

Demineralization and Desulfurization of Subbituminous Coal with Hydrogen Peroxide

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The effect of hydrogen peroxide solution alone and in the presence of dilute sulfuric acid on desulfurization and demineralization of coal collected from the Makum coalfield situated at North-Eastern region, India, was investigated and the process conditions (temperature, time, and hydrogen peroxide and sulfuric acid concentrations) were optimized. Hydrogen peroxide (15%) alone leads to removal of over 76% pyritic sulfur and 70% sulfate sulfur and around 5% organic sulfur and 14% ash at 25 °C, which increases to almost complete removal of pyritic and sulfate sulfur and over 26% organic sulfur and 43% ash in the presence of 0.1 N H₂SO₄. The oxidation rate was found to increase significantly with increasing temperature (15 to 40 °C) and hydrogen peroxide concentration (2.5 to 15%). The rate of reaction was found to be well represented by a continuous reaction model that was second order with respect to pyritic sulfur. The activation energy for pyritic conversion in Boragolai and Ledo coal are, respectively, 19.33×10^6 J kmol⁻¹ and 39.72×10^6 J kmol⁻¹.

Introduction

Sulfur is present in coal in three forms: pyrite, organic, and sulfate. The organic sulfur directly bound in the coal matrix is in the form of thiols, sulfides, disulfides, thiophenes, and cyclic sulfides¹. Pyritic sulfur (FeS₂) occurs in mineral phases as agglomerates of pyrite and marcasite crystals. The sulfate exists mostly as sulfates of iron and calcium. Silica in different forms such as quartz, cristobalite, etc., clay minerals such as kaolinite, illite, etc., carbonates such as calcite, dolomite, siderite, etc., sulfate and sulfides, etc., are the major ash-forming minerals in coal.

Combustion of high sulfur coal produces SO₂ which is toxic and corrosive. Sulfur dioxide is subsequently converted to SO₃, which in contact with water forms sulfuric acid. In weathered coal, acidic mine water percolates into the ground and makes the groundwater highly acidic. SO₃ leads to formation of acid rain, and corrosion of boilers, underground pipelines, metallic installations, mine machinery, etc. Coal ash lowers the combustion efficiency of boilers and causes other deleterious effect. Ash handling and disposal of ash are also problem. Therefore, it is necessary to remove the mineral matter and sulfur from coal prior to its utilization. Presently, control of sulfur oxide emissions is achieved mainly by stack gas scrubbing and (or) physical coal cleaning techniques. The former process is both expensive and energy intensive. The latter, although relatively inexpensive and simple to operate, is less effective.

Various chemical processes employing either oxidizing agents such as ferric sulfate,^{2–3} ferric chloride,^{4–5} hydrogen peroxide,^{6–12} potassium dichromate,¹³ potassium permanganate,^{14,15} cupric chloride,^{16,17} sodium hypochlorite,^{18–21} peroxyacetic acid (PAA),²² perchloric acid,²³ performic acid,²⁴ oxygen,^{25,26} etc., basic solutions

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such as sodium carbonate,^{27–28} sodium hydroxide,^{13,29–35} calcium hydroxide,³⁶ etc., or mineral acids such as nitric acid³⁷ have been suggested to reduce the ash and sulfur in coal.

Mukai et al.⁶ investigated desulfurization of bituminous coal from Japan by treatment with 3 wt % aqueous hydrogen peroxide solution. They reported complete removal of pyritic sulfur, but no data on organic sulfur removal was provided. Nalwalk and co-workers⁷ also reported that pyrite in coal can be slowly oxidized to sulfate by treatment with 30 wt % H₂O₂. Smith⁸ investigated desulfurization of coals of U.S. origin with 10–15 wt % H₂O₂ alone and in the presence of sulfuric acid. He observed high level pyritic sulfur and ash removal by peroxide alone, and a mixture with sulfuric acid had little effect on organic sulfur removal. Prolonged treatment with peroxide resulted in oxidative breakdown of the organic material. Boron and Taylor⁹ investigated mild oxidation of Pittsburgh Bed coal with hydrogen peroxide or mixtures of hydrogen peroxide and acid. The treatment led to slight changes in pyritic and organic sulfur content in the coal. Boron et al.¹⁰ also reported that pyritic sulfur is rapidly oxidized and oxidation of organic matter in coal starts after consumption of pyrite. Vasilakos et al.¹¹ investigated chemical beneficiation of high volatile bituminous coal with aqueous solutions of hydrogen peroxide/sulfuric acid solution at ambient temperature. They observed almost complete removal of inorganic sulfur and substantial reduction in ash. However, organic sulfur was hardly affected. Ahnonkitpanit and Prasassarakich¹² followed the similar treatment for desulfurization of subbituminous high volatile coals from Thailand. They observed removal of a small amount of organic sulfur, most of the inorganic sulfur, and a substantial amount of ash.

