See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/231271303

Aqueous Leaching on High Sulfur Subbituminous Coals, in Assam, India

ARTICLE in ENERGY & FUELS · JUNE 2006

Impact Factor: 2.79 · DOI: 10.1021/ef049701y

READS

CITATIONS

29 73

4 AUTHORS, INCLUDING:



Bimala prasad Baruah

Council of Scientific and Industrial Research.



SEE PROFILE



Binoy K Saikia

CSIR-North East Institute of Science & Techn...

52 PUBLICATIONS 257 CITATIONS

SEE PROFILE



Paruchuri Gangadhar Rao

Council of Scientific and Industrial Research ...

21 PUBLICATIONS 308 CITATIONS

SEE PROFILE

Aqueous Leaching on High Sulfur Sub-bituminous Coals, in Assam, India

Bimala P. Baruah,* Binoy K. Saikia, Prabhat Kotoky, and P. Gangadhar Rao

Regional Research Laboratory (CSIR), Jorhat-785006, Assam, India

Received November 22, 2004. Revised Manuscript Received April 26, 2006

Aqueous leaching of high sulfur sub-bituminous coals from Ledo and Baragolai collieries of Makum coal fields, in Assam, India, has been investigated with respect to time at different temperatures. Leaching at 25 °C up to 120 h showed that the physicochemical characteristics viz., conductivity, acidity, TDS, and SO_4^{-2} ions, increase with the increase in time of leaching. The generation of highly acidic leachates at 1-1.5 h (pH 2.5) and 2 h (pH 3.1) for Ledo and Baragolai coals was observed, respectively. However, it remains stable up to 120 h. The concentration of major, minor, and trace elements and their mobility along with the loss of pyritic sulfur or depyritization were also reported. The release of metals (Fe, Mg, Bi, Al, V, Cu, Cd, Ni, Pb, and Mn) above the regulatory levels during leaching was evidenced. Depyritization was found to be 79.8, 82.9, 84.7, and 89.7% for Ledo and 70.49, 73.77, 75.41, and 77.05% for Baragolai coal at 15, 25, 35, and 45 °C, respectively. A pseudo-first-order kinetic relationship with activation energies (E) of 8.1477 and 5.2378 kJ mol⁻¹ with frequency factors (A) of 8.8405×10^{-4} and 2.6494×10^{-4} dm³ mol⁻¹ s⁻¹ was attributed to aqueous oxidation of pyrites in Ledo and Baragolai coals, respectively. The X-ray diffraction analysis and Fourier transform infrared spectroscopy patterns indicate the presence of illite, α-quartz, hematite, chlorite, rutile, calcite, and albite as mineral phases. This investigation justifies the formation of acid mine drainage by weathering of pyrites from coal during the mining of high sulfur Makum coal fields, in Assam, India, and demonstrates one of the possible routes for its formation.

Introduction

The presence of high sulfur coals has been reported throughout the world with the exception of Australia.¹ Generally, the coals contain three forms of sulfur, mainly sulfate, pyritic, and organic. However, the existence of another two forms of sulfur, elemental and secondary sulfur, has also been reported for the high sulfur coals of Northeast (NE) India.² From the view of environmental perspectives, these coals have severe limitations upon their utilization, leading to environmental degradation. A large number of processes have also been developed for desulfurization of high sulfur coals of NE India.^{3–13} The major part of inorganic sulfur in coals consists of pyrite (FeS₂), which

- * To whom correspondence should be addressed. E-mail: bpcoal2002@ vahoo.co.in.
- (1) Yurovskii, A. Z. Sulphur in Coals; Academy of the Sciences of the USSR, Moscow, Russia, 1960 (English translation by INSDOC, New Delhi, India, 1974).
- (2) Baruah, M. K.; Gogoi, P. C. Fuel 1998, 77, 979.
- (3) Baruah, B. P.; Bordoloi, C. S.; Saikia, P. C.; Sain, B.; Mazumdar, B. J. Mines, Met. Fuels **1987**, 102, 102–105.
- (4) Saikia, P. C.; Sain, B.; Baruah, B. P.; Bordoloi, C. S.; Mazumdar, B. J. Mines, Met. Fuels 1988, May.
- (5) Mazumdar, B.; Saikia, P. C.; Sain, B.; Baruah, B. P.; Bordoloi, C. S. Fuel 1989, 68, May.
- (6) Sain, B.; Saikia, P. C.; Baruah, B. P.; Bordoloi, C. S.; Mazumdar, B. Fuel, 1991, 78.
- (7) A process for desulphurisation of high sulphur coals; Indian Patent number 167205.
- (8) A process for desulphurisation of high sulphur coals; Indian Patent number 167309.
- (9) A process for desulphurisation of coals; Indian Patent number 186402.
- (10) Baruah, B. P. International Seminar on Mineral Processing Technology, MPT-2003; Feb 6–8, 2003; India.
 - (11) Mukherjee, S.; Barthakur P. C. Fuel **2003**, 82, 783–788.
- (12) Mukherjee, S.; Mahiuddin, S.; Barthakur, P. C., et al. *Energy Fuels* **2001**, 1418–1424

