrosion, pollution, and other problems. Although such problems are usually associated with the combustion of coal to produce electrical power, they are also common in coal gasification and liquefaction, cokemaking, and iron production.

The current paper will briefly review research on this topic.

Nature of the Inorganic Constituents of Coal

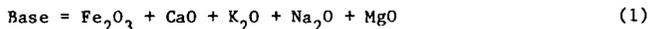
It is common practice to make a distinction between the inorganic constituents of so-called "Eastern" and "Western" coals. By definition, Western coals are those for which the CaO+MgO content exceeds the Fe₂O₃ content of the ash, while the reverse is true for Eastern coals. The inorganic constituents in Eastern coals, which are principally bituminous in rank, are predominantly in the form of discrete mineral particles. Clay minerals (kaolinite, illite) are usually dominant, followed by quartz and pyrite. The range and typical values of the mineral distribution and ash chemistry of Eastern coals are shown in Table I. These data were determined from computer-controlled scanning electron microscopy (CCSEM), Mössbauer spectroscopy, and other measurements on over a hundred coals.

Western coals are usually lignites or subbituminous coals. The range and typical values of the inorganic phase distribution and ash chemistry of approximately 20 Western coals examined in this laboratory are shown in Table II. In a recent paper, we discussed the differences between the inorganic constituents of low-rank coals and those of bituminous coals. These differences occur in the calcium-, iron-, and alkali-containing phases. In bituminous coals, the calcium content is typically low (CaO <5% of ash) and all calcium is contained in the mineral, calcite. The calcium content of lignites is high (CaO ~10 to 30% of ash) and the calcium is molecularly dispersed throughout the coal macerals as salts of carboxylic acids. The latter point has been directly confirmed by EXAFS (extended X-ray absorption fine structure) spectroscopy. Similar differences occur for the alkali elements. Minerals such as illite, which accounts for most of the potassium in bituminous coal, are usually low in lignite and subbituminous coal (see Tables I and II). In lignites, sodium and potassium are believed to occur as salts of humic or carboxylic acids. Montmorillonite and halite (NaCl) are the dominant Na-containing minerals, and they occur in both bituminous and lower rank coal. The iron-bearing minerals in unoxidized bituminous coals include pyrite, ferrous-bearing clays (illite, chlorite), and carbonates (siderite, ankerite). In lignites, only pyrite and its weathering products (iron sulfates and oxyhydroxides) are normally observed.

The diversity of transformations and reactions that such complex assemblages of inorganic matter can undergo when coal is combusted or otherwise converted to a more useful form of energy is too complex to be discussed in any detail in a short article. Our intention, therefore, is simply to outline some of the major phenomena and to provide the reader with useful references. Most of the article will deal with reactions and transformations related to coal combustion, with a short section devoted to other conversion processes.

Slagging Behavior; Ash Melting

During pulverized-coal combustion, atmospheric conditions within the coal flame are considered to be reducing in the sense that the stable ionic form of iron is ferrous. After ash particles have left the flame region, they encounter a more oxidizing environment, yielding deposits and fly ash in which the iron may be predominantly ferric or a mixture of ferrous and ferric, dependent on the air-to-fuel ratio. Consequently, it is important to understand the high temperature reactions of ash constituents in both types of environment. This point is recognized in the ASTM ash-fusion test⁵⁾ which specifies measurement of the fusion temperatures of ash cones in both a reducing (60% CO, 40% CO₂) and an oxidizing (air) atmosphere. Numerous empirical formulae have been developed to predict ash-fusion temperatures (AFTs) and the viscosities of molten coal-ash slags at higher temperatures from ash composition. Detailed discussions of these formulae and their physical basis have been given by Winegartner and his associates,^{1,6,7)} by Watt and Fereday,^{8,9)} and in a recent review article by Reid.¹⁰⁾ The dominant parameter in these relationships is usually the base-to-acid ratio, where "base" and "acid" are simply the sums of the weight percentages of the basic and acidic oxides:



