

CHARACTERIZATION OF IRON BEARING MINERALS IN COAL

Pedro A. Montano

Department of Physics, West Virginia University, Morgantown, WV 26506

Introduction

Due to the importance of coal as a major source of energy and the environmental hazards involved in its use, considerable research has become necessary in order to a) fully understand the different compounds appearing in the coal and their transformation during processing; and b) know how those compounds contribute to the pollution of the environment, i.e., acidity of water streams near the coal mines and pollution by power plants. Some positive properties can be associated with the mineral matter in coal. For example, recently several researchers have shown that the mineral matter in the coal may play an important role in the liquefaction process (1). Of all the minerals in the coal, the iron bearing minerals seem to be the most important. In most coal utilization techniques the coal is used as raw material, and as a result both the organic and inorganic components may be critical in the acceptance or rejection of a coal for a particular process. Owing to the great importance of iron as a major constituent of the mineral matter in many coals the Moessbauer effect becomes a powerful tool in the characterization of the iron bearing minerals.

The most common use of the Moessbauer effect in mineralogy and geology has been the determination of the oxidation states of iron in various minerals (2). The study of the Moessbauer spectral area also gives valuable information on the concentration of the different minerals in rocks (2). Recently the Moessbauer effect was applied to the study of iron bearing minerals in coal and to determine the amount of pyritic sulfur (3,4,5).

In what follows the application of Moessbauer spectroscopy (^{57}Fe) to determine the iron bearing minerals will be described and a critical view of the advantages and disadvantages of the technique will be presented. In this study more than 200 coal samples were investigated and more than 2000 Moessbauer runs were carried out on those samples. Before going into the experimental results, a brief description of the Moessbauer parameters which give the necessary information to determine the compounds seems appropriate.

Moessbauer Parameters

Isomer Shift (IS): The shift observed in the Moessbauer lines with respect to zero velocity is produced by the electrostatic interaction of the nuclear and s-electrons charge distributions. It is given in the non-relativistic approximation by (6)

$$IS = \frac{2\pi}{5} ze^2 (R_{ex}^{-2} - R_{gd}^{-2}) \{ |\psi_{\text{ahs}}(0)|^2 - |\psi_{\text{source}}(0)|^2 \} \quad 1)$$

The IS gives valuable and unique information on the valence states of iron, in special for high spin Fe^{2+} and Fe^{3+} .

Besides the IS there exists a shift of the Moessbauer lines due to the second order Doppler effect (7). This shift is given by

$$\delta E_{\text{SODS}} = \frac{E_0}{2} \frac{\langle v^2 \rangle_T}{c^2} \quad 2)$$

where $\langle v^2 \rangle_T$ is the thermal average of the square of the velocity of the Moessbauer atom in the solid. It is a parameter that strongly depends on the lattice dynamical properties of the solid.

The hyperfine interactions affecting the Moessbauer effect are the quadrupole and magnetic interactions (2). The quadrupole interaction exists when the electrons and/or the neighboring atoms produce an inhomogeneous electric field at the nucleus, and when the nucleus possesses a quadrupole moment, Q. This interaction produces a splitting of the Moessbauer lines for ^{57}Fe given by (2)

$$\Delta E_Q = \frac{1}{2} e^2 q Q (1 + \eta^2/3)^{1/2} \quad 3)$$

where q is the electric field gradient, and η the asymmetry parameter. When q arises from the electrons of the Moessbauer atom, the temperature dependence of the QS is very pronounced, like in high spin Fe^{2+} compounds. This temperature dependence is very useful in the identification of the electronic ground state of the ion.

The hyperfine magnetic interaction arises from the interaction of the nuclear magnetic dipole moment with a magnetic field due to the atom's own electrons. In many cases Moessbauer studies at low temperatures are necessary to fully characterize a compound. In such cases one usually applies an external magnetic field. This technique is particularly useful for the study of the electronic ground state of iron ions in minerals (8,9).