The coals available in Assam and other states in North-Eastern region of India are subbituminous in rank and characterized by low ash, high sulfur, high volatile matter, and high caking index (for the coking coals). The coals contain 2–6% (occasionally more) sulfur, and over 70% of the sulfur is in organic form.³⁸ These coals are friable and perhydroprous in nature.²³

Although there are large reserves (over 250 million tonnes) of coal in the North-Eastern region of India, the high sulfur content restricts their large scale utilization. Various chemical methods were attempted by different workers to desulfurize the coal. Mukherjee and Borthakur³⁹ observed complete removal of inorganic sulfur and 10% organic sulfur from the coal by treatment with

Table 1. Analysis of Coal Samples

	Boragolai	Ledo
proximate analysis (wt % as received)		
moisture	5.4	4.9
ash	8.4	10.4
volatile matter	41.4	41.5
fixed carbon	44.8	43.1
ultimate analysis (wt % dry basis)		
carbon	68.8	70.0
hydrogen	5.1	5.2
sulfur	4.3	4.3
nitrogen	1.5	1.5
oxygen (diff)	20.3	19.0
forms of sulfur (wt % dry basis)		
pyritic	0.64	0.52
sulfate	0.52	0.41
organic	3.11	3.38
calorific value (kcal/kg)	7526	7326

aqueous sodium hydroxide followed by acid. Sain et al.⁴⁰ reported complete removal of inorganic sulfur and about 50% organic sulfur from some Assam coal samples by chlorinolysis in aqueous medium. But chlorine is a poisonous and highly corrosive chemical and therefore it is necessary to find an alternative suitable method to desulfurize Assam coal. This communication reports the results of desulfurization and demineralization of two coal samples collected from different collieries by using aqueous hydrogen peroxide/sulfuric acid under ambient condition. An attempt has also been made to apply an available reaction model to represent pyrite oxidation.

Experimental Section

The coal samples used in the investigation were collected from Boragolai and Ledo collieries of Makum coalfield, Assam, India. The proximate analysis of the coal samples were done by following Indian standard methods [IS: 1350 (part I)-1984]. The percentages of carbon, hydrogen, and nitrogen were estimated by using a Perkin-Elmer (model 2400) elemental analyzer and total sulfur by following Eschka method [ASTM D 3177]. The percentage of oxygen was calculated by difference. The forms of sulfur were determined by following standard methods [ASTM D 2492]. The calorific value was determined by using a high-pressure oxygen bomb calorimeter [ASTM D 3286]. The analyses for each sample were carried out in quadruplicate and average values have been reported. The accuracy of the estimated values was ± 0.01 for pyritic sulfur, ± 0.01 for sulfate sulfur, ± 0.02 for organic sulfur, and ± 0.02 for total sulfur. The analyses of the coal samples are presented in Table 1. The samples were ground to $-212 \mu\text{m}$ fineness. The ground samples (about 100 g) were treated with 250 mL of hydrogen peroxide solution of different concentrations alone as well as in the presence of 0.1 N H₂SO₄ in a three-necked round-bottom flask fitted with condenser and stirrer. The mixtures were stirred at different temperatures for various periods. The temperatures were maintained by using a water bath. After the end of the reaction, the leached coals were recovered by filtration. The color of the filtrates was found to change from light yellow to brown, depending on the hydrogen peroxide concentration and treatment time. During the reaction, the soluble inorganic constituents have dissolved and possibly some of the organic portion of the coal gets oxidized, depolymerized, and converted into water-soluble products. The coal samples were washed several times with water until neutral to litmus paper, dried at 90 °C, and analyzed for ash, heating value, and forms of sulfur. Prior to the analysis, the treated coal samples were tested for elemental sulfur likely to be formed during the treatment. For this

