

Demineralization and Desulfurization of High-Sulfur Assam Coal with Alkali Treatment

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Demineralization and desulfurization of high-sulfur coal from Assam (Makum coalfield), India, was investigated using aqueous solutions of sodium hydroxide, potassium hydroxide, and their mixtures (1:1) alone as well as followed by mild hydrochloric acid treatment. Compared to the alkali and acid alone, successive treatments with the alkali and acid resulted in significant removal of mineral matter and sulfur from the coal. Demineralization and desulfurization was found to increase with the increase in alkali concentration. Alkali treatment resulted in formation and precipitation of sodium/potassium aluminosilicates, which subsequently undergo decomposition and solubilization in the presence of acid-forming soluble salts. It is possible to remove 50–54% of the ash, total inorganic sulfur, and around 25% organic sulfur from the coal by treatment with mixtures (1:1) of 16% sodium hydroxide and potassium hydroxide solution followed by 10% hydrochloric acid.

Introduction

High-ash and high-sulfur coals are unsuitable for efficient use in carbonization, combustion, gasification, liquefaction, etc., purposes. Utilization of such coals leads to environmental pollution and other deleterious effects. The high-quality coal reserves in the world are gradually being depleted and therefore there is a growing interest in utilizing the inferior grades of coal which contain high ash and sulfur. It is necessary to demineralize and desulfurize such coals prior to utilization.

The major minerals commonly found in coals are silicates; clay minerals such as kaolinite, illite, etc.; quartz; sandstone; pyrites; and carbonates such as siderites and ankerites, etc.¹ Demineralization and desulfurization of coal can be achieved by both physical and chemical methods. The effectiveness of the different methods of demineralization and desulfurization depends on the structure and composition of the minerals and on the place and time of their deposition and formation.^{1,2} Physical methods are based on the differences in the physical properties of the minerals and the carbonaceous part of the coal. Chemical methods are effective for removing mineral matters which are finely distributed and bound strongly to the coal.

Chemical cleaning of coal with alkali and acid solution has proved effective in reducing significant amounts of ash-forming minerals, pyritic sulfur, and organic sulfur from coal.^{3–15} Norton et al.¹¹ reported removal of 60–90% ash and sulfur from some bituminous coals from

New Zealand using fused caustic. Markuszewski et al.⁹ treated several bituminous coals with molten mixtures of NaOH and KOH at 350–370 °C and could remove 80–90% ash and 70–80% total sulfur. In TRW Gravimelt process^{5,7} revealed that mixtures of NaOH and KOH rather than NaOH alone desulfurize coal more efficiently. Kusakabe et al.¹⁵ also reported that sulfur removal from coal samples depends on the KOH content in the NaOH and KOH mixtures used in leaching.

Leaching with aqueous solutions of caustic soda alone or followed by mild acid at a relatively low temperature and pressure also removes considerable amounts of ash

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and sulfur from various coals. Arya et al.¹⁶ achieved 29 and 30 wt % reductions in ash and total sulfur, respectively, from a subbituminous coal from Chile by treatment with 10% sodium hydroxide solution at 80 °C for 8 h. Kara and Ceylan¹⁷ achieved removal of 60 wt % total sulfur and 65 wt % ash from some lignite samples of Turkey by treatment with 20% sodium hydroxide solution at 70 °C. Bolat et al.¹⁸ achieved about 46% demineralization of a high-ash, low-sulfur bituminous coal from Turkey by treatment with 2% aqueous sodium hydroxide solution followed by 10% mineral acid under mild conditions. Warzinski et al.¹⁹ achieved complete removal of pyritic sulfur and 40% organic sulfur from coal by treatment with aqueous sodium hydroxide solution at 300 °C. Yang et al.²⁰ reported that both pyritic and organic sulfur in bituminous coal react with sodium hydroxide solution at 190–200 °C. Mukherjee and Borthakur²¹ achieved removal of 43–50% of the ash, total inorganic sulfur, and around 10% organic sulfur from Assam coal by treatment with 16% sodium hydroxide solution followed by 10% hydrochloric acid at 95 °C. Mukherjee and Borthakur²² reported removal of 23–32% mineral matter at ambient temperature and 25–40% at 95 °C using mineral acids. The acids at 10% concentration level can remove 8–23 and 14–39% sulfur from the coal samples. Mukherjee and Borthakur²³ also reported removal of 28–45% ash, 22–35% total sulfur, and 11–15% organic sulfur with 16% potassium hydroxide solution followed by 10% hydrochloric acid at 95 °C. Mukherjee et al.²⁴ also observed complete removal of sulfate, pyritic, about 26–31% organic sulfur, and 43–45% ash from the coal samples by treatment with H₂O₂ in the presence of 0.1 N H₂SO₄. Sain et al.²⁵ 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 demineralize and desulfurize Assam coal.

