High Temperature Transformations of Minerals in Coal and the Relationship to the Organic Structure

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I. Introduction

The major use of coal is in direct combustion for the generation of electricity. Because of the environmental hazards involved in its use, considerable research has become necessary to fully understand the behavior of the different compounds appearing in coal and the ways in which they transform throughout the course of processing.

Of all the minerals present in coal, iron disulfides (pyrite and marcasite) are the most deleterious. They are one of the major sources of SO_2 pollution. Clay minerals represent a large percentage of the inorganic matter in coal. These minerals are transformed at high-temperature to ferrous and ferric glass phases. Mössbauer spectroscopy can be very helpful in understanding the transformation of iron-bearing minerals during combustion. Such a technique was used to study the oxidation of pyrite[1] at moderate temperatures (maximum 400°C). The oxidation of pyrite in an IL#6 coal occurs in three steps: a) to iron sulfates between 25° to 310°C, b) to γ-Fe_2O_3 between 310° and 325°C, and c) to α-Fe_2O_3 above 325°C.[1,2] It was also observed that the rate of oxidation is strongly particle size dependent. Wendeborn[3] enumerates no less than sixteen concurrent reactions for the oxidation of pyrite. Schwab and Philinis[4] observed that in the range of 400-500°C, the oxidation of pyrite proceeds mainly through the formation of oxides. Sulfate formation amounted to only 12% of the oxide formation at the lower temperature and decreased with increasing temperature. From thermodynamics and kinetics of the reaction of sulfur in coal, Attar[2] suggested that the final products of the reaction depend on temperature, pyrite particle size and oxygen partial pressure.

The Mössbauer effect has also been used by Huffman and Huggins[5] to study the residual ashes in coal. They observed the transformation of pyrite to hematite, siderite to hematite, and of ankerite and Fe^{2+} in clays to ferric ions in glassy materials. The composition of the ashes was strongly dependent on the original minerals and the cooling conditions.

In this work we report a series of *in situ* Mössbauer measurements in four well-characterized bituminous coals. We intend to study the sequence of chemical reactions taking place during the transformation of the iron-bearing minerals. Special emphasis is placed upon the valence state of the iron and the identification of the intermediate states.

II. Experimental Description

The coals used in this study were: Blacksville #2, Powhatan #5, Ky 9/14 and IL #6 obtained from St. Clair County, Illinois. Table I gives the ultimate analysis of these four coals. The oxidation process was carried out in a specially built reactor. The reactor chamber consists of a quartz cylinder with an outer diameter of 2.5 cm. The sample was mounted in the center of the cylinder allowing the flow of air through it. The quartz tube was placed inside a horizontal furnace capable of reaching 1200°C. A chromel-alumel thermocouple was inserted into the middle of the reactor near the sample to detect the temperature. The reactor was held

horizontally. The sample, a coal pellet, was mounted between two graphite holders in the center of the reactor. For the process of oxidation, air was allowed to flow through the sample at a constant rate. A computerized Mössbauer spectrometer was used in this study to accumulate, record and fit the data. The fitting is based on a non-linear least-square procedure assuming Lorentzian-like shapes. The source used was a ~100 mCi ^{57}Co in a rhodium matrix. A krypton (3% CH_4) proportional counter was used as a detector (care was taken to cool the windows of the detector during the measurements). In situ ^{57}Fe Mössbauer spectra of all the samples were recorded during oxidation at various temperatures between 22°C and 710°C. All the isomer shifts are given in reference to α-Fe (the zero velocity standard). The reduction measurements were performed under hydrogen flow as well as under a nitrogen atmosphere.

