

Iron content of pyrrhotites produced in continuous liquefaction units

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Abstract

The pyrrhotites formed during the liquefaction of coal in continuous reactors (which process 10 lb/day and 400 lb/day of coal) have been studied by X-ray diffraction. No systematic relationship was observed between the atomic percentage of iron in the pyrrhotite and the quality of the coal liquid, as measured by viscosity, benzene solubles, or distillate yield. There is some indication that the total amount of iron in the coal may affect the distillate yield. Pyrrhotites produced under certain reactor conditions show highly asymmetric peaks, attributed to stacking disorder. No previous studies have reported stacking disorder detectable by X-ray diffraction.

Introduction

Early German work on the production of liquid fuels from coal showed that the presence of iron had beneficial effects on the process, but the reasons for the improvement were never elucidated. The world energy situation has caused renewed interest in the direct liquefaction of coal and therefore in understanding how iron, and especially pyrite, which occurs abundantly in many coals, may be helpful in this process. During liquefaction, pyrite (FeS_2) is converted to pyrrhotite (Fe_{1-x}S , where $x = 0$ to 0.12), however, it is not known if pyrite, the transformation to pyrrhotite, or a specific pyrrhotite itself is the beneficial agent. The purpose of this work was to determine if the atomic percent iron in pyrrhotites from liquefaction residues showed any systematic relationship to the percentage of coal converted to liquids or to the viscosity of the product. In the course of the study, it was found that the pyrrhotites in the residues were not easily characterized but were mixtures of several iron compositions and/or showed stacking disorder. Since no previous X-ray diffraction studies have reported stacking disorder in pyrrhotites, mineralogists as well as chemists studying coal liquefaction may be interested in these results.

Earlier studies, described below, of pyrrhotites and pyrite in liquefaction products have, with only one exception, all been carried out on samples from autoclaves. This work reports data mainly from

continuous units processing 10 lb/day and 400 lb/day of coal and run at conditions more similar to those that would be used in commercial size liquefaction units. Mukherjee *et al.* (1970) concluded from X-ray diffraction and chemical studies that pyrrhotites with 47.6–49.0 atomic percent iron had the maximum catalytic activity. Yarzab *et al.* (1980) showed that a statistical correlation existed between conversion of medium-rank, high-sulfur coals to liquids and the total sulfur in the coal; Appell *et al.* (1979) found that coals with the highest pyrite content had the highest reactivity and product quality. From Mössbauer studies of autoclave samples, Montano and Granoff (1980) found that the iron content in a series of pyrrhotites, ranging from 47.5 to 48.2 atomic percent, was inversely proportional to the benzene soluble fraction, which varied between 64 and 78%. Keisch *et al.* (1977), the first workers to publish data on a pyrrhotite from a continuous unit, using Mössbauer spectroscopy found that it had a composition between $\text{Fe}_{0.88}\text{S}$ and FeS . Since X-ray diffraction is a much older technique and a more direct method for measuring the atomic percent Fe in pyrrhotites, it has been more widely used by geologists and mineralogists studying the origin of ore bodies. Arnold and Reichen (1962) were the first to prepare a curve relating the iron content of pyrrhotites to the position of the (102) peak. Yund and Hall (1969), after compiling and evaluating the results of all published studies, determined a slightly different expression.

Experimental

The powders used in this work were obtained from coal liquids by extraction with pyridine, methylene chloride, or benzene to remove the organic soluble fractions. X-ray diffraction measurements were carried out on samples held in a glass holder with a cavity $16 \times 18 \times 2$ mm, using a Rigaku¹ horizontal diffractometer equipped with a copper tube and operated at 40 kV and 35 mA. The slit system of the goniometer consisted of a one-degree divergent slit and 0.3-mm receiving slit, and the detector was a scintillation counter equipped with pulse height discrimination mounted behind a graphite receiving monochromator.