is usually very finely disseminated¹⁴ and occurs both in macroscopic and microscopic forms. However, particulate to agglomerated forms of pyrite has also been identified in Assam coals.¹⁵ During depyritization of coal by leaching of coal wastes, the formation of elemental sulfur and its presence during pyrite oxidation has also been detected.¹⁶

A large volume of overburden (OB) materials generated during mining of coals is exposed to the environment. The pyrites present in coal and OB or reject materials from mines are oxidized and hydrolyzed, resulting in the formation of acid mine drainage (AMD) in the natural environment and leached out to form acidic, sulfate-rich drainage water. The formation of AMD is also enhanced by the metabolic activity of *Thiobacillus ferooxidans*. Chemical or biological pyrite oxidation^{16,17} by molecular oxygen or Fe^{III} ions has the potential to generate a noticeable amount of sulfate to form AMD.^{18,19} The behavior of trace elements during leaching or simulated weathering tests

⁽¹³⁾ Gogoi, P.; Saikia, B. K.; Baruah, B. P.; Rao, P. G. National Seminar on Coal Science and Technology, Vision 2020; April 2003; Abstract number p 46/s-III-7.

⁽¹⁴⁾ Couch, G. R. *Biotechnlogy and Coal: Report ICTIS-TR38*; IEA Coal Research: London, U.K., 1987.

⁽¹⁵⁾ Choudhary, S. G.; Gosh, S.; Chandra, D. Fuel Sci. Technol. 1982, 1, 41–46.

⁽¹⁶⁾ Schippers, A.; Jozsa, P. G.; Sand, W. Appl. Environ. Microbiol. **1996**, 62, 3424–3431.

⁽¹⁷⁾ Evangelou, V. P.; Zhang, Y. L. Crit. Rev. Environ. Sci. Technol. 1995, 25/23, 141–199.

⁽¹⁸⁾ Nordsorm, D. K. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In *Acid Sulphate Weathering*, *Pedogeochemistry and Relationship to Manipulation of Soil Minerals*; Hossner, L. R., Kittrick, J. A., Faming, D. F., Eds.; American Society of Agronomy: Madison, WI, 1982; pp 37–55.

⁽¹⁹⁾ Bogenschneider et al. Desulfurization of coal: Lignin, humic substances and coal. In *Biopolymers*; Steinbuchel, A., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 1, pp 431–458.

has also been reported.^{20,21} Irrespective of pH, Fe^{III} as a pyriteattacking agent instead of a molecular oxygen has also been reported elsewhere from the kinetic and molecular orbital considerations. 16,22,23

A substantial deposit of high sulfur sub-bituminous coals, mostly of tertiary origin, is existent in NE India. These coals are rich in organic sulfur content (75–90%), with a less amount of pyritic content. However, the formation of acidic drainage in these coal mines and its effect on the environment is wellrecognized. To assess the problem of formation of AMD in these coals, an aqueous leaching study has been taken up. In this exploratory investigation, the variation of pyritic sulfur contents in coal during atmospheric oxidation in aqueous media at different temperatures has been reported. This investigation also reports the acid generation quality of the coal samples from two underground mines, build-up of heavy-metal contamination, and extent of depyritisation in aqueous medium and reaction kinetics for oxidation of pyrites in coals. It is expected that the output of this investigation will be useful as pathfinder to the extent of AMD generation from high sulfur coals and metal mobility and will help to open up an avenue toward the management of the already existing problem in the environment.

