

IMPROVED METHODS FOR DETERMINATION OF FERROUS SULFIDES IN COAL CHARs

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INTRODUCTION

A fundamental research investigation of the behavior of mineral matter in fluidized bed gasification of coal is in progress at IGT under a program largely supported by the U.S. Department of Energy. Special attention has been focused on the gasification of high sulfur and high iron containing coals, and the mechanism of ash agglomeration which facilitates the selective removal of ash from a reactor bed without loss of unacceptable amounts of char carbon.

Sulfur occurs in coal mineral mostly as iron disulfides, mainly pyrite with some marcasite. The disulfides quickly decompose to pyrrhotites ($Fe_{(1-x)}S$) and hydrogen sulfide in the charring process with an inert atmosphere or in the absence of air (1-3). The same transformation was also observed when the coal, especially bituminous coal, is fed into the fluidized bed of a gasifier typically at about 1850°F (4). The resulting pyrrhotites may partly transform to troilite (FeS) on cooling to room temperature.

It has been noted that ferrous sulfides, especially pyrrhotite, play a variety of important roles in coal conversion processes. Their possible catalytical activity in coal liquefaction (5) and coal gasification (6,7) was reported recently. In our pilot plant studies we have occasionally found that ferrous sulfide may play an independent role in agglomeration, acting as a binding medium between shale particles in the bed when run-of-mine coal is fed (Fig.1) (4). Under some circumstances, ferrous sulfide has formed deposits in the hot cyclone, which, returns entrained char particles to the bed. In order to better understand their functions in coal conversion, an accurate quantitative method for ferrous sulfides determination is needed.

Mossbauer spectroscopy has been employed as a useful method for the semi-quantitative determinations of various iron-containing species including ferrous sulfides in coal chars and gasification residues (8,9). It's accuracy highly depends upon the complexity of the Mossbauer spectra and the concentration level of ferrous sulfides.(10) The major disadvantage of this method is that it can not detect non-iron containing sulfide species, such as calcium sulfide.

X-ray diffraction spectroscopy has also been used to analyze the mineral contents of chars and residues. But, it's utility in the analysis of non-stoichiometric ferrous sulfides is often limited to the qualitative determination, because these sulfides may or may not be present in crystalline forms and their x-ray spectra is often complicated and obscured by the spectra of other major minerals.

In the past IGT has developed a wet chemical method, involving determination of hydrogen sulfide evolved by treating a sample with 6N hydrochloric acid. Although this method was successfully employed to determine the sulfide sulfur contents of chars prepared at 1700°F and gasification residues that had been subjected to higher temperature, it was found to be unsatisfactory when applied to ferrous sulfide-rich coal chars prepared at 1400°F for use as feed for gasification. In most of cases only a fraction of sulfur from ferrous sulfide (sulfide sulfur) could be recovered as hydrogen sulfide. The calculated total sulfur of these chars from sulfide sulfur, pyritic sulfur and organic sulfur is usually 5 to 20% lower than the total sulfur determined by the Eschka method, depending on the types of ferrous sulfides present and their concentration.

In the search of a more accurate method, we have re-evaluated a number of potential existing methods and developed a few new methods for ferrous sulfides analysis. The most successful method uses a reducing agent to enhance the recovery of ferrous sulfide as hydrogen sulfide in a hydrochloric acid evolution procedure. Results from the analyses of six 1400°F coal chars using different methods are presented and discussed.

EXPERIMENTAL

Two model coal char compounds synthesized from high purity carbon plus a composite 1400°F coal char sample were prepared for the initial study of the recovery of sulfide sulfur during hydrochloric acid digestion. The first model consists of troilite and the second a natural pyrrhotite. Using an acid-evolution train, the efficiencies of hydrogen sulfide evolution were examined for these three samples at four hydrochloric acid concentrations (1,2,4 and 6 normal) with and without the addition of the reducing agent, stannous chloride. The hydrogen sulfide evolved was collected in an alkaline trap composed of 10% cadmium chloride in water and subsequently determined by an iodometric method with thiosulfate back titration. The hydrochloric acid extract was then filtered and analyzed by atomic absorption method for the HCl-soluble iron. The residue collected was examined by an x-ray diffraction spectroscopic (XRD) method for the amount of ferrous sulfide left intact.