A very important Moessbauer parameter is the Debye-Waller factor (DWF). The DWF depends on the temperature and is given in the harmonic approximation by (2)

$$\text{DWF} = \exp(-k^2 \langle x^2 \rangle_T) \quad 4)$$

where $\langle x^2 \rangle_T$ is the mean square displacement of the atom along the direction of the γ -ray emission. The DWF is frequently evaluated in Moessbauer spectroscopy using an effective Debye model. The DWF can be different for the same compound if the particle size is very small. One has to be aware of this problem when using the Moessbauer effect as a quantitative analytical tool.

The Moessbauer effect can be used not only for the identification of mineral species, but also for a quantitative analysis of the mineral contents. The Moessbauer spectral area is given for a single line source and absorber by (10)

$$A = p^{-1} f_s \Gamma_a \frac{\pi}{2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n!} \frac{(2n-3)}{(2n-2)!} t^n \quad 5)$$

$p = 1 - B/N(\infty)$

$t = n \frac{\sigma_a f_a}{\Gamma_a}$

where B = background (non-Moessbauer radiation); $N(\infty)$ = counting rate at infinity velocity; Γ_a = full width of half-height of the absorption line; $f_s f_a$ = DWF of absorber and source; σ_a = absorption cross-section at resonance; n_a = number of Moessbauer atoms per square centimeter. The above formula has to be corrected for lines splitted by hyperfine interactions (11). When using the Moessbauer effect as a quantitative analytical tool, care must be taken that B, f_s and f_a are known. A discussion on the quantitative method of analysis will be given at the end of the paper.

Experimental Procedures

The coal samples used in this work were collected following strictly ASTM procedure D2013-72. The samples were mounted in lucite containers that were hermetically sealed. Pressed pellets of the grinded coal were also used as samples. The average surface densities of the samples used were between 150 to 300 mg/cm². Several samples from the same seam were analyzed in order to check for consistency of the results. Some runs were carried out on raw coals (not grinded) as well, for testing purposes. The bulk of the samples used in this study were from West Virginia coals. The Moessbauer spectrometer used in this work was a conventional constant acceleration spectrometer. A 50mC ⁵⁷Co:Pd source was used. The Moessbauer spectra were analyzed using a non-linear least-square fit program and assuming Lorentzian lineshapes. The measurements covered a wide temperature range. Many runs were carried out at low temperatures (4.2 K) and in the presence of an external magnetic field (40 kOe). The velocity calibration is given with respect to α -Fe at room temperature (RT).

Experimental Results and Discussion

The different iron bearing minerals detected in coal using Moessbauer spectroscopy are classified below according to their major groups, i.e., sulfides, clays, carbonates, and sulfates.

Sulfides: Iron disulfide (pyrite) is the most important of the iron bearing minerals in coal. In pyrite the iron ion is in the low spin configuration, Fe^{II}. The six d-electrons are occupying the T_{2g} ground state and no magnetic moment is present at the iron site (8). In pyrite^{2g} each cation has a distorted octahedral coordination of six nearest neighbors sulfur, the octahedron being slightly compressed along one of the axis. Consequently, the crystalline field at the iron site is lower than cubic and an electric field gradient exists at the ⁵⁷Fe nucleus, producing a characteristic QS in the Moessbauer spectrum.

There is a metastable phase of FeS₂, marcasite, which is the orthorhombic dimorph of pyrite and appears also in several coals. Marcasite has slightly different IS and QS (Table 1). When the amount of marcasite in coal is more than 20% of the total iron disulfide content its detection using Moessbauer spectroscopy is possible. In general, petrographical techniques seem to be more appropriate for identification of marcasite (at least for qualitative measurements). In table 1 a list of the different iron sulfides and their respective Moessbauer parameters is given.