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Table 2. Effect of H₂O₂ Concentration on Demineralization and Desulfurization of Coal; Leached for 4 h at 25 °C (all results on dry basis)

H ₂ O ₂ concn (%)	heating value (kcal/kg)	ash (%)	sulfur distribution (%)				reduction in total sulfur (%)	reduction in ash (%)
			pyritic	sulfate	organic	total		
Boragolai coal								
<i>a</i>	7526	8.8	0.64	0.52	3.11	4.27		
2.5	7765	7.3	0.25	0.24	3.08	3.57	16.4	17.2
5	7751	7.2	0.21	0.21	3.04	3.46	19.0	17.9
10	7735	7.1	0.19	0.20	3.00	3.39	21.0	18.6
15	7723	7.0	0.15	0.15	2.93	3.23	24.3	19.9
Ledo coal								
<i>a</i>	7326	11.0	0.52	0.41	3.38	4.31		
2.5	7537	9.8	0.18	0.15	3.20	3.53	18.1	11.0
5	7528	9.6	0.15	0.11	3.16	3.42	20.6	12.1
10	7516	9.5	0.12	0.08	3.10	3.30	23.4	13.8
15	7503	9.4	0.09	0.05	3.08	3.22	25.3	14.6

^a Values for unleached coal.**Table 3. Effect of H₂SO₄ Concentration on Demineralization and Desulfurization of Coal**

normality of H ₂ SO ₄	heating value (kcal/kg)	ash (%)	sulfur distribution (%)				reduction in total sulfur (%)	reduction in ash (%)
			pyritic	sulfate	organic	total		
Boragolai coal								
<i>a</i>	7526	8.8	0.64	0.52	3.11	4.27		
0.1	7595	8.0	0.48	0.40	3.09	3.97	7.0	8.5
0.5	7583	7.9	0.46	0.38	3.06	3.90	8.7	10.4
1.0	7572	7.7	0.43	0.35	3.03	3.81	11.0	12.2
1.5	7564	7.6	0.41	0.33	3.00	3.74	12.4	13.0
2.0	7555	7.5	0.38	0.30	2.96	3.64	14.7	14.5
Ledo coal								
<i>a</i>	7326	11.0	0.52	0.41	3.38	4.31	-	
0.1	7393	10.3	0.33	0.28	3.35	3.96	8.1	6.6
0.5	7385	10.1	0.32	0.27	3.31	3.90	9.5	7.6
1.0	7376	10.0	0.30	0.25	3.28	3.83	11.1	9.0
1.5	7370	9.9	0.27	0.23	3.26	3.76	13.0	9.5
2.0	7362	9.8	0.22	0.18	3.20	3.60	16.5	10.6

^a Values for unleached coal.

purpose, a small amount of the sample was mixed with carbon disulfide and the mixture was stirred for about 3 h at room temperature and filtered using a filter cloth, and the filtrate was treated with piperidine. None of the samples gave red color due to elemental sulfur.⁴¹ FTIR spectra of some of the leached coal samples in the range 4000–375 cm⁻¹ were recorded in a Perkin-Elmer Spectrophotometer (model 2000) in KBr disk.

Results and Discussion

Effect of Concentration of Hydrogen Peroxide.

The effect of H₂O₂ concentration at 25 °C on demineralization and desulfurization of both the coal samples is shown in Table 2 and Figure 1S and 2S (Supporting Information). It could be seen from Table 2 that reduction in total sulfur in Boragolai coal increases from 16.4% to 24.3%, pyritic sulfur from 60.9% to 76.6%, and organic sulfur from 1.0 to 5.8% with the increase in H₂O₂ concentration from 2.5 to 15%. In the case of Ledo coal, total, pyritic, and organic sulfur reduction increases from 18.1 to 25.3%, 65.4 to 82.7%, and 5.3 to 8.9%, respectively, for the same increase in H₂O₂ concentration. The corresponding reduction in ash increases from 17.2 to 19.9% and 11.0 to 14.6% for Boragolai and Ledo coal, respectively.