For the composite coal char, a complete sulfur-by-types analysis was also carried out to check the sulfur mass balance. A modified method of ASTM D-2492 procedure for forms of sulfur in coal was employed to analyze the sulfate, pyritic, organic, and total sulfur. The sulfate sulfur was determined by a gravimetric method as barium sulfate. The pyritic sulfur was calculated from the concentration of pyritic iron found in the dilute nitric acid extract of the residues, which was determined by an atomic absorption method. The organic sulfur was determined by digesting the residue from the dilute nitric acid digestion with concentrated nitric acid and analyzing the resulting sulfate as barium sulfate gravimetrically. The total sulfur was determined by the Eschka method.

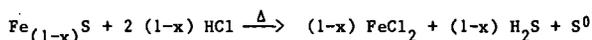
In the course of a gasification investigation, five coal chars were prepared at 1400°F in a 4-inch diameter devolatilizer purged with nitrogen from washed bituminous coals with 1/4-inch top size. The residence time of the feed coal at 1400°F was approximately 30 minutes. A -200 mesh fraction of Kentucky No. 9 coal was used to prepare the sixth coal char. All samples were ground to about 325 mesh and analyzed for their contents of sulfide sulfur, residual sulfur, 6N HCl-soluble iron and total iron. Both the residual sulfur and total sulfur were determined by the Eschka method. The 1N, 1.6N (5%) and 2N HCl-soluble iron were also determined separately and used to calculate the sulfide sulfur content.

A Phillips vertical goniometer and a copper x-ray source were employed for the x-ray diffraction analysis of all coal char samples. The total concentration of iron sulfides was determined using potassium chloride as an internal standard. The diffraction peak at a 2 theta angle of about 43.3 degree was used for the quantitation. The same peak was also profile-fitted in an attempt to deconvolute the complex peaks, measuring their precise d-spacings at the 102 crystal plane and consequently estimating the iron content of various hexagonal pyrrhotites (11).

A Ranger Scientific MS-900 Mossbauer spectrometer with a 5 mCi Co-57 source was used to acquire Mossbauer spectra of all char samples. The relative percentage of sulfide iron in total iron as ferrous sulfides was measured by a spectral subtraction technique. The concentration of sulfide sulfur in each coal char was calculated by multiplying the total iron percentage of coal char by the relative percentage of sulfide iron and a S/Fe conversion factor of 0.574.

RESULTS AND DISCUSSION

Figure 2 represent the effects of hydrochloric acid and the reducing agent, stannous chloride, on the recovery of sulfide sulfur by the described evolution method. By comparison of the mole ratios of sulfide sulfur to HCl-soluble iron, we found that the troilite (FeS) could be easily decomposed to hydrogen sulfide and determined quantitatively. However, pyrrhotite was not completely converted to hydrogen sulfide even though all ferrous sulfides would be completely decomposed in hydrochloric acid with a concentration higher than 2 normal as indicated by XRD analysis of the digested residue, unless a suitable reducing agent, such as stannous chloride, was present. We believe that pyrrhotite is partially degraded to elemental sulfur in the hydrochloric acid medium as the following equation. The stannous chloride and possible other reducing agents may inhibit this competitive degradation mechanism, converting all sulfide sulfur to hydrogen sulfide.



The results in Table 1 indicate that a good sulfur mass balance was obtained when 10% or more stannous chloride was used. The insignificant difference between the calculated total sulfur of 2.02% and 2.05% while using 4N and 6N HCl respectively suggests that either concentration is adequate for effective hydrogen sulfide evolution. The variation of the mole ratios of sulfide sulfur to HCl soluble iron in the same table further confirms that stannous chloride definitely promotes the hydrogen sulfide evolution. The sulfide sulfur calculated from 2N HCl-soluble iron provides good agreement with the determined sulfide sulfur using stannous chloride. This method could be used as a quick method to determine the sulfide sulfur in coal char, provided that there are little other types of HCl-soluble iron, such as iron oxides, iron sulfates, illites and chlorites, present in the sample.