Recently, we examined the behavior of ash fusion temperatures in the context of ternary phase diagrams.¹¹⁾ Significant similarities were observed between the dependence of AFTs on chemical composition and the liquidus curves in appropriate regions of the FeO-SiO₂-Al₂O₃, CaO-SiO₂-Al₂O₃, and K₂O-SiO₂-Al₂O₃ phase diagrams. The development of the Base-SiO₂-Al₂O₃ phase diagrams for the prediction of ash behavior appears to be a fruitful area for future research. An example of such a phase diagram is shown in Figure 1 where ash-softening temperatures (ST, reducing) are plotted in what is effectively the "mullite" region of a Base-SiO₂-Al₂O₃ phase diagram. The curves of equal ST exhibit great similarity to the liquidus curves in true ternary diagrams.

The arrow in Figure 1 illustrates the use of the phase diagram to predict STs. In this instance, a bituminous coal with a low ST was blended with two other coals to yield a product with a much higher ST. The blend was chosen with the aim of moving the composition of ash in a direction approximately normal to the equal ST curves. The predicted and observed STs of the original coal and the blend are shown in the inset of Figure 1. The predicted values are probably not as accurate as could be obtained with existing empirical formulae,⁶⁾ but they are nevertheless quite reasonable.

Ternary and more complex phase diagrams can also contribute to interpretation of the reactions that lead to ash melting. In a reducing environment

(60%CO-40%CO₂), the important reactions for Eastern coals occur primarily within the FeO-SiO₂-Al₂O₃ phase diagram.^{13,14} Using a variety of techniques [Mossbauer spectroscopy, computer-controlled scanning electron microscopy (CCSEM), X-ray diffraction (XRD)] to investigate quenched ash samples heat treated under conditions similar to the ASTM ash-fusion test, it was established that most Eastern coal ashes exhibit behavior similar to that shown in the schematic diagram of Figure 2. Here, phases that are molten at elevated temperatures appear as glass phases in the quenched specimens. The potassium-containing clay mineral, illite, appears to be the first phase converted to a partially molten form; presumably this is because of the numerous low-temperature eutectic points in the K₂O-SiO₂-Al₂O₃ phase diagram.¹² At approximately 900°C, wustite, derived from pyrite and other iron-rich minerals, begins to react with quartz and aluminosilicates derived from clay minerals to produce a mixture of wustite, fayalite (Fe₂SiO₄), and ferrous-containing melt phase. At somewhat higher temperatures (~1050°C), fayalite has been largely incorporated into the melt phase, and ferrous iron may react with aluminosilicates to form hercynite (FeAl₂O₄). This reaction retards melting somewhat and its importance is related to the Al₂O₃ content of the ash. Essentially all of the iron is contained in the melt phase for samples quenched from above 1200°C, as shown in Figure 3. Above 1200°C, reducing, most Eastern ashes (%Base <30%) are a mixture of molten aluminosilicates, mullite, quartz, and minor constituents such as iron sulfide, which is also molten, but is immiscible with the viscous silicate melt.

Similar, but less extensive experiments have also been performed on ash samples quenched from high temperatures in air.¹³ Below approximately 1200°C, essentially all of the glass observed in the samples is derived from the potassium-bearing clay mineral illite. Melting accelerates above approximately 1300°C and approaches completion for most Eastern ashes at temperatures of the order of 1500°C. In an oxidizing environment, calcium appears to be a more effective flux than ferric iron.