Effect of Sulfuric Acid. The effect of leaching the coal samples with sulfuric acid on ash and sulfur removal are presented in Table 3 and Figure 3S and 4S (Supporting Information) and that of acidified hydrogen peroxide in Table 4 and Figure 5S and 6S

(Supporting Information). The ash and sulfur removal increases with increase in concentration of sulfuric acid. The acid alone, depending on concentration, can remove various amounts of ash, total sulfur, pyritic sulfur, and organic sulfur. Presence of acid in the peroxide solution significantly enhances the removal of total, pyritic, and organic sulfur as well as ash from both the coal samples at all concentrations of hydrogen peroxide solution. As an example, 15% H₂O₂ removes 24.3 and 25.3% of total sulfur from Boragolai and Ledo coal, respectively, which increases to 45.0%, respectively, in the presence of 0.1 N H₂SO₄. The removal of organic sulfur from the coal samples increases from 5.8 and 8.9% to 26.7 and 31.4%, inorganic sulfur from 74.1 and 85.0% to 94.0 and 94.6%, and ash from 19.9 and 14.6% to 45.0 and 43.0%, respectively, on acidification of the peroxide solution. Figure 7S and 8S (Supporting Information) show that increase in concentration of H₂SO₄ beyond 0.1 N has little effect on removal of both inorganic and organic sulfur but increases the ash removal to a small extent.

FTIR spectra (Figures 1 and 2) of the hydrogen peroxide-treated samples do not exhibit prominent peak at ~1700 cm⁻¹ due to the -COOH group. The intensity of the peaks at ~2920 and 2865 cm⁻¹ due to aliphatic -CH groups are also not significantly affected by the treatment. The treatment therefore did not lead to addition of significant amount of oxygen to the residual coal samples to cause concern for dilution of the sulfur levels.

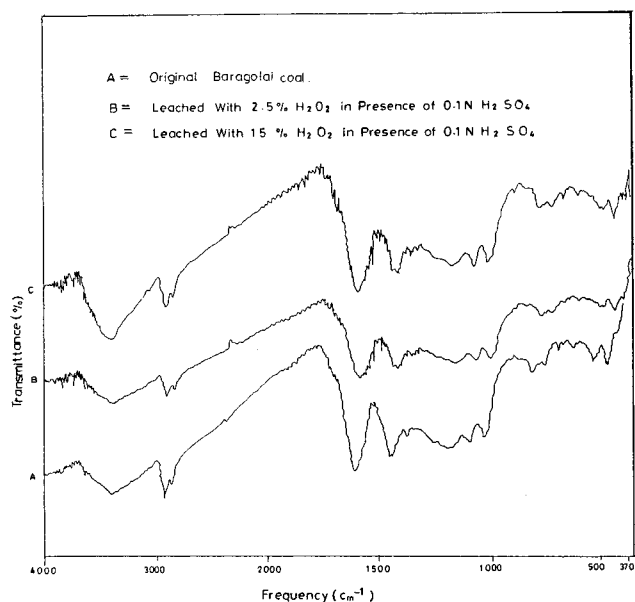
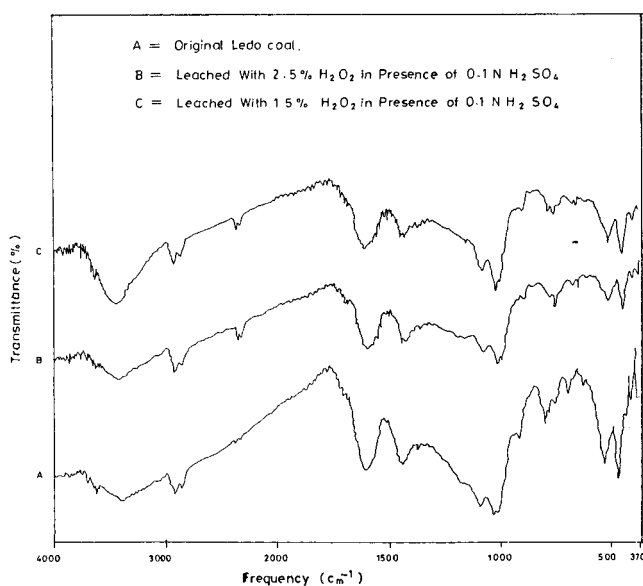
Effect of Leaching Time. The effect of leaching time could be seen from the results in Table 5 and Figure 9S

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Table 4. Effect of H₂O₂ Concentration (with 0.1 N H₂SO₄) on Demineralization and Desulfurization of Coal; Leached for 4 h at 25 °C (all results on dry basis)

