MÖSSBAUER SPECTROSCOPY OF IRON IN COAL AND COAL HYDROGENATION PRODUCTS

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ABSTRACT

The chemical states of iron in a Kentucky coal and in the products of its hydrogenation were determined by Mössbauer spectroscopy. The iron in the coal was present chiefly as pyrite, FeS_2. There was, however, evidence for some non-pyritic iron, most likely present as szomolnokite ($FeSO_4.H_2O$). The products from hydrogenation of this coal by the SYNTHOIL process at 723 K and 28 MPa contained all the iron as FeS_x where x = 1.0 to 1.14. There was no evidence for unreduced FeS_2 or $FeSO_4$. There was also no evidence for elemental iron. At the experimental conditions for hydrogenation of coal in this work, the reactor gas contained 0.32 percent H_2S. Evidently, FeS_x is not reduced to elemental iron in the presence of this concentration of H_2S in the reducing gas.

INTRODUCTION

Iron is a major constituent of the mineral matter in many U. S. Coals (1). The metal occurs principally as iron pyrite, FeS_2, in coal although small quantities of the element may be present as sulfate, oxide, carbonate or silicate (2, 3). In several Australian brown coals, significant quantities of iron occur as salts of carboxylic acids (4, 5, 6). An investigation of iron in coal by Mössbauer spectroscopy was first reported by Lefelhocz *et al*. (7). From an examination of seven U. S. coals ranging in rank from lignite to anthracite, they concluded that, in some coals, iron occurs exclusively as FeS_2, and non-pyrite iron, when present, occurs as Fe(II) in a high-spin configuration.

The purpose of the present investigation was to determine, by Mössbauer spectroscopy, the iron compounds in a coal utilized in the SYNTHOIL process and in the process products. In this process, a feed paste consisting of pulverized coal in recycle oil is reacted with hydrogen at 723K (450°C) and 14-28 MPa (2000-4000 psi) in a turbulent-flow reactor packed with pellets of $Co\text{-}Mo/SiO_2\text{-}Al_2O_3$ catalyst. The product stream is cooled and the gross liquid product, after separation from gases, is centrifuged to remove the unreacted solids. The centrifuged liquid product is a low-sulfur, low-ash fuel oil a portion of which is used as recycle oil to prepare more feed paste for continuous process operation (8, 9).

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EXPERIMENTAL

Samples of feed coal, feed paste, gross liquid product, centrifuged liquid product and centrifuged residue were drawn from a 1/2 ton per day SYNTHOIL plant currently in operation at the Pittsburgh Energy Research Center. The basics of the plant and the sampling points are shown in figure 1. A detailed description of the procedure and precautions required for obtaining representative samples has been published by Schultz et al. (10). The origin and analysis of the coal are given in table 1. The hydrogenation was conducted at 723K and 28MPa.

Samples were placed in circular plastic containers, 25 mm in diameter and 3 mm deep, for Mössbauer analysis. The containers were covered with plastic discs and mounted horizontally in the spectrometer so that any settling of the solids from the liquid samples was uniform with respect to the gamma ray beam. The source was ^{57}Co diffused in Cr. The Mössbauer spectrometer used was of conventional design (Nuclear Science Instruments, Inc.*) and the spectra were obtained by transmission. Iron foil was used for velocity calibration and also provided the reference for isomer shifts. All spectra were recorded at room temperature (∿ 300K).

RESULT AND DISCUSSION

The weights of samples, the results of chemical analyses for iron in each of them and the spectrometer run times are given in table 2. Isomer shifts, quadrupole splittings, ΔS's and approximate strengths of the internal magnetic fields are given in table 3. The literature values of the Mössbauer parameters for a number of pertinent iron compounds are presented in table 4.

The Mössbauer spectrum of the feed coal showed two strong peaks with an isomer shift of 0.32 mms^{-1} and a quadrupole splitting of 0.64 mms^{-1}. These values agree well with the isomer shift and quadrupole splitting values reported in literature for pyrite and marcasite, two naturally occurring minerals of composition FeS_2 (7, 13). The Mössbauer parameters for the two minerals are so similar that their spectra cannot be resolved if both are present. Although Mössbauer analysis is unable to distinguish pyrite from marcasite, petrographic and X-ray diffraction studies have shown that FeS_2 in coals is generally pyrite (20, 21). Specifically, the FeS_2 in the present coal has been shown by Ruch, et al. to be iron pyrite (22).