A typical spectrum of a coal is given in figure 1. The sample has been treated with HCl (following ASTM standard D-2492) to get rid of the non-pyritic iron (sulfates). The spectrum is typical of pyrite. All the ca. 2000 spectra run in this work show the presence of pyrite (contents ranging between 7 to 0.1%). While studying several coal macerals a new Moessbauer spectrum associated with pyrite was observed in three different samples (9) rich in framboidal pyrite. The extra Moessbauer doublet showed the same magnetic behavior as pyrite (low spin). However, its Moessbauer parameters are different and the IS suggests a smaller electronic density at the nucleus than for FeS₂. The low temperature measurements indicate that the spectrum cannot be associated with any of the other minerals. It is possible that this phase is highly disordered (or "amorphous") FeS₂.

Other iron sulfides are produced during coal processing. They are mainly pyrrhotites. For compositions varying between FeS (troilite) and Fe₇S₈ (monoclinic pyrrhotite), the compounds are referred to generally as pyrrhotites (12). The Moessbauer spectrum of iron pyrrhotites can be observed in the coal liquefaction

mineral residue. The study of these pyrrhotites is of considerable importance due to their potential use as disposable catalysts in coal liquefaction (1). It is to be noted that the presence of pyrrhotites was observed in some severely "weathered" coal. In studies carried out under a reducing hydrogen atmosphere (between RT and 400°C) the conversion of all the pyrite to pyrrhotites was observed.

Clay minerals: Clay minerals represent a large percentage of the inorganic mineral content in coal. Illite, kaolinite and mixed clays are the major clay minerals present in coal. The crystal structures of the clay minerals are basically derived from two types of sheets. A tetrahedral sheet typically made of SiO_4 units, and an octahedral sheet typically made of $\text{Al}(\text{O}, \text{OH})_6$ units (13). The ideal formula, i.e., for kaolinite is $\text{Al}_2^{3+}\text{Si}_2^{4+}\text{O}_5^{2-}(\text{OH})_4$, but as in all clay minerals, a certain amount of cation substitution is possible. In mica and its derived clay minerals, illites, the octahedral sheet contains only Al^{3+} , but in the tetrahedral sites one quarter of the Si^{4+} is replaced by Al^{3+} . The net negative charge of the layer is balanced by interlayer alkali cations which also bond the layers together. The interlayer in montmorillonite or vermiculite is occupied by H_2O and/or cations, whereas in chlorite there is a complete sheet of aluminum (magnesium) hydroxide, the brucite sheet. Continuous ranges of chemical composition are often possible between the different clays and there is a great variety of mixed layer structures. Iron can be substituted in the octahedral layer in its high-spin ferrous and ferric forms, and occasionally in the tetrahedral layer. However, the iron concentration in clays is relatively small (a few % by weight) for kaolinite and illite, the most frequently found clays in coal (14).

In general the clays appearing in the coal show slightly different Moessbauer parameters than pure clays. The usual method utilized to identify the clay minerals in coal is X-ray diffraction of the LTA, but due to the poor crystallinity of the clays in the coal the technique cannot be used for quantitative measurements. The Moessbauer effect is not much of an improvement due to the small iron content of the clays. A coal rich in clays is shown in figure 2 (about 10% mineral matter). The appearance of two peaks at higher velocity is not due to the presence of two sites in the clay or to two different clays, it is produced by szomolnokite. By treating the sample with HCl, the sulfate was washed away and the clay (possibly illite) could be clearly seen (Figure 3). Treating the coal with HNO_3 dissolves the pyritic iron and the spectrum of the clays can be detected more clearly. Figure 4 shows the Pittsburgh coal (230 mesh) shown in Fig. 1 after treatment with HNO_3 . The spectrum (notice the smaller effect) is identified as that of kaolinite (a small QS is detectable).

In general, to study the clays in coal one should treat the samples as described above, or run the experiments at low temperatures in order to resolve the overlapping lines (measurements in an external magnetic field become necessary) (8,9). Moessbauer parameters for the principal clay minerals, pure and as they appear in coal, are given in table 1.

Sulfates: The iron sulfates were detected in more than 90% of the coal samples studied. The sulfates are considered to be produced by "weathering" of the coal. The amounts detected in this study ranged from 0.2 to 0.005% of total weight.