H ₂ O ₂ concn (%)	heating value (kcal/kg)	ash (%)	sulfur distribution (%)				reduction in total sulfur (%)	reduction in ash (%)
			pyritic	sulfate	organic	total		
Boragolai coal								
a	7526	8.8	0.64	0.52	3.11	4.27		
2.5	7849	5.3	0.11	0.05	2.48	2.64	38.2	40.0
5.00	7758	5.2	0.09	0.03	2.41	2.53	40.7	41.1
10.0	7773	5.0	0.08	0.01	2.33	2.42	43.3	42.9
15.0	7787	4.8	0.07	0.00	2.28	2.35	45.0	45.0
Ledo coal								
a	7326	11.0	0.52	0.41	3.38	4.31		
2.5	7705	6.8	0.08	0.06	2.51	2.65	38.5	37.6
5.0	7622	6.7	0.06	0.04	2.44	2.54	41.1	39.3
10.0	7638	6.5	0.05	0.02	2.37	2.44	43.4	41.0
15.0	7659	6.3	0.04	0.01	2.32	2.37	45.0	43.0

^a Values for unleached coal.

**Figure 1.** FTIR spectra of original (Boragolai) and leached coal.**Figure 2.** FTIR spectra of original (Ledo) and leached coal.

and 10S (Supporting Information). Increase of leaching time from 0.25 to 4 h increase the removal of total sulfur from 37.9 to 45.0% and 38.2 to 45.0 and organic from

19.3 to 26.7% and 27.2 to 31.4% from Boragolai and Ledo coal, respectively. Removal of pyritic sulfur also improves from 84.4 to 89.1% and 76.9 to 92.3% from the respective coal samples. Sulfate sulfur from the coal can be almost completely removed by increasing the leaching time to 1.5–2 h. The ash reduction from the coal samples also gradually increases with leaching time. Increase of leaching time from 0.25 to 4 h results in about 7% increase in ash removal. The heating values accordingly changes.

Effect of Temperature. The effect of temperature could be seen from Table 6 and Figures 11S and 12S (Supporting Information). Removal of pyritic sulfur from Boragolai and Ledo coal increases from 87.5 to 95.3% and 90.4 to 98.1% and total sulfur from 39.6 to 48.7% and 38.3 to 48.9%, respectively, on increase of temperatures from 15 to 40 °C. The ash reduction from the coal samples also increases from 40.0 to 47.2% and 38.8 to 46.7%, respectively, from the two coal samples. Increase of temperature beyond 30 °C had little effect on removal of the pyritic sulfur but there was a small increase in organic sulfur removal from Boragolai coal. In the case of Ledo coal, increase of temperature from 30 to 40 °C improves removal of pyritic sulfur and organic sulfur to a small extent.

The amount of organic sulfur removed from Assam coal by treatment with hydrogen peroxide in acidic conditions are in general greater than from other coal samples as reported in the literature.^{9–12} This may be due to differences in the nature of the coal samples and relative abundance of different organic sulfur functionalities in the samples. Organo sulfur compounds such as sulfide (carbon–sulfur), disulfides (sulfur–sulfur), thiols, and simple thiopenes undergo oxidation to soluble sulfonic acid and/or sulfones whereas compounds such as dibenzothiophene is highly resistant to oxidation under similar conditions.^{42–45} Assam coal probably contains a relatively high amount of reactive sulfur functionalities accounting for more organic sulfur removal than those reported so far. Distribution of organic sulfur in some Assam coal samples revealed the pres-

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Table 5. Effect of Reaction Time on Demineralization and Desulfurization of Coal; Leached with 15% H₂O₂ in 0.1 N H₂SO₄ at 25 °C (all results on dry basis)