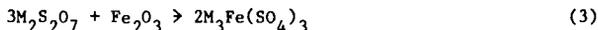
In both reducing and oxidizing atmospheres, significant partial melting of ash occurs at temperatures well below the initial deformation temperature (IDT). It is not uncommon to observe up to 50 percent of the ash in the form of glass at quenching temperatures as low as 200 to 400°C below the IDT. Such partial melting is important in deposit formation. Not surprisingly, the amount of glass observed at a given temperature in an oxidizing atmosphere is significantly less than that in a reducing atmosphere.^{13,14}

Fouling; Volatile Species

Fouling generally refers to the formation of deposits on convective heat-transfer surfaces at relatively low temperatures (600 to 1000°C). Excellent discussions of this problem have recently been given by Wibberly and Wall¹⁵ and in the general review article by Reid.¹⁰ Alkali elements (Na, K) are the principal culprits in the formation of such deposits. Within the flame, these elements become volatilized. The ease of volatilization is related to the form in which the alkalis are present in the coal. Organically bound alkalies would be expected to be easily volatilized at typical flame temperatures (1400-1500°C), as would NaCl, the most common form of sodium in bituminous coal. Potassium contained in illite would not be expected to volatilize as readily; illite should rapidly convert to a molten slag at these temperatures. For this reason, the water-soluble alkali content of coal is considered to be a more reliable indicator of fouling than the total alkali content, at least for Eastern coals. Wibberly and Wall¹⁵ list Na, NaOH, and NaCl as likely gaseous species, dependent on chlorine content of

the coal, flame temperature, and oxygen potential. Nonchloride species are probably rapidly converted to oxides (Na_2O , K_2O) on leaving the flame front. The volatile alkalis may condense on the surfaces of fly-ash particles carried by the flue gas or on cooler boiler surfaces. Wibberly and Wall¹⁵⁾ performed drop-tube experiments in which silica particles were exposed to synthetic combustion gases containing sodium at temperatures of 1200 to 1600°C. Sodium silicate layers ranging in thickness from 0.03 to 0.3 μm were observed on the particle surfaces, and sintered deposits formed rapidly on stainless steel probes inserted into the lower part of the furnace. Such alkali-silicate layers are molten at the temperatures of interest. The thickness of the sodium silicate layers was decreased by a factor of three when the sodium was introduced in the form of NaCl , rather than in chlorine-free forms.

An excellent review of the role of alkali sulfates is given by Reid.¹⁰⁾ Below 1100°C, alkali oxides and chlorides react rapidly with SO_2 and O_2 or SO_3 to form condensed sulfates on fly-ash particles and metal surfaces. Because of their low melting points, alkali sulfates are very corrosive, and form strongly bonded deposits. The melting points of the most easily formed sulfates, Na_2SO_4 and K_2SO_4 , are 882°C and 1075°C, respectively, and the minimum melting point of Na_2SO_4 - K_2SO_4 mixtures is 833°C. K_2SO_4 - CaSO_4 and Na_2SO_4 - CaSO_4 are also commonly observed mixtures, which exhibit melting points in the range from 870 to 970°C. If the SO_3 content of the atmosphere is sufficiently high, the pyrosulfates, $\text{K}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{S}_2\text{O}_7$, may be formed from K_2SO_4 and Na_2SO_4 . These phases melt at very low temperatures: 400°C for $\text{Na}_2\text{S}_2\text{O}_7$ and 300°C for $\text{K}_2\text{S}_2\text{O}_7$. Crossley¹⁶⁾ has suggested that rapid metal wastage is caused by the reaction of the pyrosulfates with Fe_2O_3 to form low-melting point (<600°C) alkali-iron trisulfates:



where $\text{M} = \text{Na}$ or K . This point of view is supported by the work of Coats et al.¹⁷⁾ which established that liquid melts containing up to 90 percent pyrosulfate can be formed from Na_2SO_4 - K_2SO_4 mixtures in SO_3 pressures of 100 to 300 ppm at temperatures down to 335°C. Such SO_3 levels¹⁰⁾ can be readily reached via catalytic oxidation of SO_2 in the presence of Fe_2O_3 .

CCSEM analyses of fouling deposits from a boiler furnace in which a North Dakota lignite had been fired are given in Table III. Although the deposits consisted principally of calcium-enriched aluminosilicates, they also contained small but significant amounts of alkali sulfates, intermixed with calcium sulfate. Recently, we conducted potassium K-edge X-ray absorption spectroscopy (XAS) measurements on one of these samples at the Stanford Synchrotron Radiation Laboratory. The X-ray absorption near-edge structure, or XANES, shown in Figure 4, is nearly identical to that of a $\text{K}_2\text{S}_2\text{O}_7$ standard sample. It appears that XAS will be a very useful method of investigating the structure of individual elements in complex deposits.