The spectrum of the coal also showed a single, very weak peak with a velocity of 2.83 mms^{-1} relative to the source. This, no doubt, corresponds to one peak of the doublet for non-pyrite iron reported by Lefelhocz et al. in several coals (7). They determined an isomer shift of about 1.1 mms^{-1} (recalculated with reference to iron) and a quadrupole splitting of about 2.6 mms^{-1}. Unfortunately, the second peak for non-pyrite iron in our spectrum is completely obscured by one of the strong pyrite peaks, probably that with a velocity of 0.22 mms^{-1} relative to the source. Lefelhocz et al. concluded that the non-pyrite iron may be organic iron or inorganic iron as a silicate (7). Montano (27), however, observing similar

*Use of brand name facilitates understanding and does not necessarily imply endorsement by the U. S. Department of Energy.

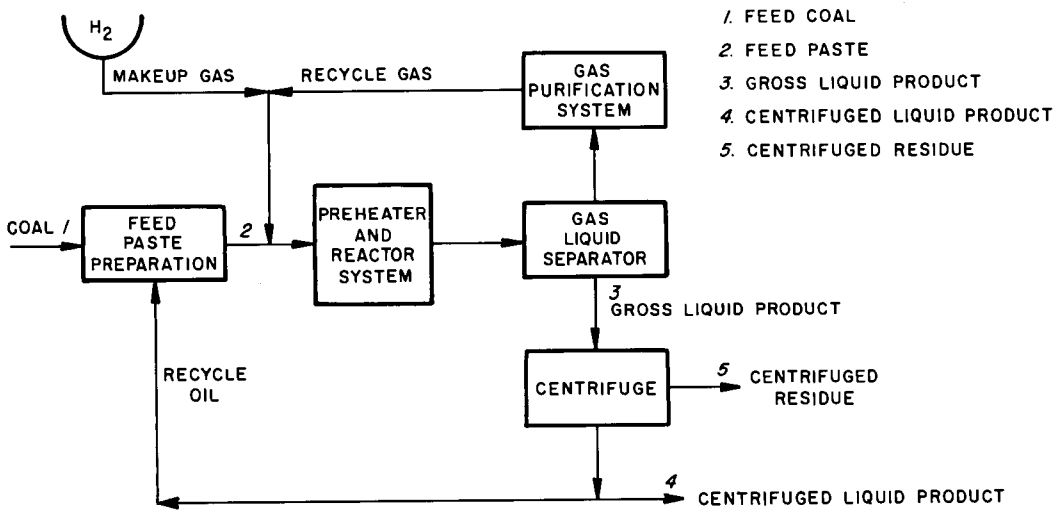

Figure 1 - Sampling points in the SYNTHOIL ½ ton per day unit

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Table 1. - Analysis of the as-received feed coal[1]

Proximate analysis, (wt. pct.)	
Moisture	6.1
Volatile matter	36.3
Fixed carbon	42.1
Ash	15.5
Ultimate analysis, (wt. pct.)	
Hydrogen	4.9
Carbon	60.3
Nitrogen	1.2
Oxygen (By difference)	12.8
Ash	15.5
Sulfur	5.3
as sulfate	0.58
as pyrite	2.69
as organic	2.03
Rank: hvBb	

[1]A blend from Kentucky seams No. 9, 11, 12 and 13 which are mined together; Homestead mine, Western Kentucky. The coal was pulverized to a fineness of 70 percent through 200 mesh, U. S. Standard Sieve, and 100 percent through 100 mesh.

Table 2. - Samples analyzed by Mossbauer spectrometry

Material	Weight (g)	Iron content (wt. pct.)	Spectrometer run time (hr.)
Feed coal	1.24	3.58	113
Feed paste	2.60	1.47	160
Gross liquid product	2.40	1.84	139
Centrifuged liquid product	2.16	0.55	189
Centrifuged residue	3.20	10.1	∿100

Table 3. Results of Mössbauer Analysis

Material	Isomer shift[1/] (mms^{-1})	Quadrupole splitting (mms^{-1})	ΔS[2/] (mms^{-1})	Approximate internal magnetic field[3/] H_i, (kOe)
Feed coal	0.32[4/]	0.64	--	--
Feed paste	0.32[5/]	0.63	--	--
	0.59	--	0.55	280
Gross liquid product[6/]	0.70, 0.74	--	0.00, 0.15	310, 270
Centrifuged liquid product	0.72	--	0.28	280
Centrifuged residue[6/]	0.69, 0.72	--	0.05, 0.69	310, 270