time (h)	heating value (kcal/kg)	ash (%)	sulfur distribution (%)				reduction in total sulfur (%)	reduction in ash (%)
			pyritic	sulfate	organic	total		
Boragolai coal								
<i>a</i>	7526	8.8	0.64	0.52	3.11	4.27		
0.25	7827	5.5	0.10	0.04	2.51	2.65	37.9	37.3
0.50	7842	5.4	0.09	0.04	2.50	2.63	38.4	38.3
1.00	7851	5.3	0.09	0.03	2.48	2.60	39.1	39.0
1.50	7856	5.2	0.08	0.01	2.44	2.53	40.7	40.9
2.00	7860	5.2	0.08	0.00	2.38	2.46	42.4	41.4
3.00	7765	5.1	0.07	0.00	2.33	2.40	43.8	42.0
4.00	7787	4.8	0.07	0.00	2.28	2.35	45.0	45.0
Ledo coal								
<i>a</i>	7326	11.0	0.52	0.41	3.38	4.31		
0.25	7687	7.0	0.12	0.04	2.46	2.62	38.2	35.8
0.50	7693	6.9	0.10	0.03	2.46	2.59	39.9	36.4
1.00	7707	6.8	0.09	0.02	2.39	2.50	42.0	37.8
1.50	7717	6.7	0.07	0.02	2.37	2.46	42.9	38.8
2.00	7714	6.6	0.05	0.01	2.36	2.42	43.8	39.5
3.00	7688	6.5	0.05	0.01	2.32	2.38	44.8	40.6
4.00	7659	6.3	0.04	0.01	2.32	2.37	45.0	43.0

^a Values for unleached coal.**Table 6. Effect of Temperature on Demineralization and Desulfurization of Coal; Leached with 15% H₂O₂ in 0.1 N H₂SO₄ for 4 h (all results on dry basis)**

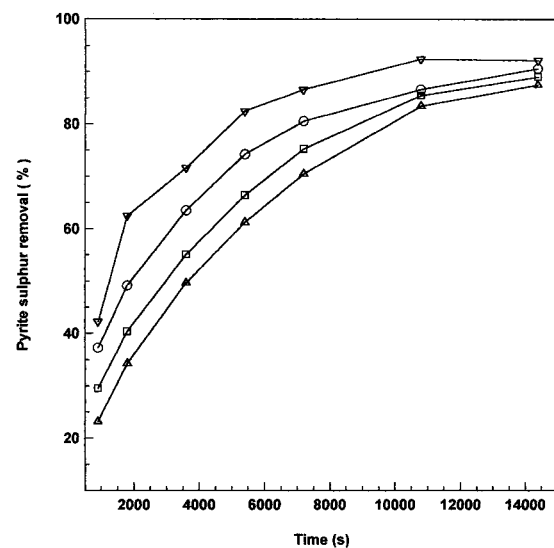
temp (°C)	heating value (kcal/kg)	ash (%)	sulfur distribution (%)				reduction in total sulfur (%)	reduction in ash (%)
			pyritic	sulfate	organic	total		
Boragolai coal								
<i>a</i>	7526	8.8	0.64	0.52	3.11	4.27		
15	7779	5.3	0.08	0.08	2.42	2.58	39.6	40.0
25	7787	4.8	0.07	0.00	2.28	2.35	45.0	45.0
30	7766	4.8	0.04	0.00	2.25	2.29	46.4	45.7
40	7755	4.6	0.03	0.00	2.16	2.19	48.7	47.2
Ledo coal								
<i>a</i>	7326	11.0	0.52	0.41	3.38	4.31		
15	7615	6.7	0.05	0.10	2.51	2.66	38.3	38.8
25	7659	6.3	0.04	0.01	2.32	2.37	45.0	43.0
30	7622	6.1	0.03	0.00	2.25	2.28	47.1	44.8
40	7615	5.8	0.01	0.00	2.19	2.20	48.9	46.7

^a Values for unleached coal.

ence of mercaptan, disulfide, thiol, sulfide, simple thiophene, and complex thiophene; of which the first five constitute over 70% of the organic sulfur.⁴⁶ These functionalities are possibly more in Ledo than Boragolai coal.

Kinetics of Oxidation of Pyritic Sulfur. The results presented above show that hydrogen peroxide in the presence of mild acid leads to removal of over 90% pyritic sulfur and therefore the principal reaction occurring during the process is oxidation of pyrite.

Figures 3 and 4 illustrate the conversion of pyritic sulfur in Boragolai and Ledo coal at different temperatures. It could be seen from the figures that the removal of pyritic sulfur is rapid at the initial period. More than 60% of the pyrite in Ledo coal and 40% of that in Boragolai coal are converted within 15 min at 40 °C. Pyrite in powdered coal can exist as free particles or it may be embedded inside the coal particles. Since the concentration of pyrite is very small, the intraparticle diffusional resistance will be negligibly small. As a result, the oxidation of pyritic sulfur can be assumed to follow a continuous reaction model.⁴⁷ This model has successfully been used by several authors^{12,25,26,48} to study the kinetics of pyritic sulfur removal from coal.