Table 1. Sulfur-by-types analysis of a composite 1400°F Coal Char

Digestion Acid Promoting Agent	4N HCl	4N HCl 10% SnCl ₂	4N HCl 20% SnCl ₂	6N HCl	6N HCl 10% SnCl ₂
Sulfate Sulfur %	<0.01	<0.01		<0.01	<0.01
Sulfide Sulfur %	.66	1.04	1.07	.74	1.04
Pyritic Sulfur %	.06	.05		.06	.04
Organic Sulfur %	1.06	.93		1.05	.97
Total S % (calc.)	1.78	2.02		1.85	2.05
Total S % (detrn.)	2.09	2.09		2.09	2.09
HCl Soluble Fe %	1.81	1.84	1.86	1.92	1.88
S/Fe Mole Ratio	.64	.98	1.00	.67	.96
2N HCl-Soluble Fe	1.81	1.84	1.86	1.92	1.88
Sulfide S % (calc. from Fe)	1.05	1.07	1.08	1.11	1.09

We found also that the organic sulfur contents determined in the procedure without stannous chloride are higher than those found in the procedure with stannous chloride. This is probably because the elemental sulfur, formed during the hydrochloric acid digestion, may be partially associated with the solid residue and recovered as organic sulfur in the subsequent concentrated nitric acid digestion. This indicates that the acid evolution method without stannous chloride is likely to give a high estimation of organic sulfur in char in addition to a low quantitation of sulfide sulfur.

Table 2 presents the concentrations of sulfide sulfur, residual sulfur and total sulfur of six coal chars. The total sulfur calculated from the sulfide and residual sulfur was again found to agree well with the determined total sulfur in all analyses when stannous chloride was used in the evolution procedure. The mole ratios of sulfide sulfur to the HCl-soluble iron deviate significantly from unity in four analyses, indicating the presence of other 6N HCl-soluble iron species in those char samples. However, the quick method to determine the sulfide sulfur using the percentage of iron soluble in 1N, 1.6N (5%) and 2N HCl seems to be quite satisfactory in most of the cases (Table 3). Further studies should be conducted to select an optimum hydrochloric acid concentration for this method.

Another method, using the relative percentage content of the sulfide iron determined by Mossbauer spectroscopy and the total iron percentage in char to calculate the sulfide sulfur, was successfully employed. However, only the results of two coal char samples with high ferrous sulfide content were reported in Table 3. They agree quite well with the data reported by the evolution method. Greater difficulties were encountered in analyzing the rest of the samples because of their relatively low iron concentration and the presence of various other iron species. During this study, we found that pyrrhotites ($\text{Fe}_{(1-x)}\text{S}$) with varying stoichiometric quantity of sulfur may give different Mossbauer spectra, rendering the Mossbauer spectral subtraction technique inaccurate, especially when no suitable pyrrhotite standards were available.

Table 2. Determination of sulfide sulfur of 1400°F coal chars using HCl evolution method

1400 °F Coal Char	Sulfide S %	Residual S %	Total S %		HCl-Soluble Fe %	S/Fe (Mole)
			(Calc)	(Detn.)		
Kentucky No. 9						
(with SnCl_2)	.90	1.38	2.28	2.50	2.00	.78
(w/o SnCl_2)	.57	1.53	2.10		1.97	
Kentucky No. 9 (prepared from -200 mesh coal fines)						
(with SnCl_2)	.74	1.30	2.04	2.14	1.65	.78
(w/o SnCl_2)	.24	1.35	1.59		1.64	
Pittsburgh No. 8						
(with SnCl_2)	2.11	.90	3.01	2.96	3.76	.98
(w/o SnCl_2)	1.70	1.12	2.82		3.70	
Kentucky No. 13						
(with SnCl_2)	.30	.68	.98	1.02	.60	.87
(w/o SnCl_2)	.04	.85	.89		.60	
Illinois No. 6						
(with SnCl_2)	1.44	1.35	2.79	2.79	2.46	1.02
(w/o SnCl_2)	.87	1.61	2.48		2.40	
Rosebud						
(with SnCl_2)	.56	.74	1.30	1.33	1.20	.81
(w/o SnCl_2)	.30	.93	1.23		1.18	

Table 3. Comparison of methods for sulfide sulfur analysis of 1400°F Coal Chars

1400 °F Coal Char	Sulfide S % (determined)		Sulfide S % (calculated)				
	w/o SnCl ₂	with SnCl ₂	From	From HCl-soluble Fe			
			Mossbauer	(1N)	(1.6N)	(2N)	(6N)
Kentucky No. 9	.57	.90	ND	.87	.80	.88	1.13
Kentucky No. 9 (-200 mesh coal)	.24	.74	ND	.76	.81	.84	.94
Pittsburgh No. 8	1.70	2.11	2.07	2.08	2.05	1.98	2.12
Kentucky No. 13	.04	.30	ND	.30	.30	.30	.34
Illinois No. 6	.87	1.44	1.41	1.35	1.37	1.33	1.38
Rosebud	.30	.56	ND	.61	.60	.57	.68

NOTE: ND = not determined.