Reactions and Transformations of Interest for Other Coal Conversion Processes

In this section, examples of the high-temperature behavior of inorganic phases in other conversion processes will be given.

Liquefaction - Montano et al.¹⁸⁾ have investigated the transformation of pyrite to pyrrhotite in coal liquefaction environments. They conducted in situ Mossbauer

spectroscopy measurements on coals maintained at 1.24 MPa nitrogen pressure and observed changes in the isomer shift at approximately 300°C that signalled the beginning of the transformation of pyrite to pyrrhotite. The transformation accelerated between 300 and 400°C, and from 20 to 80 percent of the pyrite in four different coals was transformed after one hour at 440°C. From close examination of both the in situ spectra and the spectra of cooled residues, they concluded that the pyrrhotite underwent covalent bonding to the coal molecules, causing a catalytic effect on coal liquefaction.

Carbonization - When coal is heated to temperatures ~900 to 1200°C in the absence of air, most of the volatile matter is driven off, leaving a char, or, in the case of metallurgical bituminous coal, a coke. The atmosphere in a coke oven consists principally of hydrogen and methane. Consequently, pyrite is reduced to a mixture of iron sulfide (troilite and pyrrhotite) and iron metal. The amount of iron metal formed depends on both the temperature and the composition of the coke-oven gas. The reduction of iron sulfide to iron metal is desirable since blast furnace operation is more efficient with low sulfur coke. Calcite reacts with the liberated sulfur to form calcium sulfate, thus retaining sulfur in the coke. In Figure 5, the calcium XANES spectrum of a coke produced from a Pittsburgh seam coal in which all calcium was initially present as calcite is shown. The spectrum establishes that approximately 70 percent of the calcite was converted to calcium sulfate during coking.

Gasification

Iron exhibits a great diversity of reactions at elevated temperatures when the reaction environment encompasses both reducing and oxidizing conditions at different stages of the process. For example, it is not unusual to observe five or six different iron-bearing compounds in three different oxidation states in char and ash samples obtained from coal-gasification systems. In Figure 6, the Mossbauer spectrum of a char residue from a bench-scale gasification system at the Institute of Gas Technology is shown. The input atmosphere to the gasifier was approximately 5.2% O₂, 21.2% H₂O, and the remainder N₂, and the average temperature was 1800°F. As indicated in Figure 6, six iron-bearing phases exhibiting three different oxidation states are observed: iron metal, iron sulfide (principally FeS), fayalite (Fe₂SiO₄), magnetite (Fe₃O₄), hematite (Fe₂O₃), glass, wustite, and possibly other minor phases. A more detailed discussion of this work has been given by Mason et al.

Conclusions

Even from this brief overview, it is clear that much remains to be done in the area of understanding mineral-matter behavior in coal combustion and other conversion technologies and even more in combating the sticky problems arising from this component in coal. In particular, we feel there is a great need for much more detailed investigations of full-scale technological processes, especially now that a number of relatively new and sophisticated techniques are available that can be used to characterize mineral-matter related phenomena in ways that were not possible a few years ago. Such techniques include Mossbauer and EXAFS spectroscopies, which we have highlighted in this article, that have the ability to focus on specific critical elements (Fe, K, S, etc.), and reveal very detailed information about the behavior of that element. However, the observed phenomena in full-scale processes will also need to be interpreted in terms of both kinetic (e.g., drop-tube experiments) and thermodynamic (e.g., phase diagram analysis) approaches, as

well as to take into account the form of the mineral matter and its distribution in the original coal. These areas, we feel, should be important areas for research on mineral-matter related problems in the immediate future.