**Figure 3.** Percent pyrite sulfur removal versus time for Boragolai coal (15% H₂O₂, 0.1 N H₂SO₄): Δ , 15 °C; \square , 25 °C; \circ , 30 °C; ∇ , 40 °C.

The experimental data were found to correlate well with a second-order rate equation of the following form:

$$dC/dt = k C^2 \quad (1)$$

where k is the intrinsic kinetic rate constant whose

(46) Kumar, A.; Srivastava, S. K. *Fuel* **1992**, *71*, 718.(47) Levenspiel, O. In *Chemical Reaction Engineering*, 2nd ed.; John Wiley & Sons: New York, 1973.

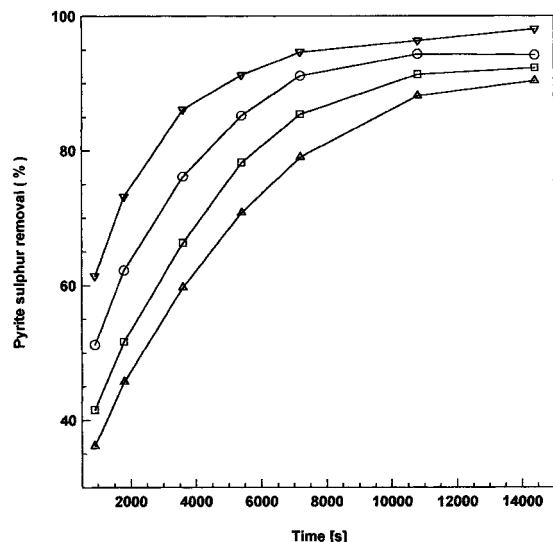


Figure 4. Percent pyrite sulfur removal versus time for Ledo coal (15% H₂O₂, 0.1 N H₂SO₄): Δ , 15 °C; \square , 25 °C; \circ , 30 °C; ∇ , 40 °C.

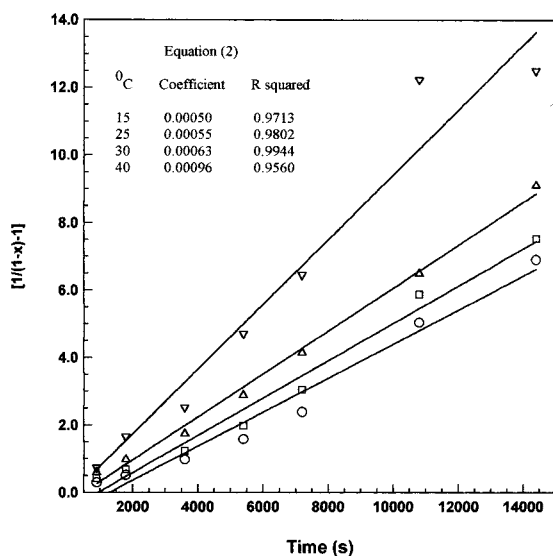


Figure 5. Second-order kinetic plot for pyrite sulfur reaction: continuous reaction model. Boragolai coal (15% H₂O₂, 0.1 N H₂SO₄): \circ , 15 °C; \square , 25 °C; Δ , 30 °C; ∇ , 40 °C.

value depends on both the temperature and concentration of hydrogen peroxide. Integration of eq 1 gives

$$[1/(1-x) - 1] = C_0 kt \quad (2)$$

where x is the pyrite conversion, and C_0 and C are the initial and instantaneous concentrations of pyrite in coal (kmol m⁻³), respectively. The validity of eq 2 is illustrated in Figures 5 and 6. The rate constants at different temperatures were calculated from the regression analysis of the kinetic data.