Analysis of the pyrrhotites consisted of two parts: first, a qualitative analysis to identify the compounds present and ensure that only pyrrhotite was contributing to the intensity in the region of the pyrrhotite (102) peak; and second, accurate measurement of the peak position. The qualitative analyses were carried out on step-scans made over the range 2° to 60° two-theta using 0.1° steps and five-second counts. For measurement of peak positions, a 0.02° step and 5- to 20-second counting times were employed, depending on the peak intensities. From this latter measurement, the atomic percent Fe was estimated using the calibration curve of Arnold and Reichen (1962). The quartz (101) peak at 26.64° two-theta was used as an internal standard. (Although some of the pyrrhotites may have super-cells, for convenience the reflection used to estimate the atomic percent iron is always referred to as (102).) Peak position was estimated to the nearest 0.01° , and iron content to 0.1 atomic percent. Quartz was not added to the residues, since they retain the quartz originally present in the coal. Preliminary work on synthetic mixtures of quartz added to residues showed that identical corrections were obtained from the quartz (101), (110), and (200) reflections. Since the latter two peaks usually were too weak to measure, only the (101) was used.

Crystallite size was estimated using the relationship for three-dimensional crystallites described by Klug and Alexander (1974):

$$D = \frac{0.9 \lambda 57.3}{B \cos \theta}$$

where, D = crystallite size, λ = wave length, B =

peak width-at-half-maximum, θ = Bragg angle. The factor 57.3 is used to convert degrees to radian measure.

A correction for instrumental broadening was made by subtracting the width-at-half-maximum of lines measured from a quartz sample having a crystal size of 5–25 μm . The correction varied between 0.2° and 0.3° two-theta.

Results

The mineral matter remaining after the oils and soluble organic portions have been removed from coal-derived liquids reflects the starting composition of the coal and generally consists of quartz, kaolinite, illite, anhydrite (CaSO_4), other clays, and pyrrhotite. Most of the calcite and gypsum originally in the coal is usually transformed to anhydrite, although calcite is occasionally present. Pyrite and troilite occur very rarely. Before presenting the relationship between conversion and composition of the pyrrhotites produced during liquefaction, differences in the diffraction patterns of these pyrrhotites will be described, which will help in understanding the following results.

Peak Shapes

Figures 1–3, smoothed step-scans that have been redrawn, contain examples of the diffraction peak shapes that have been observed in the pyrrhotites from liquefaction residues. The most symmetrical peaks are from samples produced in autoclaves or continuous reactors at 450°C . In Figure 1 are shown three diffraction peaks from Robena pyrite heated in an autoclave at 425°C under 2000 psi hydrogen. There is a slight amount of asymmetry on the high angle side of the (101) and (102) peaks, Figure 1B and 1C, but none for the (100), Figure 1A. For comparison, the smoothed, redrawn step-scan of the (200) peak of quartz is shown in Figure 1D, indicating that from 40° to 44° two-theta, the instrumental broadening is less than that shown in Figure 1C.

In Figure 2 are shown pyrrhotite peaks from a vacuum bottom sample produced in the Hydrocarbon Research Inc. (HRI) H-Coal process. The coal-derived liquid which contained this pyrrhotite was produced at 450°C and 2000 psi hydrogen in an ebullating bed reactor, and then later heated in a vacuum still to 450°C . Figures 2A, the (100), and 2B, the (101), are very similar to 1A and 1B, but 2C has a much greater width-at-half maximum. This increase is not due to a smaller crystallite size, since

¹ Use of brand names facilitates understanding and does not necessarily imply endorsement by the U. S. Department of Energy.

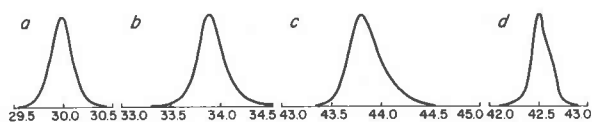


Fig. 1. Smoothed, redrawn X-ray step-scans of pyrrhotites produced after heating Robena pyrite in an autoclave at 2000 psi hydrogen and 425°C: a. (100) peak, b. (101) peak, c. (102) peak, d. (200) peak of quartz from pure quartz sample.