There are large reserves (over 250, million tones) of coal in Assam and other states in the North-Eastern region of India.²⁶ These coals are subbituminous in rank, characterized by high (2–7%) sulfur, high (30–50%) volatile matter, high (18–30) caking index (for the coking coals), high (6500–8000 kcal/kg) calorific value, high fluidity, and low (1000–1050 °C) ash fusion temperature. The ash content of the coal is usually low (3–15%), but due to open cast and mechanical mining and wining of the coal from lower horizons the ash content is gradually increasing. The coals contain sulfur in the forms of sulfate, pyritic, and organic.^{27–29} Another form,

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	43.2
ultimate analysis (wt % dry basis)		
carbon	68.8	70.0
hydrogen	5.1	5.2
sulfur	4.2	4.3
nitrogen	1.5	1.4
oxygen (diff)	20.4	19.1
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)	7527	7327

termed secondary sulfur containing Fe–S moiety associated with organic matter has also been reported.²⁹ The high sulfur restricts large-scale utilization of these coals. Assam coal with low ash finds major use as a blend in metallurgical coke preparation for steel making. The coke for the purpose should have low (5–7%) ash and low (maximum 0.7%) sulfur.

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. 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. The present communication reports the effect of aqueous solution of sodium hydroxide, potassium hydroxide, and their mixtures (1:1) alone and followed by mild hydrochloric acid treatment on demineralization and desulfurization of high-sulfur subbituminous Assam coal.

Experimental Section

The coal samples used in the investigation were collected from Boragolai and Ledo collieries of Makum coalfield, Assam, belonging to North-Eastern coalfields, India. The samples were stored under atmospheric conditions for a few months, ground, and fractionated to –212 μm fineness. The proximate analysis of the coal samples was done by following standard methods [ASTM D 3172]. The percentages of carbon, hydrogen, and nitrogen were estimated by using a Perkin-Elmer (model 2400) elemental analyzer and total sulfur by following the 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 of 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 ground samples (about 10 g) were mixed with 50 mL of alkali [NaOH, KOH, and NaOH + KOH (1:1)] solution of different concentrations and refluxed

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Table 2. Chemical Analysis of Coal Ash

source	constituents (wt %)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	SAR
Boragolai	57.9	18.9	11.9	3.9	4.7	0.1	1.4	0.8	3.06
Ledo	54.8	21.8	12.7	2.6	3.8	0.2	1.2	1.3	2.51

SAR (silica/alumina ratio).

with stirring for 8 h at 95 °C. The reaction mixtures were cooled, filtered, and the residues were washed repeatedly with distilled water until free of alkali. The color of the filtrates was found to change from light yellow to brown, depending on the alkali concentration. During the reaction, the soluble inorganic constituents have dissolved and been converted into water-soluble products. The alkali-treated coal samples were subsequently dried and then suspended in 50 mL of 10% hydrochloric acid solution. The mixtures were stirred under reflux for 8 h at 95 °C, filtered, washed, and dried by adopting the same procedure as detailed above. The coal samples were again washed several times with water until neutral to litmus paper, dried at 90 °C, and analyzed for ash and forms of sulfur. The cation-exchange capacity of the samples was determined by following reported method. About 0.2 g of finely ground sample was mixed with 25 mL of 0.1 N CaCl₂ solution in an Erlenmeyer flask. The mixture was allowed to stand for 18 h at room temperature with intermittent shaking for equilibration. It was filtered and the residue was washed four to five times with 75% methanol followed by until free from chloride. The calcium ion absorbed was displaced by slow leaching the residue with 30 mL of 0.1 N KCl (5 times) and estimated using EDTA. XRD patterns and FTIR spectra were used to characterize the mineral present in the coal. The XRD patterns were obtained using a Philips Analytical X-ray B.V. diffractometer. The FTIR spectra in the range of 4000–375 cm⁻¹ were recorded in a KBr disk using an FTIR 2000 Perkin-Elmer spectrophotometer.