An Arrhenius plot (Figure 7) based on the rate constants from Figures 5 and 6 gave an activation energy of 19.33×10^6 J kmol⁻¹ and 39.72×10^6 J kmol⁻¹ for the pyrite reaction of Boragolai and Ledo coal, respectively. The intercepts of the plots yielded frequency factors (A_0) of 6.19×10^{-1} and 2.33×10^{-4} at

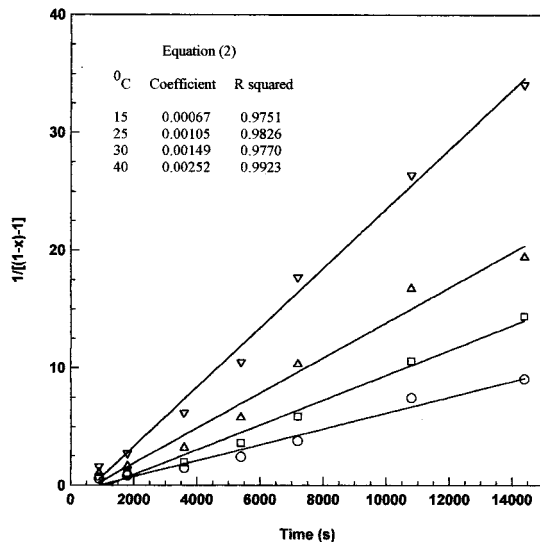


Figure 6. Second-order kinetic plot for pyrite sulfur reaction: continuous reaction model. Ledo coal (15% H₂O₂, 0.1 N H₂SO₄): \circ , 15 °C; \square , 25 °C; Δ , 30 °C; ∇ , 40 °C.

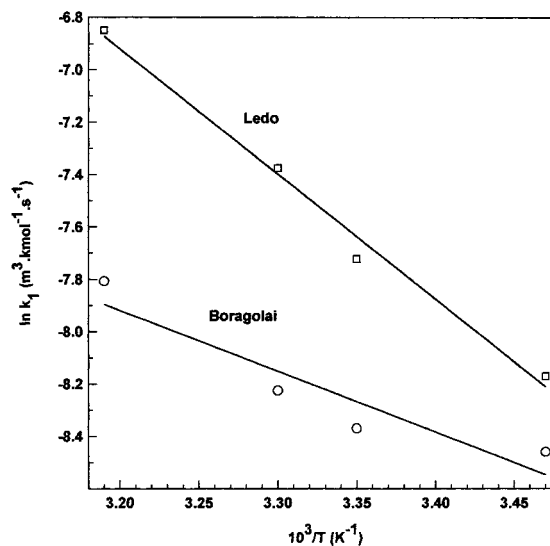


Figure 7. Arrhenius plot for pyrite sulfur reaction: continuous reaction model. Boragolai and Ledo coal (15% H₂O₂, 0.1 N H₂SO₄).

15% H₂O₂ concentration, leading to eqs 3 and 4 for Boragolai and Ledo coal, respectively:

$$k = 6.19 \times 10^{-1} \exp(-19.33 \times 10^6/RT) \quad (3)$$

$$k = 2.33 \times 10^{-4} \exp(-39.72 \times 10^6/RT) \quad (4)$$

Ahnonkitpanit⁴⁸ and Ahnonkitpanit and Prasassar-akich¹² studied kinetics of desulfurization of two high volatile subbituminous coal samples of Thailand origin from different sources and expressed the following rate expressions:

$$k = 3.88 \times 10^6 \exp(-49.7 \times 10^6/RT) \quad (5)$$

$$k = 12.02 \times 10^6 \exp(-52.6 \times 10^6/RT) \quad (6)$$

Differences in activation energy of desulfurization of pyritic sulfur from Boragolai and Ledo coal as well as from that of Thailand coal samples (49.7×10^6 and 52.6×10^6 J kmol⁻¹) may be due to differences in their

(48) Ahnonkitpanit, E. MSc. Thesis, Chulalongkorn University, Bangkok, Thailand, 1986.

mineralogical characteristics. The North Eastern coals are friable which may also lead to lower values of the activation energy.

Conclusions

Almost complete removal of sulfate and pyritic sulfur, about 26–31% organic sulfur and about 43–45% ash from Boragolai and Ledo coal may be achieved at ambient temperature by treatment with aqueous hydrogen peroxide in the presence of 0.1 N H₂SO₄. The oxidation of pyritic sulfur is represented by a continuous reaction model. The experimental data found to correlate well with a second-order expression, with an activation energy of 19.33×10^6 J kmol⁻¹ and 39.72×10^6 J kmol⁻¹ for Boragolai and Ledo coal, respectively.

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Supporting Information Available: Twelve figures showing the effects of hydrogen peroxide and acidified hydrogen peroxide as well as the effects of leaching time and temperature on the demineralization and desulfurization of coals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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