The standard technique used for detection of sulfates is X-ray diffraction of the LTA. Nevertheless, we have observed that in some cases sulfates are present in the coal and the X-ray does not show any line attributable to them (15). The most abundant divalent iron sulfate observed in the coals studied is $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (szomolnokite), a monoclinic crystal with a tetramolecular unit cell (16). This compound

orders antiferromagnetically around 10K with an effective interval field of 359 kOe (9). Other sulfate minerals found less frequently are $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite), and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite); anhydrous ferrous sulfate was detected when the coal was stored under vacuum. The ferric sulfates commonly observed in several coals are coquimbite and jarosites.

A word of caution concerning the presence of trivalent sulfates in the coal is appropriate here. These sulfates have in general lines which overlap with the Moessbauer pyrite lines. The result is the detection of a slightly asymmetric pyrite spectrum. If one treats the samples with HCl it will appear as if some of the pyrite has dissolved in HCl, but this is of course not true, and is the result of the presence of the iron sulfates. The ferric sulfates are easily distinguishable from pyrite. When Moessbauer measurements are carried out at 4.2K in the presence of a large external field, the characteristic hyperfine field of Fe^{3+} is detected (about 500 kOe). It was observed also that many of the ferric sulfates are formed during LTA (3).

In figure 5 a Moessbauer spectrum for a mixture of szomolnokite (A) and rozenite (B) is shown. The sample was characterized by X-ray diffraction as well as Moessbauer spectroscopy. After LTA (17) the Moessbauer spectrum shows the presence of szomolnokite (no rozenite) and ferric sulfate. This was observed for all the runs carried on the coal samples studied. In table 1 a list of the iron sulfates and their respective Moessbauer parameters is given.

Carbonates: The Moessbauer spectra of some of the coal samples show the presence of FeCO_3 (siderite). Siderite has a rhombohedral structure with an octahedron of oxygens around the iron with a small trigonal distortion along the c-axis. Siderite is magnetically ordered at low temperatures ($T_N = 38\text{K}$) with a very distinctive Moessbauer spectrum (18). During the study it was observed on several occasions that a Moessbauer spectrum appeared to be that of FeCO_3 ; however, by carrying out low temperature measurements the presence of either clay or ankerite was inferred. Ankerite $[\text{Ca}(\text{FeMg})(\text{CO}_3)_2]$ is another carbonate that appears in some coals. It is nearly impossible to distinguish ankerite from siderite using Moessbauer spectroscopy at room temperature (RT). One has to carry out low temperature measurements. In table 1 the relevant Moessbauer parameters are given for the iron carbonates observed in coal. In all the measurements no more than 0.1% siderite by weight was detected.

Other minerals: In this work no other minerals were detected using Moessbauer spectroscopy, except the ones mentioned above. However, in heavily weathered coals and coal refuse the presence of iron oxides (hematite and to a lesser extent magnetite) were observed. Pyrrhotite was also detectable in some of the heavily weathered coals. Other minerals like spharelite, chalcopyrite and arsenopyrite were not detectable in these experiments. Some of the latter minerals have been identified using scanning electron microscopy, but their presence in the coal is too small to make their contribution to the Moessbauer spectrum significant. Other sulfides like Fe_3S_4 or Fe_2S_3 (19) were not detectable in any of the samples at RT or 4.2K. No evidence of organically bound iron in coal was found for all the studied samples (20).

Moessbauer Spectroscopy as a Tool for Quantitative Determination of Pyritic Sulfur