Results and Discussion

The chemical analysis (Table 2) shows that the major constituents of coal ash are silica (over 50%) followed by alumina and iron oxide. These three together constitute around 89% of the ash. Boragolai coal ash is more siliceous (SiO₂/Al₂O₃, weight ratio 3.06) than Ledo coal ash (SiO₂/Al₂O₃, weight ratio 2.51).

XRD patterns and FTIR spectra (Figures 1 and 2) indicate presence of quartz as the major and dominant crystalline material in both the coal samples followed by clay minerals. The clay minerals identified are kaolinite, illite, chlorite, etc. The coal samples also contain small to trace amounts of calcite, pyrite, marcasite, and amorphous materials. Ledo coal in addition contains gypsum and feldspar. The high silica/alumina ratio in Boragolai coal ash suggests that the coal contains relatively high amount of free silica, which may be both crystalline (quartz) or amorphous.

The effect of leaching the coal samples with different reagents on ash removal is presented in Tables 3 and 4. It shows that 10% hydrochloric acid treatment leads to around 28 and 20 wt % demineralization of Boragolai and Ledo coals, respectively. Carbonates and many oxides, sulfates, sulfides, many zeolites, sodalites, etc., are soluble in hydrochloric acid.^{30–32} Aqueous sodium hydroxide alone has a very small effect on reduction of the ash content and that too at relatively low concentration. In the case of Boragolai coal, demineralization (3.4 wt %) was observed only with 2% sodium hydroxide

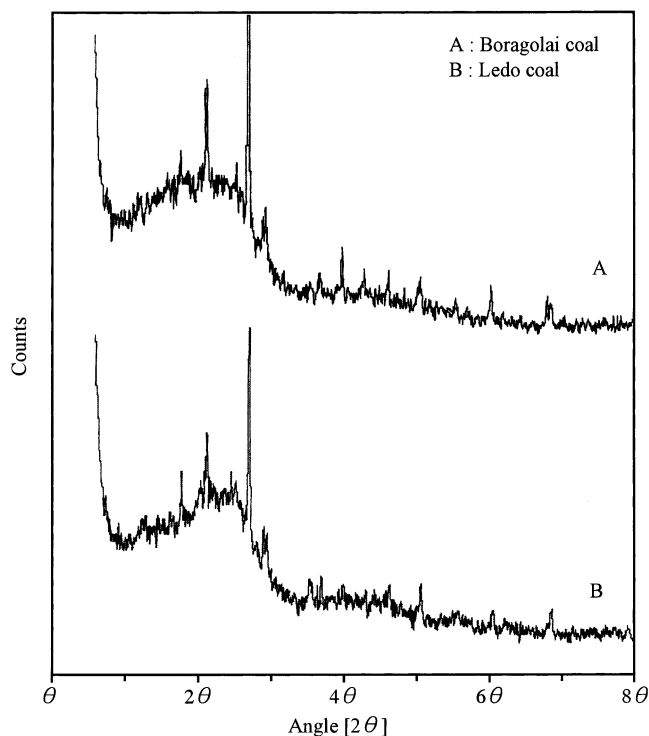


Figure 1. XRD patterns of coal samples.