III. Experimental Results and Discussion

The Mössbauer spectra of all the coals at room temperature show the presence of FeS_2 (pyrite) in various amounts. The spectrum of pyrite is known to give a characteristic quadrupole split doublet, isomer shift (IS) = 0.31 mm/sec and quadrupole splitting (QS) = 0.61 mm/sec. In all the coals depending on the degree of weathering (room temperature oxidation), the presence of $FeSO_4 \cdot H_2O$ (szomolnokite) was observed, IS = 1.18 mm/sec and QS = 2.69 mm/sec. In some samples minor amounts of jarosite and coquimbite (ferric sulfates) were also observed. The major iron-bearing clay minerals detected in the present experiments were illite and mixed clays (as detected by x-ray diffraction). The amount of iron in such minerals is very small and detection becomes easier after analyzing the high temperature ashes. On heating the coal in air, FeS_2 will be oxidized to a mixture of sulfates and oxides, and we would expect the Mössbauer spectrum to consist of a superposition of a magnetically split six-line pattern due to the iron oxides and doublets resulting from unreacted FeS_2 and iron sulfates. The above reactions could be summarized as:

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2 \qquad 1)$$

$$3FeS_2 + 10\ O_2 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 2SO_2 \qquad 2)$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

In Figures 1 and 2 the in situ Mössbauer spectra for the Blacksville #2 and IL#6 coal are shown. On heating the coals through the various temperatures it was observed 1) for FeS_2, the QS remains almost unchanged but its isomer shift decreases rapidly. The decrease in the IS is attributed mainly to the second order Doppler shift. 2) For $FeSO_4 \cdot H_2O$, the QS is observed to decrease at high temperatures. This decrease is mainly due to the temperature dependence of the electric field gradient (through population of excited electronic states). The area fraction of iron sulfates increased with temperature; this is due to the formation of sulfates through reactions (1) and (2). On increasing the temperature above 300°C and for short periods of time, the formation of ferrimagnetic γ-Fe_2O_3 is observed (see reference 1). The formation of γ-Fe_2O_3 has also been reported by other authors.[6] On further heating the coal to 350°C, the conversion of γ-Fe_2O_3 to α-Fe_2O_3 is observed (easily detected by the difference in magnetic hyperfine fields). The conversion of γ-Fe_2O_3 to α-Fe_2O_3 is complete at 400°C, and a characteristic six-line pattern due to α-Fe_2O_3 is observed. The presence of γ-Fe_2O_3 as an intermediate state depends on the coal as well as oxidation time. The longer the time, the more γ-Fe_2O_3 to α-Fe_2O_3 conversion is observed. Of course at higher temperatures only α-Fe_2O_3 is stable. How the coal composition affects the amount of γ-Fe_2O_3 formed is not well understood, although one is inclined to believe that particle size and impurities in the pyrite (or marcasite) would be important factors in this process. The above was also observed in all the coals studied. Two typical room temperature spectra for the Blacksville #2 and IL#6 coals are shown in Figures 3 and 4. The six-line spectrum characteristic of α-Fe_2O_3 is easily observed as the dominant feature in the figures. Noted is the presence of

two extra doublets containing Fe^{3+}, attributed to decomposition of the clays and formation of amorphous materials with Fe^{3+} as an impurity. The doublets are not identical in both spectra indicating that the environment of Fe^{3+} is different. This is indicative of a variation in clay composition between the two coals. Because of the small amounts of iron in such phases, their clear identification is rather difficult and still remains a challenging problem for the spectroscopist. Similar spectra were also observed for the other two coals.

The Mössbauer spectral area of each species was used to determine the relative amounts of FeS_2, Fe^{2+}, Fe^{3+} (not as oxide) and Fe_2O_3. In this analysis we will neglect any variation in Debye-Waller (D-W) factors between the different species. Consequently the relative amounts will indicate the qualitative variation in sample composition at the different temperatures. The absolute amounts vary depending on their respective D-W factors. Since such a correction is very difficult, we limit ourselves to the assumption that all the species show a similar temperature dependence for the D-W factors. Figure 5 shows the decomposition of FeS_2 as a function of temperature for all the coals under study. Figure 6 shows the amount of Fe^{2+} as a function of temperature for all the coals; the divalent ion contribution is mainly from the ferrous sulfates. In Figure 7 the variation in Fe^{3+} and iron oxides (both γ and α) are shown as a function of temperature. It is evident that for the most weathered coals, there is more ferric sulfate present (e.g. IL#6). For the fresher coal (BL#2), the amount of ferric sulfate is smaller and the transformation from iron sulfides to sulfates to oxides is rapid. At 710°C the ferric ion is present mainly as α-Fe_2O_3. At this temperature we are above the antiferromagnetic to paramagnetic transition temperature of α-Fe_2O_3 and no magnetic splitting is observed. The α-Fe_2O_3 particle sizes seems to be very similar in all the coals studied. This is evident from Figure 8 where the normalized magnetic hyperfine field at the ^{57}Fe nucleus is plotted versus temperature. The temperature dependence is very similar for all the samples (only α-Fe_2O_3 plotted) indicating similar particle sizes. Most likely sintering has occurred during combustion. Weathering of the coal seems to be one of the major factors hindering the rapid conversion of FeS_2 to oxides at low temperatures. Eventually at higher temperatures the ferric sulfate particles are converted to oxides. It appears that the presence of particles of ferrous and ferric sulfates slows down the rapid oxidation of FeS_2. There is also a physical factor present. It is highly probable that the smaller sulfide particles were oxidized at room temperature in a weathered coal and the remaining particles are larger and more difficult to oxidize.[1,2] It is evident that the fresher coal oxidized faster than the others (see Figure 7).