The use of Moessbauer spectroscopy to determine the amount of iron in a sample presents several serious problems to the experimentalist. One has to know the Debye-Waller factor of pyrite and the background radiation accurately. The DWF of FeS_2 can be determined from the temperature dependence of the spectral area for pure crystals of known thicknesses. However, in many coals pyrite is highly dispersed

and form very small particles which have low crystallinity; consequently, the DWF might differ considerably from that of large FeS_2 crystals. Also, a very important source of error is the determination of the non-resonant radiation background. In all the runs carried out in this study it was observed that variations of 10 to 30% occur in background counting rates for samples of coals with the same weight per unit area. The differences are due to the heterogeneity of the mineral composition of the coals. Both photoelectric scattering (mainly by the 14.4 keV) and Compton scattering of the high energy γ -rays contribute to the background radiation. This, of course, indicates that a full analysis of the γ -ray spectrum for each sample is necessary. Any use of standards to determine the amount of pyritic sulfur will have to take into consideration the problems mentioned above (5). The use of Moessbauer spectroscopy for quantitative analysis has to go hand in hand with the standard chemical procedures (ASTM D 2492-68), as a *complementary technique and not as a substitute*. In general, the most accurate Moessbauer quantitative measurement will give an error of about 10%.

Conclusions

The Moessbauer effect has been used as an analytical tool to characterize the different iron bearing minerals in coal. It has been pointed out that by the use of low temperature measurements (in the presence of a large external magnetic field) and treatment of the coal samples all the iron bearing minerals can be correctly identified. The use of Moessbauer spectroscopy as a quantitative analytical tool presents several experimental difficulties. It is recommended that this spectroscopy be used as a *complement* to and not as a substitute for the standard techniques.

Acknowledgements

The author thanks Drs. A.H. Stiller and J.J. Renton of the West Virginia Geological Survey for their invaluable help in carrying out this investigation. The technical assistant of William Dyson in some of the measurements is gratefully acknowledged.

References

1. Thomas, M.G., Granoff, B., Baca, P.M., and Noles G.T., 1978. Division of Fuel Chemistry, American Chemical Society, 23(1):23.
2. Bancroft, G.M., 1973. Moessbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists. New York: John Wiley.
3. Montano, P.A., 1977. Fuel 56:397.
4. Levinson, L.M., and Jacobs, I.S., 1977. Fuel 56:453.
5. Huffman, G.P., and Higgins, F.E., in press. Fuel.
6. Kistner, O.C., and Sunyar, A.W., 1960. Phys. Rev. Letters 4:412.
7. Pound, R.V., and Rebka, G.A., Jr., 1960. Phys. Rev. Letters 4:274; Josephson, B.D., 1960. Phys. Rev. Letters 4:342.
8. Montano, P.A., and Seehra, M.S., 1976. Solid State Communications 20:897.

9. Russell, P., and Montano, P.A., 1978. *Journal of Applied Physics*. 49(3):1573; 49(8):4615.
10. Lang, G., 1963. *Nucl. Instr. Methods* 24:425.
11. Housley, R.M., Grant, R.W., and Gonser, V., 1969. *Phys. Rev.* 178:514.
12. Power, L.F., and Fine, H.A., 1976. *Minerals Sci. Engng.* 8:106.
13. Millot, G., 1970. *Geologie des Argiles*. Paris: Masson.
14. Rao, C. Prasada, and Gluskoter, J. Harold, 1973. *Illinois State Geological Survey, Circular* 476.
15. Stiller, A.H., Renton, J.J., Montano, P.A., and Russell, P.E., 1978. *Fuel* 57:447.
16. Pistorius, C.W.F.T., 1960. *Bull. Soc. Chim. Belg.* 69:570.
17. The LTA was carried out by J.J. Renton at the West Virginia Geological Survey.
18. Ono, K., and Ito, A., 1964. *Journal of the Phys. Soc. of Japan* 19:899.
19. Schrader, R., and Pietzsch C., 1969. *Kristall und Technik* 4:385; Stiller, A.H., McCormick, B., Jack, Russell P., and Montano, P.A., 1978. *Journal of the American Chem. Soc.* 100:2553.
20. Lefelhocz, J.F., Friedel R.A., and Kohman, T.P., 1967. *Geochim. Cosmochim. Acta* 31:2261.
21. Thiel, R.C., and van den Berg, C.B., 1968. *Phys. Stat. Sol.* 29:837.
22. Goncharov, G.N., Ostonevich, Yu. M., Tomilov, S.B., and Cser, L., 1970. *Phys. Stat. Sol.* 37:141; Novikov, G.V., Egorov, V.K., Popov, V.I., and Sipavina, L.V., 1977. *Phys. Chem. Minerals* 1:1; Gosselin, J.R., Townsend, M.G., Tremblay, R.J., and Webster, A.H., 1976. *Solid State Chem.* 17:43.
23. Vaughan, D.J., and Ridout, M.S., 1971. *J. Inorg. Nucl. Chem.* 33:741.
24. Jefferson, D.A., Tricker, M.J., and Winterbottom, A.P., 1975. *Clays and Clay Minerals* 23:355.
25. Coey, J.M.D., 1975. *Proc. Int. Conf. on Moessbauer Spectroscopy* 333, Cracow.
26. Vertes, A., and Zsoldos, B., 1970. *Acta Chim. Acad. Sci. Hung.* 65:261.
27. Greenwood, N.N., and Gibb, T.C., 1971. *Moessbauer Spectroscopy*. London: Chapman and Hall, Ltd.
28. Hryniewicz, A.Z., Kubisz, J., and Kulgawczuk, D.S., 1965. *J. Inorg. Nucl. Chem.* 27:2513.