Experimental Section

Chemical Analysis. The freshly mined coal samples were collected from two of the most AMD-affected areas of Ledo (L) and Baragolai (B) collieries of Makum coal fields, in Assam, India. The samples are ground to -72 BSS, preserved in desiccators, and used for all subsequent analyses under study. The proximate analyses of the coal samples were carried out by standard methods [IS: 1350 (part I, 1984)]. An elemental analyzer, Perkin-Elmer, model 2400, estimated the elements C, H, and N contents, while total sulfur was determined by a sulfur determinator (Leco, SC132) and the percentage of oxygen was calculated by the difference. The forms of sulfur were determined by following standard methods (ASTM D 2492). The calorific values (CVs) were determined by using a Bomb calorimeter (ASTM D 3286). The ash analysis of the coal samples was carried out by standard methods.^{24,25} The averages of quadruplicate analyses for ultimate, proximate, and ash composition of the coal samples are given in Tables 1 and 2, respectively.

The Fourier transform infrared spectroscopy (FTIR) spectra of the coal samples are recorded by Perkin-Elmer System 2000, model 640B by using a KBr pellet, and the X-ray diffraction analysis (XRD) patterns are recorded by a X-ray diffractometer, model JDX11 PZA, JEOL, Japan, using Cu Kα Fe-filtered X-ray radiation ($\lambda = 1.5426 \text{ Å}$).

Static Aqueous Leaching. A simulation study by static leaching for the generation of AMD has been carried out in the laboratory by taking 50 g each of the coal samples and adding 250 mL of deionized water in a 1 L conical flask at atmospheric conditions. The mixture was stirred at a temperature of 25 °C for a period of 120 h. Using a microprocessor-based water and soil analysis kit, model 1160E, pH, conductivity, and total dissolved solids (TDS) of the leachate at different time intervals were recorded, while the SO₄⁻² ion concentrations were determined by standard gravimetric

Table 1. Ultimate and Proximate Analysis of Raw Coals (as Received, wt %)

parameters (wt %)	Ledo	Baragolai
proximate		
moisture	3.07	2.40
ash	10.35	5.70
volatile matter	43.38	47.40
fixed carbon	43.20	44.50
forms of sulfur		
total sulfur	3.57	5.30
pyritic sulfur	0.58	0.61
sulfate suphur	0.43	0.53
organic sulfur	2.56	4.16
ultimate analysis		
C	70.00	68.50
Н	4.80	5.20
N	1.10	1.20
O (by the difference)	20.53	19.80
CV (kcal/kg)	5633.00	5839.00

Table 2. Ash Composition of Raw Coals (wt %)

coal	SiO_2	Fe_2O_3	MgO	CaO	SO_3	TiO_2	Al_2O_3	others
Ledo	63.1	9.7	0.7	1.1	0.5	0.5	23.60	0.80
Baragolai	60.6	10.0	1.7	0.7	0.4	1.2	21.76	3.64

methods²⁵ (Table 3). The aqueous leachates for Ledo and Baragolai coals after 4, 8, and 120 h, respectively, are collected and analyzed for the presence of metals (Tables 4 and 5). In another set of experiments, aqueous leaching of samples up to 120 h at different temperatures of 15, 25, 35, and 45 °C was carried out. The leachates L1, L2, and L3 and B1, B2, and B3 for Ledo and Baragolai coals at 25 °C were designated as aqueous leachates obtained after 4, 8, and 120 h of leaching, respectively. The elemental concentrations in the leachates were determined by using an atomic absorption spectrophotometer (Perkin-Elmer AAS, model 2380).

Aqueous Depyritisation. The catalytic effect of bacteria has been well-documented. Many compounds are screened as bactericides. To compare the effect of biological and normal aqueous oxidation of pyrite in coals and bactericides, sodium dodecyl sulfate (SDS) was introduced to understand the nature of biological oxidation of pyrite in coal26 during leaching. The effect of bactericides on pH during leaching of the coal samples has been compared (Table 6). However, the present study attributed the nonsignificant effect of bactericide on the aqueous leaching of high sulfur coals.

After leaching at 15, 25, 35, and 45 °C, the coals were recovered and pyritic sulfur contents were determined by standard methods (ASTM D 2492). The results for both the coal samples are given in Tables 7 and 8. The kinetic parameters derived from the oxidation of pyrites in aqueous medium for the coal samples are given in Table 9.