Under reduction conditions and below 450°C, all the iron sulfides are transformed into pyrrhotites. The degree of transformation depends on time as well as the type of coal.[7] The major factor affecting the Fe/S ratio in the pyrrhotites is the total amount of sulfur available as H_2S. Partial H_2S pressure is the crucial quantity controlling the stoichiometry of the pyrrhotites. A high percentage of H_2S in the reactor at high temperatures assures the formation of pyrrhotites with a high number of metal vacancies. The pyrrhotite surface interacts with CO and CO_2 in the presence of hydrogen. The products are removed from the surface and the pyrrhotites retain a metal character. At temperatures higher than 450°C the pyrrhotites start to transform into troilite and eventually into iron metal. The formation of troilite (FeS) is also possible at lower temperatures if H_2S is continually removed from the reactor by flowing hydrogen. The clay minerals are also transformed during reduction with the iron ion preferring to retain a divalent state. The degree of transformation is strongly coal dependent.

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TABLE I Ultimate Analysis (WT%, dry basis)

Coal	H	C	N	S	O	HTA
IL#6	4.7	67.6	1.2	4.0	8.0	13.96
Powhatan #5	4.9	71.1	1.1	3.5	7.5	11.8
Ky 9/14	4.9	71.3	1.5	3.4	9.7	9.3
Blacksville #2	5.2	75.83	1.4	3.4	3.5	10.1

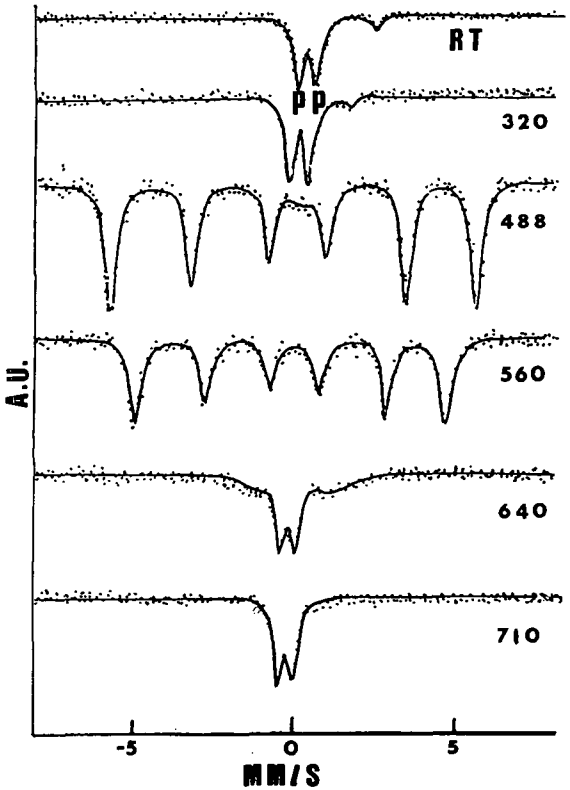

FIGURE 1 Mossbauer spectra of the Blacksville #2 coal as a function of temperature: pp indicates the position of pyrite.