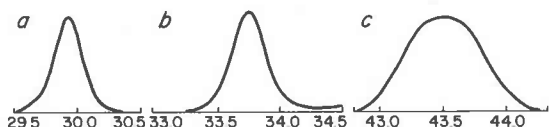


Fig. 2. Smoothed, redrawn X-ray step-scans of pyrrhotite from vacuum bottom sample produced in Hydrocarbon Research Inc. (HRI) H-Coal process: a. (100) peak, b. (101) peak, c. (102) peak.

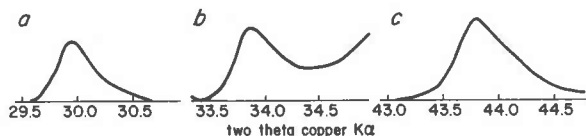


Fig. 3. Smoothed, redrawn X-ray step-scans of pyrrhotite from Homestead, Kentucky coal produced in 10 lb/day reactor at 375°C under 2000 psi hydrogen, and a gas flow rate of 103 standard cubic feet (scf) hydrogen/lb slurry: a. (100) peak, b. (101) peak, c. (102) peak.

only one reflection is broadened appreciably. The width of this (102) reflection indicates that the sample is a mixture of either two distinct iron compositions or a series of continuously varying compositions. Figure 3 contains peaks from a pyrrhotite produced in a 10-lb/day continuous unit at 375°C under hydrogen. All three peaks are highly asymmetric, with steep slopes on the low-angle side but falling off gradually on the high-angle side. Mukherjee *et al.* (1972) also found asymmetric peaks, which they attributed to mixtures of different pyrrhotite compositions. The exact cause of the asymmetry of the peaks shown in Figure 3 is not known, since several effects might produce it:

(1) If monoclinic pyrrhotite were admixed with the hexagonal pyrrhotite, asymmetric broadening of the (101) and (102) reflections would be expected, since the monoclinic form has additional peaks close to, but on the high angle side of, the above hexagonal peaks. However, this would not explain the asymmetry of the (100) peak in Figure 3 and the (220) (not shown) reflections.

(2) Mixtures of hexagonal crystallites with several compositions could also produce broadening.

Figure 2 shows peaks from a mixture of hexagonal troilite and a hexagonal pyrrhotite with 47.7 atomic percent iron (measured by X-ray diffraction and Mössbauer spectroscopy), yet the (100) and (101) do not show the same shapes shown in Figure 3. Therefore, if the sample shown in this figure contains a mixture of pyrrhotites, more than two distinct compositions or a continuous distribution over a range of compositions would be required.

(3) A third possibility is the presence of stacking disorder. If crystallites have a random-layer lattice (turbostratic) stacking, the peaks would be expected to show the observed asymmetry, but only two-dimensional (hk) reflections should be present. Since (hkl) reflections are present, the most likely possibility is that some type of stacking disorder exists in the crystallites, which may be partially, but cannot be completely, turbostratic.² In samples such as shown in Figure 1A, the relatively small amounts of asymmetry could be due either to small amounts of a second pyrrhotite composition or to stacking disorder.

If a peak is truly three dimensional, the correct d spacing can be measured from its peak position, but if it is turbostratic or two-dimensional, the measured spacing is slightly smaller than the true value. The amount of the shift increases from about 0.04° two-theta at a crystallite size of 800Å to 0.08° at 300Å. For each 0.01° shift, the iron estimate decreases by about 0.1 atomic percent iron.