1/ Relative to iron
2/ Calculated from the 4 outer peaks of a 6-peak pattern as follows: $\Delta S = (S_6 - S_5) - (S_2 - S_1)$.
3/ $Hi = (S_6 - S_1)*31$ where S_1 and S_6 are the outermost peaks of a six-peak pattern.
4/ An additional low intensity (5%) peak was observed at a velocity of 2.83 mms^{-1} with respect to the source; see text for discussion.
5/ Calculated from the predominant doublet of the 6-peak spectrum.
6/ Discussion of multiple values given in text.

Table 4. Literature Values of Mössbauer Parameters for Some Pertinent Fe Compounds.

Compound	Isomer shift[1/] δ (mms^{-1})	Quadrupole splitting (mms^{-1})	ΔS (mms^{-1})	Internal Magnetic field H_i (kO_e)	Reference[2/]
FeS (troilite)	0.77	0.28		310	(11)
$FeS_{1.14}$ (pyrrhotite)	0.64		0.16	307	(11)
	0.69		0.31	225	
$FeS_{1.00}$	0.71		-0.32	308	(12)
$FeS_{1.05}$	0.82		-0.40	276	(12)
$FeS_{1.07}$	0.77		-0.52	275	(12)
FeS_2 (pyrite)	0.28	0.60			(7)
	0.29	0.61			(13)
FeS_2 (marcasite)	0.25	0.50			(7)
	0.23	0.51			(13)
$FeSO_4.H_2O$ (szomolnokite)	1.2	2.62			(26)
Fe (metal)	0.00		0.00	330	(14)
αFe_2O_3	0.43	0.17		515	(17)
Fe_3O_4	0.30			492	(16)
	0.63			455	
FeO	1.08	0.55			(18)
αFeOOH	0.35		0.6	384	(15)
$FeSO_4$	1.25	2.94			(17)
$FeSO_4 \cdot 4H_2O$	1.32	3.17			(18)
$FeSO_4 \cdot 7H_2O$	1.31	3.20			(18)
$Fe_2(SO_4)_3 \times H_2O$	0.45	0.28			(19)
$FeCO_3$	1.25	1.80			(16)
$Fe(HCO_2)_2$ (formate)		1.86			(16)

Table 4. Literature Values of Mössbauer Parameters for Some Pertinent Fe Compounds (Continued).

Compound	Isomer shift[1/] δ (mms^{-1})	Quadrupole splitting (mms^{-1})	ΔS (mms^{-1})	Internal Magnetic field H_i (kO_e)	Reference[2/]
$Fe(C_2H_3O_2)_2$ (acetate)	0.42	0.50			(14)
$Fe_2(CO)_9$	0.08	0.37			(17)
$Fe_3(CO)_{12}$ (-85°C)	0.10 0.15	1.09			(19)

1/ Relative to iron. The following correction values were used: Stainless steel to iron -0.90 mms^{-1}, sodium nitroprusside to iron -0.26 mms^{-1}.

2/ The numbers refer to the bibliography at the end of the text.

spectra concluded that the non-pyrite fraction is anhydrous iron (II) sulfate $FeSO_4$. But the literature values (28) he quotes for isomer shift and quadropole splitting are inaccurate, as the experiment was probably inadvertently performed on $FeSO_4.H_2O$. More recent work, using carefully prepared materials, gave values for $FeSO_4$ and $FeSO_4.H_2O$ as shown in table 4. Assuming that, in our spectrum, the hidden peak of the high spin doublet is directly under the low velocity peak of the pyrite spectrum our values for the isomer shift and quadropole splitting would be $\sim$1.3 mms^{-1} and $\sim$2.6 mms^{-1}, respectively, which are in excellent agreement with $FeSO_4.H_2O$ as are Montana's and Lefelhocz's.

The spectrum of the feed paste was a composite of the spectra of its components, namely the feed coal and the recycle oil. The latter, as explained above, is a portion of the centrifuged liquid product from a previous batch. For convenience, therefore, the spectrum of the feed paste will be discussed after discussing the spectrum of the centrifuged liquid product.