TABLE 1. MOESSBAUER PARAMETERS OF MAJOR IRON BEARING MINERALS AT RT.

Name	IS (mm/sec)	QS (mm/sec)	Magnetic Hyperfine Field (kOe)	Ref.
SULFIDES:				
Pyrite (FeS ₂)	0.32(2)	0.63(2)	0	*
Marcasite (FeS)	0.28(2)	0.59(2)	0	*
Troilite (FeS)	0.77(4)	0.28	310	(21)
Pyrrhotite (FeS _{1+x}) (1<x<0.143)	0.64 - 0.69	-0.14 - 0.32	243 - 310	(22)
	0.70	0.30	322	
Greigite (Fe ₃ S ₄)	0.40 (4.2K)	0	486 (4.2K)	(23)
	0.45	0.4	465	
Fe ₂ S ₃	0.35(6)	0.82(6)		
	0.51(12)	0.88(12)	253 (4.2K)	(19)
Sphalerite (Zn, Fe)S	0.30(2)	0.61(2)	0	*
CLAYS:				
Kaolinite	0.30	0.59	492 (4.2K)	(22)
Chamosite	0.38(5)	0.78(8)		(25)
	1.14(6)	2.57(8)		
Fayalite	1.17(6)	2.85(8)		*
	0.99(7)	1.72(10)		
Montmorillonite	0.38(8)	0.50(13)		(25)
	1.15(6)	2.81(6)		
Muskovite	0.37(5)	0.75(8)	40 (4.2K)	*
	1.17(3)	3.08(7)	500	
	0.36(5)	0.52(12)		
Glaucanite	0.38(3)	1.21(5)		(25)
	1.14(6)	2.30(6)		
Chlorite	0.17(6)	0.78(8)	505 (4.2K)	*
	1.13(4)	2.67(6)	20	
	0.34(3)	0.43(4)	0	
Illite #36 (Morris)	1.24(5)	2.60(6)	20 - 30 (4.2K)	*
	1.27(3)	1.92(4)	0	
	0.28(6)	0.60(8)		
Illite #35 (Fitchian)	1.14(7)	2.77(7)	20 - 30 (4.2K)	*
	1.25(8)	2.54(8)		
	0.25(4)	0.58(6)		
Illite #35 (Fitchian)	1.05(4)	2.73(6)		*
after treatment with HNO ₃	1.20(5)	2.51(6)		*

TABLE 1. (Cont.)