Results and Discussion

Characteristics of the coal samples (Table 1) evidenced low ash, high volatile matter, and high CV. Ledo coal contains 28.2 and 71.7% of inorganic and organic sulfur, while Baragolai coal contains 21.51 and 78.49% of inorganic and organic sulfur, respectively. Chemical analysis of major oxides in ash shows that the major ash constituent of both of the coals is silica, followed by alumina and iron oxides.

Physicochemical parameters, pH, conductivity, TDS, SO₄⁻², and total acidity of the aqueous leachates for both of the coal samples at different times of leaching are given in Table 3, which increases with the time of leaching. The results show that the pH of the leachates falls immediately after the addition of water into the coal samples and was constant up to 120 h of

⁽²⁰⁾ Wewerka, E. M.; Williams, J. M.; Wagner, P.; Wanger, L. E.; Bertino, J. P. Control of trace element leaching from coal preparation wastes. In Proceedings of the Symposium on Coal Cleaning to Achieve Energy and Environmental Goals; U.S. Environmental Protection Agency: Hollywood, FL, Sept 1978; Vol. 2, p 856-874.

⁽²¹⁾ Duncan, D. W.; Bruynesteyn, A. Determination of APP of Waste Materials; Mater. Soc., AMIE, paper A, 1979; p 10.

⁽²²⁾ Singer, P. C.; Stumm, W. Science 1990, 167, 1121.

⁽²³⁾ Luther, G. W. Geochim. Cosmochim. Acta 1987, 51, 3193-3199.

⁽²⁴⁾ Himus, G. W., Ed. Fuel Testing, Laboratory Methods in Fuel Technology; Penguin: London, U.K., 1954; pp 67-78.

⁽²⁵⁾ Vogel, A. I. A Textbook of Quantitative Inorganic Analysis, Including Elementary Analysis; Wiley: New York, 1969.

⁽²⁶⁾ Erickson, P. M.; Ladwig, K. J. Control of Acid Formation by Inhibition of Bacteria and by Coating Pyrite Surfaces; Final Report to the West Virginia Department of Energy, Division of Reclamation, Charleston, WV. 1983.

2880.0

2880.0

2880.0

2880.0

2880.0

	Ledo							Barag	olai	
time (h)	pН	conductivity (ms/cm)	TDS (ppm)	acidity (mg of CaCO ₃ /L)	SO ₄ ⁻² (mg/L)	рН	conductivity (ms/cm)	TDS (ppm)	acidity (mg of CaCO ₃ /L)	SO ₄ ⁻² (mg/L)
0	7.3	0	0	ND	0	7.3	0	0	ND	0
0.5	2.6	1.7	4505.9	780.0	3559	3.5	1.5	3815.7	568.0	2534.0
1	2.6	1.7	4505.2	782.1	4161	3.3	1.5	3816.7	632.1	2854.0
1.5	2.5	1.8	4506.9	790.0	4260	3.3	1.8	3816.9	632.5	2864.0
2	2.5	1.9	4508.4	790.0	4272	3.1	1.8	3817.1	634.5	2869.0
2.5	2.4	1.9	4509.4	790.0	4272	3.2	1.8	3818.2	644.3	2869.0
3	2.5	1.9	4510.7	790.0	4272	3.1	1.9	3818.3	644.3	2870.0
3.5	2.5	2.0	4511.9	790.0	4272	3.1	1.9	3818.5	644.3	2870.0
4	2.5	2.0	4512.1	790.0	4275	3.1	1.9	3820.7	644.3	2870.0
4.5	2.5	2.2	4512.6	790.0	4275	3.1	2.0	3821.7	644.3	2879.0
5.0	2.5	2.2	4520.2	790.0	4275	3.1	2.0	3822.1	644.3	2879.0

Table 3. Physicochemical Analysis of Aqueous Leachates of Ledo and Baragolai Coals at 25 °C