No results from XRD analysis were reported at this time. The quantitative method using potassium chloride as an internal standard gave erroneous results because no effective method was developed yet to resolve and quantitate the broad and deformed x-ray peak corresponding to diffractions at the crystal 102 planes of various ferrous sulfides. The even broader XRD background induced by the char itself further complicates the XRD spectra. In order to achieve better accuracy in the quantitative measurement of total ferrous sulfide, the sensitivity of diffraction from each of the different ferrous sulfides must also be determined.

CONCLUSION

A hydrochloric acid evolution method using stannous chloride as a promoting agent was developed and employed successfully for ferrous sulfides determination in 1400°F coal char. This method not only provides an accurate analysis of ferrous sulfides, but also improves the accuracy of the organic sulfur analysis of coal char. We believe this method could be and should be employed in the sulfur-by-types analysis of all coal derivatives containing ferrous sulfides.

Among other methods studied, the methods using 1N, 1.6N (5%) and 2N HCl-soluble iron to calculate the ferrous sulfides content could be employed to determine the ferrous sulfides content in coal char, provided that little other HCl-soluble iron species are present. The method using Mossbauer spectroscopy to determine the sulfide iron concentration and atomic absorption spectroscopy to determine the total iron would be a good technique, if pyrrhotite standards as well as other iron standards resembling the iron species in coal char were found. Further Mossbauer spectroscopic studies with temperature control may provide more information and may simplify the current procedure. X-ray diffraction spectroscopy also encounters a similar problem caused by various ferrous sulfides with discrete composition and structures. However, the latter problem is even more significant and tends to be too complex to resolve.

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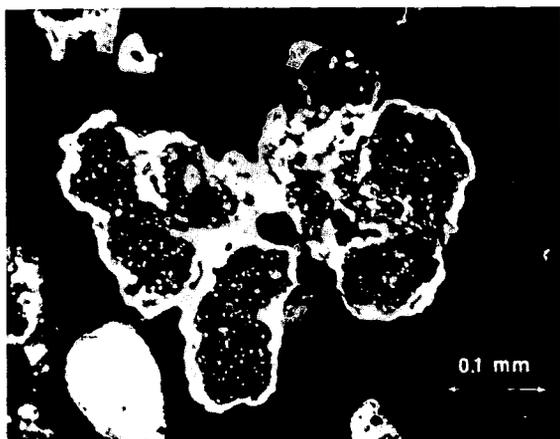


Figure 1. FeS (white) Joining Shale Particles in Bed Material From a Pilot-Plant Run on Run-of-Mine Coal

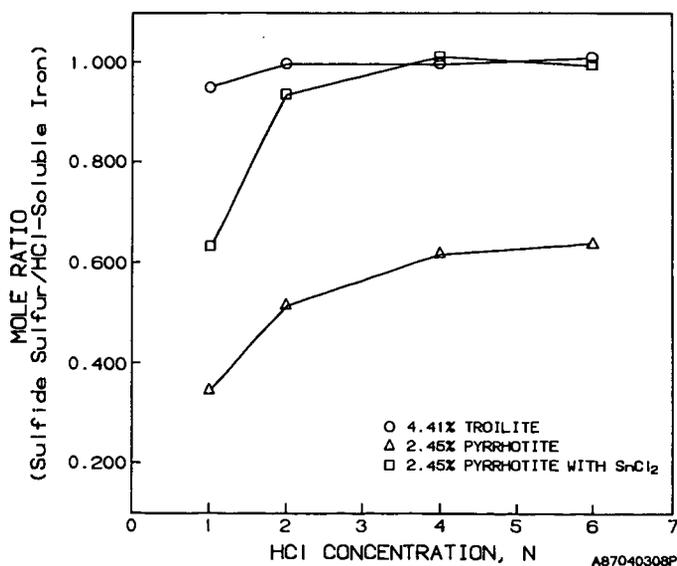


Figure 2. Recovery of Ferrous Sulfide as Hydrogen Sulfide in a Hydrochloric Acid Evolution Procedure With and Without Stannous Chloride