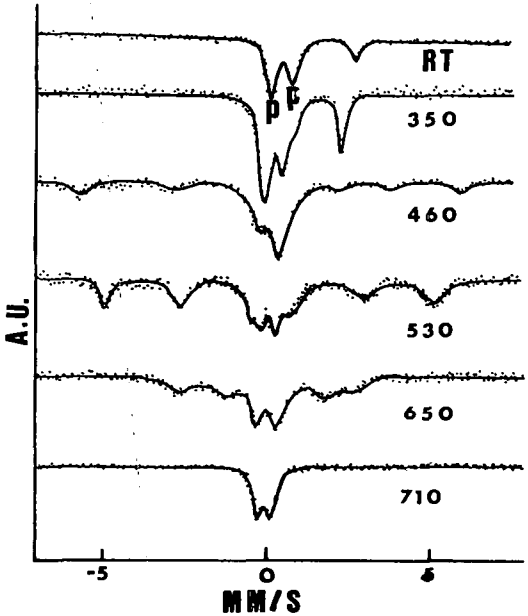

FIGURE 2 Mossbauer spectra of the IL #6 coal as a function of temperature.

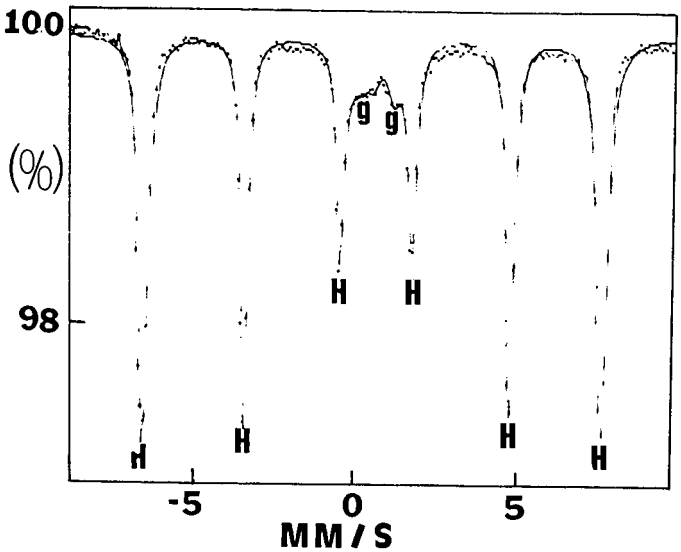

FIGURE 3 Mössbauer spectrum at room temperature after oxidation at 710°C of the Blacksville #2 coal. H: α-Fe_2O_3
g: Fe^{3+} in amorphous clay (two doublet)

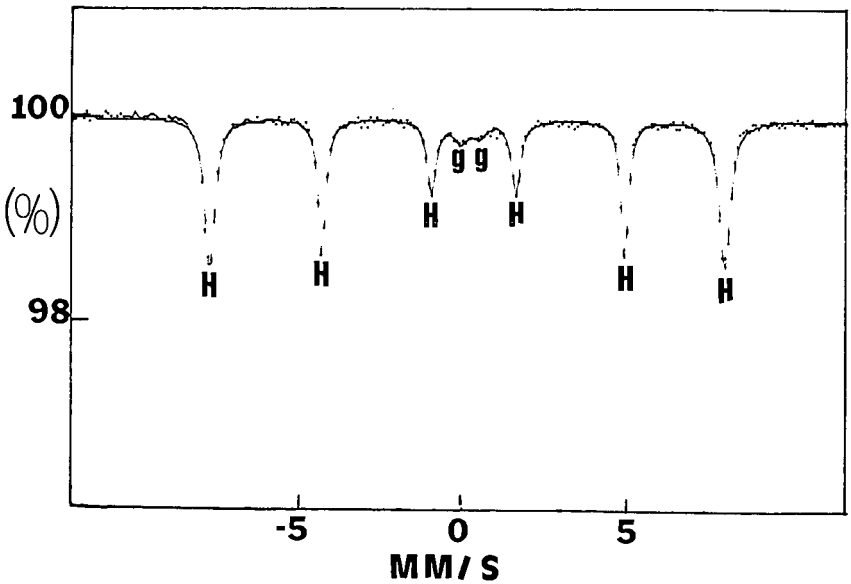

FIGURE 4. The same as above but IL #6 instead of Blacksville #2.