4275 Table 4. Distribution of Metals in the Aqueous Leachates and Ledo Coal at 25 $^{\circ}\mathrm{C}$

4275

4275

4275

4275

3.1

3.1

3.1

3.1

2.1

2.1

2.1

2.1

3822.7

3822.8

3823.0

3823.2

3823.2

644.3

644.3

644.3

644.3

644.3

metals ppm	original coal	L1 $(4 \text{ h})^a$	L2 (8 h) ^a	L3 (120 h) ^a	regulatory levels
Fe	6240	1363 (21.84)	1414.75 (22.67)	1435.25 (23.0)	1.0
Mg	424.35	345.7 (81.47)	347.0 (81.77)	348.25 (82.1)	150
Bi	1700	4.75 (0.28)	6.47 (0.39)	7.21 (0.42)	
Al	1315	399.5 (30.48)	400.75 (30.48)	401.39 (30.52)	15.0
V	140	1.5 (1.07)	2.0 (1.42)	4.4 (3.14)	
Cu	120	3.6 (3.02)	6.05 (5.04)	6.25 (5.2)	3.0
Cd	60	2.5 (4.17)	2.75 (4.58)	2.91 (4.85)	2.0
Ni	20.7	8.2 (39.85)	8.75 (42.27)	8.78 (42.4)	1.8
Pb	4	2.5 (62.5)	2.5 (62.5)	2.8 (70.0)	0.1
Mn	4	2.5 (62.5)	2.5 (62.5)	2.8 (70.0)	0.5

^a Percent of release.

2.5

2.5

2.5

2.5

6.0

6.5

7.0

8.0

120

2.2

2.3

2.3

2.3

2.3

4523.1

4530.1

4532.1

4533.0

4533.1

790.0

790.0

790.0

791.0

791.0

Table 5. Distribution of Metals in Aqueous Leachates of Baragolai Coal at 25 °C

metals ppm	original coal	B1 (4 h) ^a	B2 (8 h) ^a	B3 (120 h) ^a	regulatory levels
Fe	3990	632.5 (15.85)	792.5 (19.86)	814.0 (20.40)	1
Mg	603	535.2 (88.75)	539.7 (89.50)	541.7 (89.83)	150
Bi	1423.5	4.27 (0.29)	6.3 (0.44)	7.12 (0.50)	
A1	6320	207.2 (3.13)	209.3 (3.15)	211.2 (3.18)	15
V	58.72	2.8 (4.77)	2.8 (4.77)	4.6 (7.83)	
Cu	30.62	7.98 (26.1)	9.9 (32.50)	10.1 (32.99)	3
Cd	38.21	1.5 (3.93)	1.7 (4.50)	1.9 (4.98)	2
Ni	18.7	12.58	13.43 (71.80)	13.59 (72.67)	1.8
Pb	21.38	2.25 (11.5)	2.9 (13.56)	2.9 (13.56)	0.1
Mn	34.32	5.3 (15.4)	5.8 (16.89)	5.8 (16.89)	0.5

^a Percent of release.

Table 6. Effect of Bactericides (SDS) on pH during Normal Aqueous Leaching of Coals

coals	Ledo coal +	Ledo coal + water +	Baragolai coal +	Baragolai coal + water +
	water leachate	SDS leachate	water leachate	SDS leachate
pH (after 120 h)	2.3	2.4	3.1	3.2

aqueous leaching. Ledo and Baragolai coal leachates show the ultimate pH value of 2.5 and 3.1 after 120 h of leaching, respectively. The conductivity of coal leachates is found to be 2.3 and 2.1 for Ledo and Baragolai after 120 h of leaching, respectively. The pH values 2.5 and 3.1 of simulated acidic water (AMD) was found in good agreement with the reported pH values of effluent water from high sulfur coalmine areas.²⁷

The acidity of the leachates from the coal has significant relationships with pH and the time of leaching. It can be attributed from the study that the acidity increases with the decrease in pH and an increase in the leaching time. The precipitate of soluble iron to form Fe(OH)₃ coats the bottom of the receiving stream. The acidity after 120 h of leaching was found to increase from 780 to 791 mg/L of CaCO3 for Ledo coal leachate and from 568.0 to 644.3 mg/L of CaCO3 for Baragolai coal leachate. The TDS values were found to increase marginally and remain almost constant in both of the coal leachates (Table 3). The conductivities produced during aqueous leaching for the samples are found to increase with the time of leaching and remain constant after 6.5 and 6.0 h for Ledo and Baragolai coal leachates, respectively. The increase in conductivity is due to the presence of sulfate and other ions in the leachates. The concentration of sulfate ions found was 4.27 and 2.88 g/L for Ledo and Baragolai coal leachates after 120 h of leaching, respectively.

The release of trace and heavy metals after 4, 8, and 120 h of leaching of Ledo and Baragolai coals as shown in Tables 4 and 5 is quite high and increases with the increase in the leaching time. Cd, Ni, Pb, and Mn are identified as hazardous air

⁽²⁷⁾ Rawat, N. S.; Vishawanathan J. Mines, Met. Fuels, Jan-Feb 1990.