Name	IS (mm/sec)	QS (mm/sec)	Magnetic Hyperfine Field (kOe)	Ref.
Illite (Coal)	0.3 - 0.4	0.4 - 0.5	≈ 0	*
	1.1 - 1.2	2.6 - 2.8	15	
SULFATES:				
FeSO ₄				
Szomolnokite (FeSO ₄ ·H ₂ O)	1.28(2)	2.90(2)	185 (4.2K)	*
Rozenite (FeSO ₄ ·4H ₂ O)	1.18(2)	2.69(2)	359 (4.2K)	(9)
Melanterite (FeSO ₄ ·7H ₂ O)	1.32(4)	3.17(4)		*(26)
Coquimbite	1.31	3.20		(26)
Jarosites	0.39(3)	0.60(5)	550 (4.2K)	*(27)
	0.43(2)	1.1 - 1.2	470 - 480 (4.2K)	*(28)
CARBONATES:				
Siderite (FeCO ₃)	1.24(2)	1.87(10)	184 (4.2K)	(18)

(*) This work

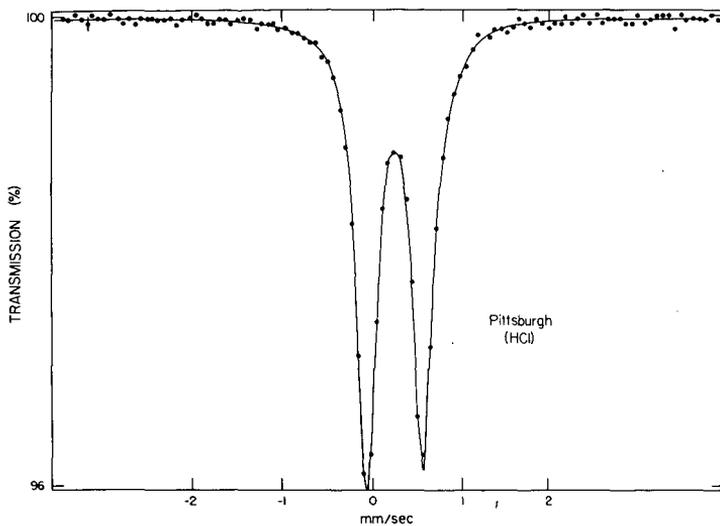


FIGURE 1. Moessbauer spectrum of a Pittsburgh coal (RT) after treatment with HCl.

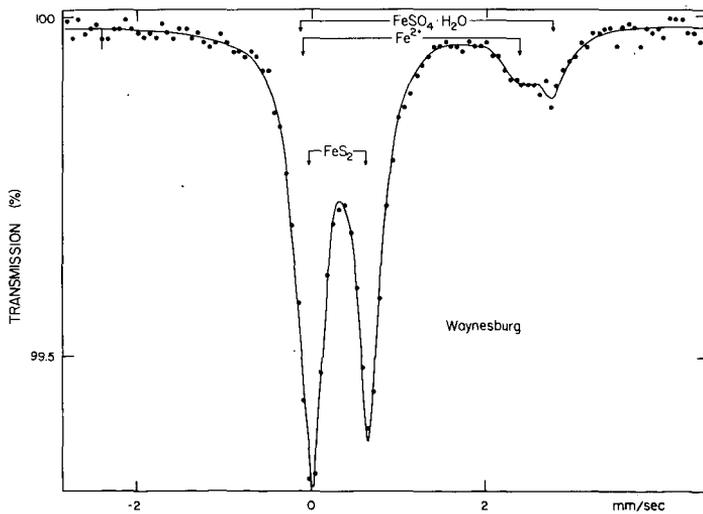


FIGURE 2. Moessbauer spectrum of a Waynesburg coal

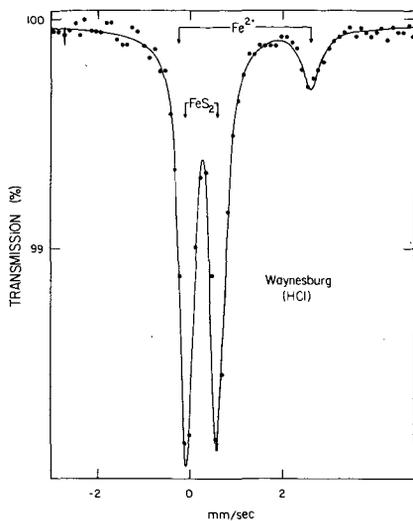


FIGURE 3. Waynesburg coal after treatment with HCl (RT).