The spectra of the gross liquid product, the centrifuged liquid product and the centrifuged residue were similar and may be discussed together. Each of the spectra showed a six-peak pattern with isomer shifts in the range of 0.69 to 0.74 mms^{-1}, ΔS's in the range of 0.00 to 0.69 mms^{-1} and the strengths of the internal magnetic fields in the range of 310 to 270 kOe. The outermost peaks in the spectra of the gross liquid product and the centrifuged residue showed partial resolution into two subpeaks. The values of the isomer shifts, the ΔS's and the strengths of the internal magnetic fields given in table 3 for these two materials are the values obtained by using the positions of the outer and inner subpeaks respectively to calculate the parameters. Hafner and Klavius observed similar fine structures in the Mössbauer spectra of two pyrrhotites and used a comparable technique for data reduction (11). A comparison of the Mössbauer parameters in tables 3 and 4 shows that the gross liquid product, the centrifuged liquid product and the centrifuged residue contain FeS_x where x = 1.0 to 1.14.

In agreement with our findings, Ruch et al. found pyrrhotite in the centrifuged residue by X-ray diffraction analysis of aliquots drawn from the samples used in this work (22).

The spectrum of the feed paste had six peaks: two strong peaks corresponding to the pyrite peaks in the spectrum of the feed coal, and four weak peaks, two on each side of the strong doublet. The four weak peaks correspond to the outer four peaks in the size-peak spectrum of the centrifuged liquid product. The two middle peaks of the centrifuged liquid product are obscured by the two strong peaks of the pyrite. Clearly the spectrum of the feed paste is a composite of the spectra of coal and centrifuged liquid product, the components of the feed paste.

None of the spectra obtained in this work showed any absorptions other than those discussed above. We estimate the precision of our measurements is such that other compounds (for example, those shown in taboe 4 starting with iron) would have been detected had they been present in significant

amounts. Elemental iron, Fe_2O_3, Fe_3O_4, or α-FeOOH would have been detectable in any of the materials analyzed if present in quantities as small as 5% of the total iron present. In the case of the feed coal, the detection limits for iron and above oxides would have been even lower and, in addition, the presence of many of the othercompounds in the lower portion of Table 4 would have also been detectable at the 5% level. Possible exceptions are the iron (III) sulfates, iron (III) acetate and $Fe_2(CO)_9$ with detectability limits of the order of 10-20%.

Although the feed coal does contain a small amount of $FeSO_4.H_2O$, the quantity of it is too small to account for all the sulfate the coal is known to contain by conventional analysis (see Table 1). Some of the sulfate is presumably combined with Ca or some other cation.

The spectra of the gross liquid product, the centrifuged liquid product and the centrifuged residue showed no evidence for elemental iron. The absence of iron is significant since Gallo has reported the reduction of FeS_2 to elemental iron by the following successive reactions (23):

$$FeS_2 + H_2 \xrightarrow{500K} Fe_2S_3 + H_2S \qquad (i)$$

$$Fe_2S_3 + H_2 \xrightarrow{550K} FeS + H_2S \qquad (ii)$$

$$FeS + H_2 \underset{}{\overset{640K}{\rightleftharpoons}} Fe + H_2S \qquad (iii)$$

These results were obtained with gavorranto, a natural pyrite, containing 97.12 percent FeS_2. It should be noted that reaction (iii) is reversible and, therefore, the reduction of FeS to Fe will not be feasible if the partial pressure of H_2S in the reducing gas is above some critical value. Rosenquist has measured K_p for reaction (iii) at 723K (24). At 28 MPa hydrogen pressure, the equilibrium H_2S pressure is 0.008 percent of the hydrogen pressure. In the present study, the reactor gas contained approximately 0.32 percent H_2S and, evidently, FeS_2 was not reduced to iron in the presence of this concentration of H_2S.

In the qualitative agreement with our results, J. T. Richardson has reported that FeS_2 is reduced to Fe_7S_8 ($FeS_{1.14}$) during coal hydrogenation (25). By theromagnetic analysis of a char from a coal liquefaction plant he concluded that the iron in char was present as a mixture of Fe_7S_8 and FeS_2. The exact composition of the mixture varied with the process conditions.

CONCLUSIONS

Mössbauer analysis of a Kentucky coal showed that iron in the coal was present mainly as FeS_2. There was some non-pyritic iron, most likely present as szomolnokite ($FeSO_4 \cdot H_2O$). Products from hydrogenation of the coal at 723K and 28 MPa contained FeS_x where x = 1.0 to 1.14. There was no evidence of elemental iron in the products.

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