Table 7. Variation of Pyritic Sulfur (wt %) with Temperature and Time of Leaching of Ledo Coal

time of stirring	pyritic sulfur (wt %) at different temperatures					
(h)	15 °C	25 °C	35 °C	45 °C		
0	0.58	0.58	0.58	0.58		
4	0.49	0.48	0.45	0.43		
8	0.39	0.37	0.35	0.34		
12	0.29	0.27	0.25	0.24		
16	0.25	0.23	0.23	0.22		
20	0.20	0.20	0.19	0.18		
24	0.18	0.15	0.16	0.15		
80	0.16	0.15	0.14	0.13		
120	0.16	0.15	0.14	0.13		

Table 8. Variation of Pyritic Sulfur (wt %) with Time and Temperature of Leaching in Baragolai Coal

time of stirring	pyritic sulfur (wt %) at different temperatures					
(h)	15 °C	25 °C	35 °C	45 °C		
0	0.61	0.61	0.61	0.61		
4	0.52	0.51	0.47	0.45		
8	0.45	0.44	0.42	0.40		
12	0.36	0.31	0.28	0.27		
16	0.31	0.27	0.22	0.20		
20	0.25	0.22	0.19	0.19		
24	0.23	0.18	0.17	0.16		
80	0.18	0.16	0.15	0.14		
120	0.18	0.16	0.15	0.14		

Table 9. Kinetic Parameters for Aqueous Oxidation of Pyritic Sulfur in Ledo and Baragolai Coals

coal samples	temp (°C)	equilibrium constant (K_c)	specific rate constant (k s ⁻¹)	activation energy (E _a) (kJ mol ⁻¹)	frequency factor (A) (dm³ mol ⁻¹ s ⁻¹)
	15	0.7759	10.26×10^{-2}		
Ledo	25	0.8273	11.91×10^{-2}	8147.72	8.8405×10^{-4}
	35	0.8448	12.61×10^{-2}		
	45	0.8966	13.54×10^{-2}		
	15	0.7049	10.24×10^{-2}		
Baragolai	25	0.7377	11.50×10^{-2}	5007.00	2.6494×10^{-4}
	35	0.7541	14.32×10^{-2}	5237.82	2.0494 × 10
	45	0.7705	14.73×10^{-2}		

pollutants (HAP) by 1990 Clean Air Act amendments (CAAA).²⁸ The distribution (wt %) of major and minor elements at different times shows that the increase in the leaching time at constant pH enhances the release of metals to the leachates (Tables 4 and 5). In this study, 120 h of leaching has been considered to be optimum, while pH is found to remain constant. Concentrations of all of the elements evaluated were observed to be above the regulatory levels.²⁹⁻³³

Because of relative abundances in coals, Fe, Mg, Al, Ni are released in high quantities. The other two fairly less abundant elements, Pb and Mn, are also observed to be released in relatively higher quantities. The variation in metal leaching from the coal samples in aqueous medium is significantly observed. Of the 10 elements (viz., Fe, Mg, Bi, Al, V, Cu, Cd, Ni, Pb, and Mn) determined, Bi and V were released from the coal with a minimum of 0.42 and 3.14% for Ledo and 0.50 and 7.83% for Baragolai coals, respectively. The release of Mg has been

found to be 82.06 and 89.83%, whereas Ni was found to be 42.41 and 72.67% for Ledo and Baragolai coals, respectively. The presence of these metals in the leachates indicated their association with the mineral or inorganic phases of the coals. It can very well be attributed that the metals present in organic phases cannot be released easily by water. Metals present in coal as disulfides³⁴ are responsible for their release in aqueous leachates. Some other minerals are also reported to be associated with pyrite such as chalcopyrite, chalcocite, bornite, arsenopyrite, tetrahedrite, galena, sphalerite, marcasite, millerite, siderite, etc.³⁵ This study has brought out a significant relationship in determining the association and mobility of metals in the AMD-affected areas. The pyritic sulfur contents in the residual coal samples after aqueous leaching with respect to time are given Tables 7 and 8 for Ledo and Baragolai coals, respectively. The variation of pyritic sulfur against time and temperature is clearly observed from the study. The loss of pyritic sulfur is due to normal atmospheric oxidation in aqueous medium.