Iron compositions from peaks that show only a slight asymmetry (such as Figure 1C) can be determined more accurately than those with high asymmetry (Figure 3C). If the asymmetry is due to a mixture of two different compositions, the effect of the several components can be taken into account by using the center of gravity of the peak or a curve-resolving technique. However, if the asymmetry is due to stacking disorder, a small correction for displacement would be needed for a narrow peak such as Figure 1C and a larger one for a broader peak such as 3C. The corrections are difficult because a good model of the structure is needed before they can be made. Measurements from all highly asymmetric peaks that result from stacking disorder give results that have about the same precision, but their true values are more highly

² Note added in proof: electron diffraction patterns of pyrrhotites from the same sample as used for Figure 3 show the presence of layer lines along the c axis which consist of streaks and diffuse spots, confirming the presence of stacking disorder.

Table 1. Sulfur forms in Homestead, Ireland Mine, and Kentucky #11 Coals

Coal	Sulfur forms, weight % (moisture-free basis)		
	Pyritic	Organic	Sulfate
Homestead, KY	2.88	2.13	0.67
Ireland Mine, WV	1.85	1.54	0.14
Kentucky #11	4.68	2.32	0.38
Kentucky #11 (Cleaned)	1.13	2.35	0.08

underestimated than the sharper asymmetric peaks. Since the actual cause of the asymmetric peaks is not known for these samples, the *d* spacing was estimated from the measured position of the upper portion of the peaks.

Atomic percent iron

The results presented here are from pyrrhotites produced in 10-lb/day and 40-lb/day continuous units. In none of the three series of experiments was there any trend indicating that improvement in product quality was related to the iron content of the pyrrhotites. (In Table 1 are listed the amounts of the pyritic, organic, and sulfate sulfur in the three coals used in this work.) Products from a 10-lb/day reactor run at high gas flow rates showed the expected increase in benzene solubles from 51 to 83% (see Table 2) as the temperature was increased from 375°C to 450°C; yet the atomic percent iron in the pyrrhotites remained constant at 47.5. Runs were also made at much lower gas flow rates, 15–20 standard cubic feet (scf) hydrogen per lb of slurry, but these results were not reproducible and are not shown here. The shapes of the (102) pyrrhotite peaks from the high gas flow samples are shown in Figure 4. The pyrrhotites produced at higher temperatures are more symmetric, which means they have less stacking disorder; they also have narrower peaks and therefore larger crystallites or more uniform stoichiometries.

Table 2. Apparent crystallite size of pyrrhotites produced in a 10-lb/day continuous unit between 375 and 450°C at high gas flow rate, 120 standard cubic feet (scf) hydrogen per lb slurry at 2000 psi. All pyrrhotites contained 47.5 atomic percent Fe. (Homestead, Kentucky Coal).

Reactor temp. °C	Crystallite size \bar{R}			% Benzene soluble
	(100)	(101)	(102)	
450	820	ND	390	83
425	680	ND	300	79
400	590	410	300	73
375	460	310	280	51

ND = Not Determined.

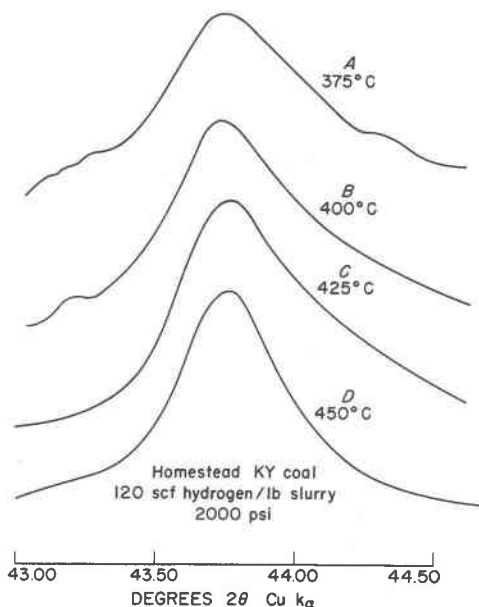


Fig. 4. (102) peak of pyrrhotites from 10 lb/day continuous reactor produced at high gas flow rates.