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Table 1
Inorganic Constituents of Eastern Coals

<u>Mineral Distribution</u>			<u>Typical Ash Chemistry</u>	
<u>Mineral</u>	<u>Range</u>	<u>Typical</u>	<u>Species</u>	<u>Weight %</u>
Quartz	5-44	18	SiO ₂	54
Kaolinite	9-60	32	Al ₂ O ₃	29
Illite	2-29	14	Fe ₂ O ₃	8
Chlorite	0-15	2	CaO	2
Mixed Silicates	5-31	17	MgO	1
Pyrite	1-27	8	K ₂ O	2
Calcite	0-14	3	Na ₂ O	1
Siderite/Ankerite	0-11	2	TiO ₂	1
Other Minerals	0-12	4	P ₂ O ₅	0.2
			SO ₃	2

Table II
Inorganic Constituents of Western Coals

<u>Mineral Distribution</u>			<u>Typical Ash Chemistry</u>	
<u>Mineral</u>	<u>Range</u>	<u>Typical</u>	<u>Species</u>	<u>Weight %</u>
Quartz	7-22	15	SiO ₂	30
Kaolinite	13-45	30	Al ₂ O ₃	15
Illite	0-12	2	Fe ₂ O ₃	10
Mixed Silicates	0-22	8	CaO	20
Pyrite	1-26	7	MgO	8
Fe Sulfates	0-5	1	K ₂ O	0.7
Fe-rich*	0-14	2	NaO	0.6
Ca-rich**	7-49	25	TiO ₂	0.7
Other minerals***	1-10	7	P ₂ O ₅	0.4
			SO ₃	15

*Principally iron oxyhydroxide.

**Principally calcium bonded to carboxyl groups in the macerals.

***Barite, apatite, montmorillonite, and others.

Table III

CCSEM Analyses of Fouling Deposits

<u>CCSEM Category</u>	<u>Sec. Superheater, 990-1050°C</u>	<u>Preheater 750°C</u>
Ca-rich aluminosilicate*	55	63
Ca- and Fe-rich aluminosilicate**	7	6
Alkali sulfate***	2	2
Calcium sulfate + alkali sulfate	4	6
SiO ₂	3	2
Ca-rich	10	6
Hematite	2	1
Ca-Fe ferrite	2	1
Ca-Mg sulfate	3	2
Al-Si rich	5	2
Unidentified, mixed phases	7	5

*Approximate average composition (mole %) determined from CCSEM energy dispersive X-ray fluorescence spectra was 37% Ca, 8% Mg, 4% Fe, 41% Si, 10% Al.

**Average composition - 31% Ca, 7% Mg, 21% Fe, 32% Si, 9% Al.

***Average composition - Na₃₃Ca₁₆K₃S₄₈.

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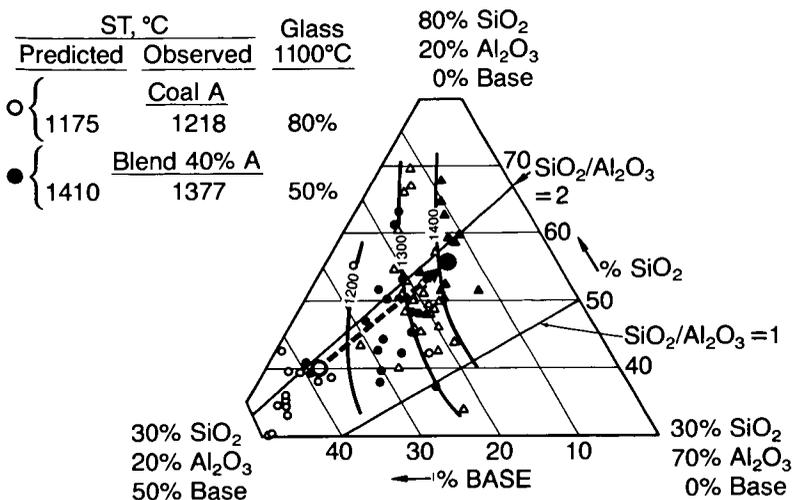


Figure 1 Pseudoternary phase diagram (Base - Al_2O_3 - SiO_2) showing spherical temperature (ST) contours. See text for discussion of points connected by arrow.