The XRD pattern (d values, in angstroms) indicates some of the mineral phases in the raw coal samples viz., illite (4.497), α-quartz (4.262, 3.353, 2.460, 2.282, 2.236, 2.130, 1.982, 1.818, 1.696, 1.545, 1.487, 1.454, 1.374, and 1.310), hematite (3.694, 2.700, 2.520, 2.282, 2.213, 1.842, 1.696, 1.545, 1.374, and 0.963), and chlorite (3.495). The FTIR data (adsorption, in cm⁻¹) of these coal samples also show the presence of α -quartz (1031.9, 1009.8, 937.4, 779.6, 694.9, 471.6, 430.4, and 394.2), rutile (471.6), hematite (1093.4, 1009.8, 798.9, 752.0, 694.9, 537.6, 471.6, 430.4, and 394.2), calcite (779.6), illite (1031.9), and albite (1164.4, 1093.6, 1009.8, 798.9, 779.6, 626.6, 537.6, 471.6, and 430.4), which is in agreement with the XRD detections of mineral phases.

Kinetics of Depyritisation. Aqueous leaching of this coal for 120 h shows pyritic sulfur removal of 77.59% at 45 °C, 75.86% at 35 °C, 74.14% at 25 °C, and 72.41% at 15 °C for Ledo and 77.05% at 45 °C, 75.41% at 35 °C, 73.77% at 25 °C, and 70.49% at 15 °C for Baragolai coals, respectively. The removal of pyritic sulfur by atmospheric aqueous oxidation increases with the rise in temperatures of the systems. Earlier work³⁶ also reports that, when coal is exposed to an oxidizing atmosphere in an aqueous media, first pyrite content in coal is rapidly converted to sulfate.

To understand the reaction kinetics of pyrite oxidation, activated complex theory (ACT) is applied. Assuming the ACT to be true for the depyritisation, the reaction proceeds with the initial formation of an intermediate activated complex (I), which is at equilibrium with the reactants, and a certain fraction decomposes, resulting in sulfur loss.³⁷

pyrite sulfur + water/air
$$\Delta$$
 [pyrite sulfur-water/O₂] \rightarrow I

pyrite sulfur loss

The formation of I is the slowest step, the rate-determining step of the reaction

$$-d[pyrite-sulfur]/dt = k[pyrite-sulfur]$$
 (1)

where k is the rate constant and is computed graphically by

⁽²⁸⁾ U.S. Public Law 101-J49, Clean Air Act Amendments, Title 3, 104 state 2531-2535, 1990.

⁽²⁹⁾ Swarup, R.; Mishra, S. N. Encyclopedia of Ecology, Environment and Pollution Control-12; Jauhari, Mittal Publication: New Delhi, India, 1992

⁽³⁰⁾ Mohammed, A.; Najar, P. A. M. J. Ind. Pollut. Control 1997, 13, 85 - 106.

⁽³¹⁾ Forster, U., Wittman, G. T. W., Eds.; Metal Pollution in the Aquatic Environment; Springer-Verlag: New York, 1981; p 30.

⁽³²⁾ Sawyer, C. N., McCarly, P. C., Eds.; Chemistry for Environmental Engineering; McGraw-Hill, Inc.: Singapore, 1978; p 517.

⁽³³⁾ Indian Standards for Industrial and Sewage Effluents' Discharge; IS: 2490, 1982.

⁽³⁴⁾ Baruah, M. K.; Kotoky, P.; Baruah, G. C. Fuel 2003, 82, 1783-1791.

⁽³⁵⁾ Dana, E. S., Ford, W. E., Eds.; A Textbook of Mineralogy; Asia Publishing House: India, 1962.

⁽³⁶⁾ Yaman, S.; Kucukbayrak, S. Fuel 2000, 79, 777-783.

⁽³⁷⁾ Rakshit, P. C. Physical Chemistry; Sarat Book House: Calcutta, India, 1995; p 632.

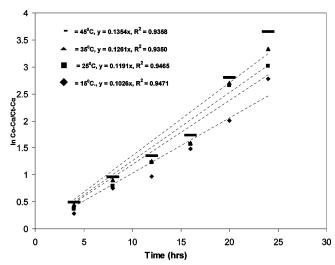


Figure 1. Pseudo-unimolecular kinetic plot for pyritic sulfur oxidation of Ledo coal at different times.