For this series of samples, crystallite size measurements estimated from the (100), (101), and (102) reflections for each pyrrhotite vary by a factor of two as shown in Table 2. In all samples, the apparent crystallite size was largest when estimated from the (100) peak, which gives the size in the plane of the S and Fe atoms. The (101) and (102) planes are inclined to this plane and are more affected by any stacking disorder or pyrrhotite inhomogeneity that may be present; thus the crystallite size estimated from these two peaks is less reliable. Benzene solubles appear to be related to crystallite size and less disordered crystals, however it is more likely that all three are directly related to reactor temperature.

Until checked by electron microscopy, these numbers should be used to indicate relative differences between the samples rather than absolute values.

Samples from two series of experiments using a 400-lb/day unit showed no correlations between iron content of pyrrhotites and product quality. In the first series, Ireland Mine Coal from West Virginia was treated at 455°C at pressures of 4000, 3000, and 2000 psi (Mazzocco, 1978, unpublished). The pyrrhotites in these residues had essentially the same composition, between 47.6 and 47.9 atomic percent Fe in 12 samples and 48.1% in two of them. The viscosity was slightly higher for the lower

Table 3. Relationship of atomic percent iron and crystallite size of pyrrhotites to distillate and Solvent Refined Coal (SRC) yield from raw, cleaned, and cleaned Kentucky Coal with two levels of added pyrite.

Sample	Weight % Fe in slurry	Atomic % Fe in pyrrhotite	Crystallite size \bar{R}			Yield	
			(100)	(101)	(102)	% Dist.	% SRC
Cleaned KY	0.54	47.6	390	500	340	36	33
Cleaned KY + pyrite	0.84	47.8	750	>1000	540	41	30
Cleaned KY + pyrite	1.67	47.8	>1000	>1000	610	42	28
Raw KY	1.57	47.8	>1000	>1000	570	39	30

SRC - Benzene soluble material not distillable at 454°C; Distillate C₅-454°C.

pressure products; yet the conversion to distillate and the quality of the product were the same for the three pressures. In a second series, samples of Kentucky #11 raw, cleaned, and, in two cases, cleaned with added pyrite were treated at 450°C and 2200 psi Mazzocco *et al.* (1981). The feed slurries of these runs, which contained 1.57, 0.54, 0.84, and 1.67% Fe, produced liquids with viscosities of 22, 156, 84, and 32 Saybolt Seconds Furol (SSF), respectively, at 82.2°C essentially inversely related to the iron content. Although the amount of pyrrhotite varied, the iron content of the pyrrhotites was very similar, 47.6 atomic percent Fe for the cleaned coal without added pyrite and 47.8 percent Fe for the other three samples. Table 2 relates the iron content and crystallite size of the pyrrhotites to the distillate and Solvent Refined Coal (SRC) yields, and total iron in slurry for these samples. Although the cleaned Kentucky coal produced the product with the lowest distillate yield and the pyrrhotite from this run had the smallest crystallite size, there is insufficient data to determine if the two are truly related. Differences in crystallite size estimates measured from the three reflections for each sample are probably due to the presence of stacking disorder and/or pyrrhotite inhomogeneity in these samples.

Summary

From measurement of the (102) peak position by X-ray diffraction, the amount of iron in several series of pyrrhotites was estimated. No systematic relationship between viscosity, benzene solubles or distillate yield of coal-derived liquids and the iron content of their pyrrhotites was observed. All the samples from the 10-lb/day and 400-lb/day units contained pyrrhotite within a narrow range of compositions (47.5–48.1 atomic percent iron), and all

but two of these fell between 47.5 and 47.9. The data for the Kentucky coal indicate that the amount of iron in the coal may affect the distillate yield. X-ray diffraction measurements also indicate that some pyrrhotites produced in a continuous liquefaction unit at high gas flows and 375°C, and possibly 400°C, 425°C, and 450°C, show crystallites with stacking disorder, but the stacking disorder has probably little or no effect on product quality.

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