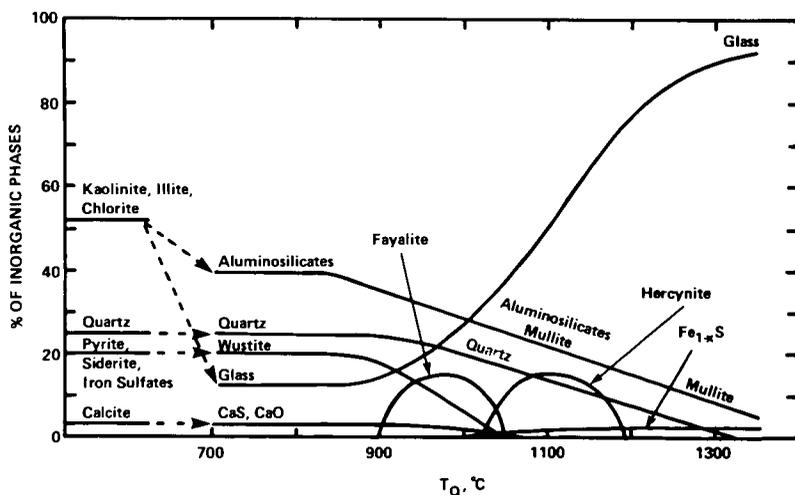


Figure 2 Schematic diagram illustrating high-temperature reactions for minerals in an Eastern-type coal under reducing conditions.

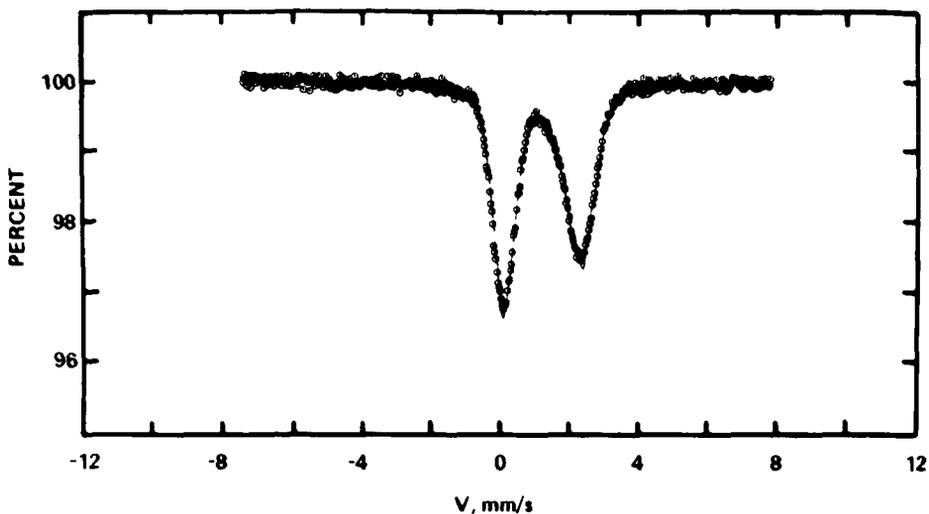


Figure 3 Mössbauer spectrum of Somerset C ash quenched from 1260°C under reducing conditions. Absorption derives entirely from Fe^{2+} in glass.