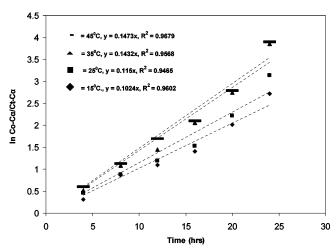


Figure 2. Pseudo-unimolecular kinetic plot for pyritic sulfur oxidation of Baragolai coal at different times.

applying appropriate regression methods. The experimental data (Tables 7 and 8) on depyritisation of the two coals have been found to follow the pseudo-first-order reaction kinetics;³⁷ thus

$$k = 1/t \ln C_0 - C_{\infty}/C_t - C_{\infty} \tag{2}$$

Here, C_0 , C_t , and C_∞ stands for the concentrations of pyritic sulfur in the coal samples at 0, t, and infinity (say 120 h).

Arrhenius plots (Figure 3) based on the rate constants from Figures 1 and 2 gave activation energies at 8.1477 and 5.238 kJ mol $^{-1}$ for the depyritisation of Ledo and Baragolai coals in aqueous media. The intercepts of the plot yield the frequency factors (*A*) of 8.8405 × 10 $^{-4}$ and 2.6494 × 10 $^{-4}$ dm 3 mol $^{-1}$ s $^{-1}$ for Ledo and Baragolai coals, respectively, leading to the oxidation of pyritic sulfur in water media.

A semiquantitative thermodynamical approach has been considered here for understanding the depyritisation of the coal samples in aqueous medium. The Gibbs free energy of activation for the formation of the activated complex I is determined by applying the reaction isotherm.³⁸

$$\Delta G^* = -RT \ln K_c \tag{3}$$

where K_c is the equilibrium constant, R is the universal gas

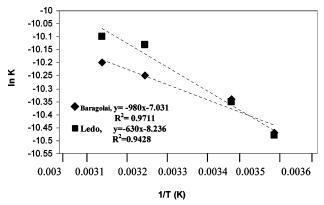


Figure 3. Arrhenius plot for the aqueous pyritic sulfur oxidation in Ledo and Baragolai coals.

constant, and T is the reaction temperature in Kelvin. K_c is expressed in terms of the pyrite sulfur loss to the total coal pyritic sulfur.

The changes in the entropy of activation H^* for the formation of the activated complex at equilibrium is calculated using the well-known Gibbs—Helmholtz equation

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{4}$$

where the heat content or enthalpy of activation for the formation of the activated complex at equilibrium is calculated by application of the ACT.³⁹

$$E_{a} = \Delta H + RT \tag{5}$$

Specific rate constants for the depyritisation in the aqueous system for the two coal samples are presented in Table 9. The linear type of plot obtained by the regression (R^2) method supported the pseudo-first-order reaction kinetics. Values of rate constants show low depyritisation, which is kinetically very slow. Yaman et al.³⁹ has also reported the very slow rate of this type of aqueous oxidation of lignite. The rate constants are found to increase with the rise of temperature of the reacting system. This is in accordance with the usual temperature dependence of the rate of a chemical reaction. Moreover, a smaller value of E_a may be due to higher effective changes on the metal concentration, resulting in a lower Fe-S formation than the dissociation energy of the pyritic compound in the activated complex.

The usual interpretation of the frequency factor is the number of successful collisions between the reacting species in forming the activated complex.³⁸ The values of the frequency factors in these systems (Table 9) suggest the associated type of the depyritisation reaction because these reactions have low frequency factors.³⁷ Because the low frequency factors govern the formation of the activated complex, it adversely controls the kinetics of pyrite oxidation in water media.

Conclusion

The aqueous leaching of these coals has shown that these coals are amenable to atmospheric weathering and lead to the formation of AMD by the oxidation of pyrites present in these coals. The highly acidic water formed during the leaching of these coals enhances the mobilization of associated trace and heavy metals.

The oxidation of pyrites in these coals follows pseudo-firstorder reaction kinetics.

⁽³⁸⁾ Moore, W. J. Basic Physical Chemistry; Prentice Hall: New York, 1989.

Such an investigation will help in attributing environmental mitigation and management approaches in relation to gainful utilization of high sulfur coals of NE India.

Acknowledgment. Financial Grant (reference number 19-79/ 98-RE, dated August 29, 2001) from the Ministry of Environment and Forests, New Delhi, India, is gratefully acknowledged. The authors are also thankful to the Director, RRL, Jorhat, for giving permission to publish the paper and Dr. H. P. Deka Baruah, Scientist, RRL, for his suggestions.

EF049701Y