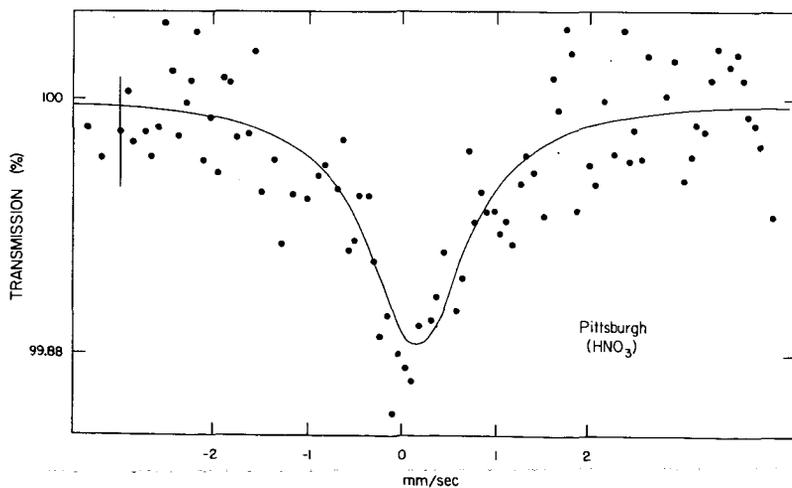


FIGURE 4. Pittsburgh coal (Fig. 1) after treatment with HNO₃

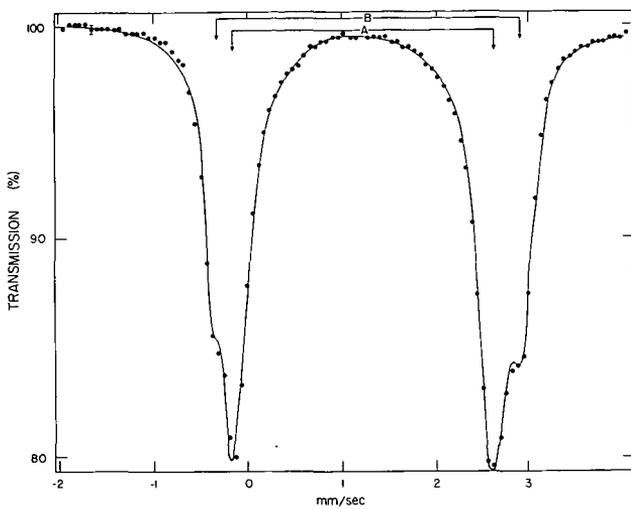


FIGURE 5. Moessbauer spectrum of szomolnokite and rozenite (RT).

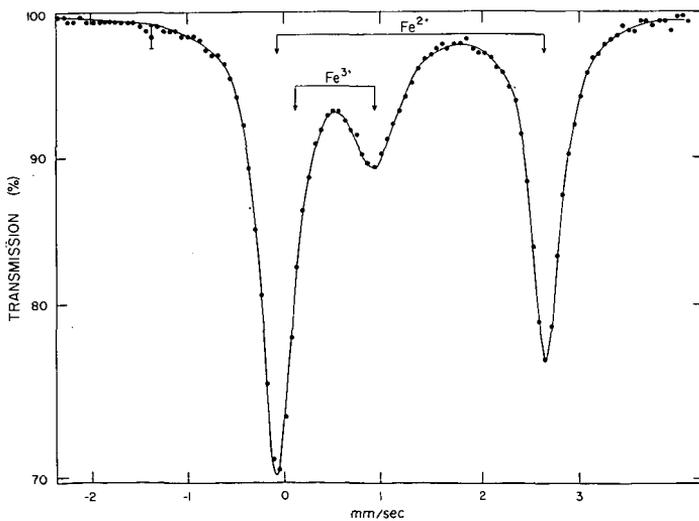


FIGURE 6. Moessbauer spectrum after LTA.