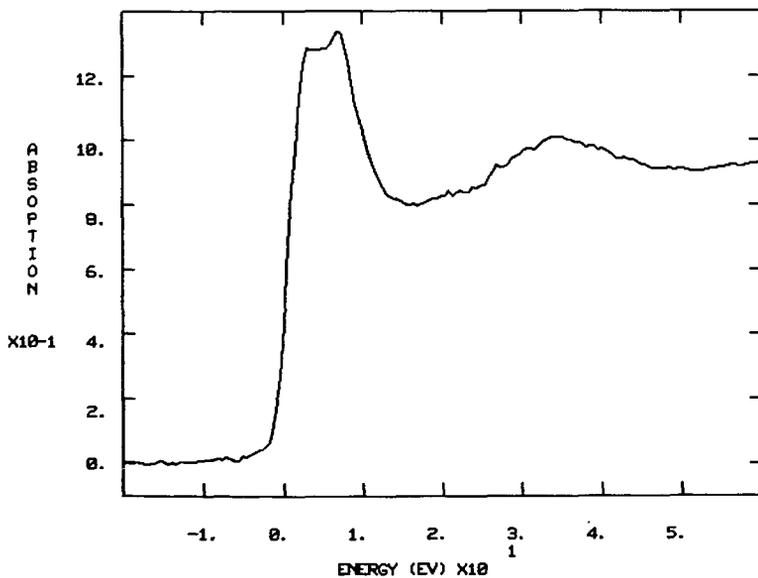


Figure 4 XANES for potassium (K edge) in the fouling deposit resulting from lignite combustion.

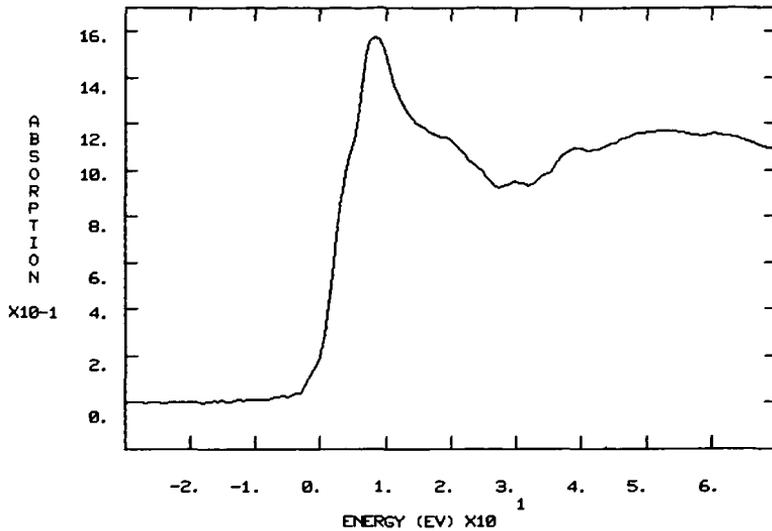


Figure 5 XANES for calcium (K edge) in coke made from high-sulfur coal from Pittsburgh seam.

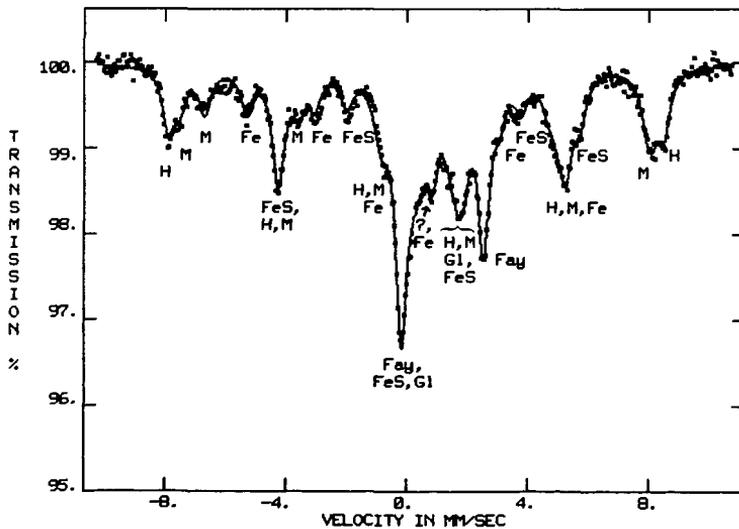


Figure 6 ⁵⁷Fe Mössbauer spectra of gasification char residue showing peaks from hematite (H), magnetite (M), iron metal (Fe), iron sulfides (FeS), fayalite (Fay), glass ± wustite (GI), and an unknown phase (?).