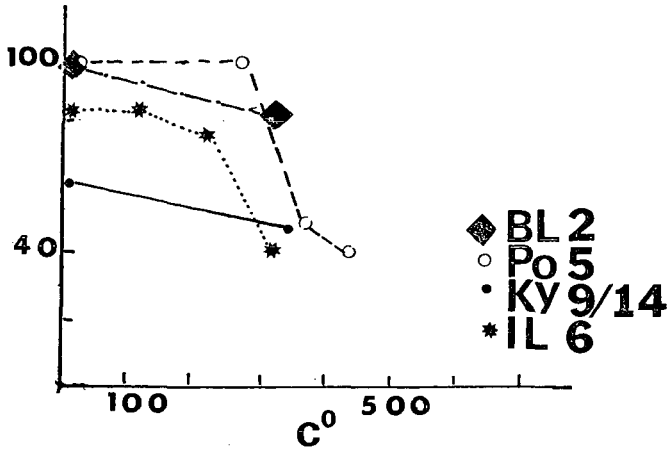

FIGURE 5 Decomposition of FeS_2 in percent as a function of temperature. BL2: Blacksville #2; Po5: Powhatan #5; Ky 9/14; and IL6: IL #6.

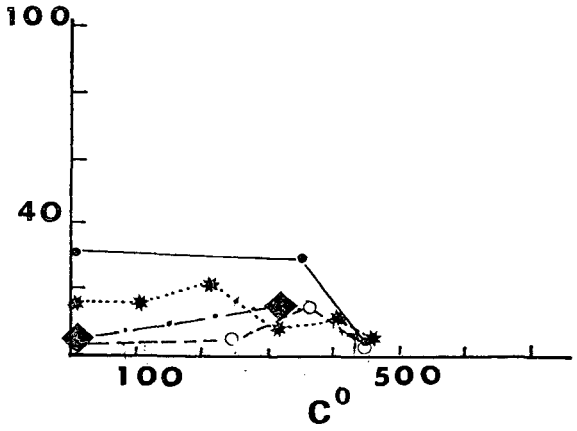

FIGURE 6 Transformation of Fe^{2+} in percentage vs. temperature. Key to the figure is found in Figure 5.

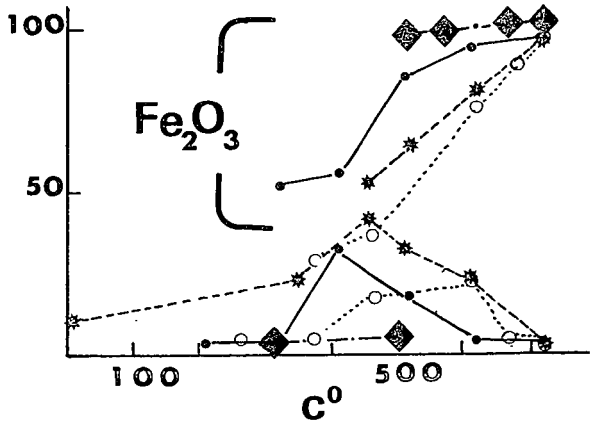

FIGURE 7 Conversion to Fe_2O_3 and Fe^{3+} (not oxides) as a function of temperature. See Figure 5 for the key to the symbols.

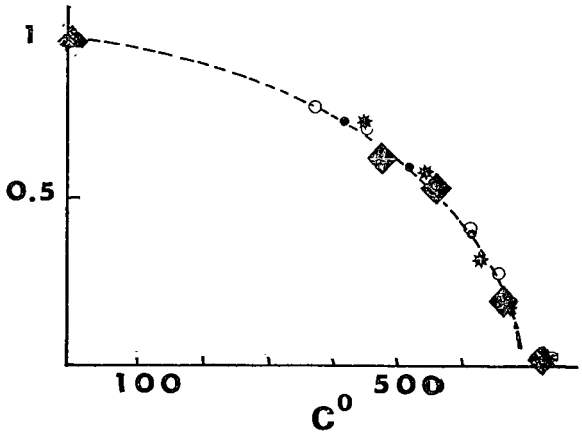

FIGURE 8 Magnetic hyperfine field normalized to room temperature for all the samples vs. temperature.