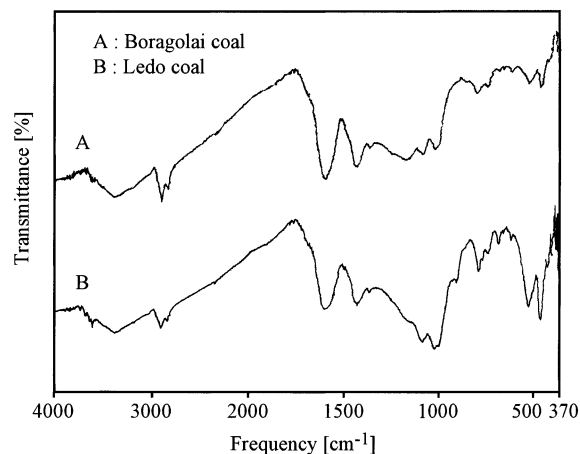


Figure 2. FTIR spectra of coal samples.

solution and at higher alkali concentration, the ash content increases. In the case of Ledo coal also maximum demineralization (10.0 wt %) was observed with 2% sodium hydroxide solution. Demineralization of the coal samples was found to decrease with increase in concentration of the alkali.

Demineralization of Ledo coal with KOH in general is more than Boragolai coal and it increases with the concentration of the alkali. 2% KOH solution removes 6.8 and 10% ash from Boragolai and Ledo coal at 95 °C. Demineralization of Boragolai coal decreases to 2.3 and Ledo coal increases to 19.1% at 95 °C on increasing the alkali concentration to 16%. But demineralization of Ledo coal with NaOH + KOH (1:1) in general is more than Boragolai coal and it increases with the concentra-

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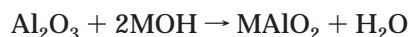
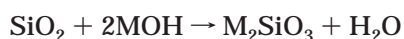
Table 3. Effect of Alkali Treatment on Demineralization of Coal Leached for 8 h at 95 °C (all results on dry basis)

treatments	Boragolai coal		Ledo coal	
	ash (%)	degree of demineralization (%)	ash (%)	degree of demineralization (%)
Nil	8.8		11.0	
NaOH				
2%	8.5	3.4	9.9	10.0
4%	9.1	<i>a</i>	10.0	9.1
8%	9.4	<i>a</i>	10.1	8.2
16%	10.6	<i>a</i>	10.2	7.3
KOH				
2%	8.2	6.8	9.9	10.0
4%	8.3	5.7	9.6	12.7
8%	8.4	4.5	9.4	14.5
16%	8.6	2.3	8.9	19.1
NaOH + KOH (1:1)				
2%	7.6	13.6	9.6	12.7
4%	7.8	11.4	9.3	15.4
8%	7.9	10.2	9.0	18.2
16%	8.1	7.9	8.4	23.6

^a Ash gain.

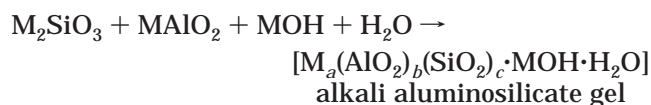
tion of the alkali. A 2% NaOH + KOH (1:1) solution removes 13.6 and 12.7% ash from Boragolai and Ledo coal, respectively, at 95 °C. Demineralization of Boragolai coal decreases to 7.9 and Ledo coal increases to 23.6% at 95 °C on increasing the alkali concentration to 16%. Alkali concentration and temperature are kinetic factors in mineral dissolution. The decreased demineralization of the coal samples with increase of these factors indicates that mineral dissolution reactions are followed by some precipitation of some substance.

The gain in ash content or decrease in degree of demineralization of the coal samples with increase in alkali concentration is attributed to alkali aluminosilicate formation. Many earlier workers also observed an increase in ash content of coal on alkali treatment and attributed it to the formation of insoluble alkali complexes, zeolite, sodalite, etc.^{1,20,30} Alkali dissolves silica and alumina from clay and other silica- and alumina-bearing materials present in the coal forming soluble alkali silicate and aluminate. The reaction may be represented in simplified ways as



where M = Na or K.

When the concentration of the silicate and aluminate ions in the alkaline solution exceeds the solubility product of alkali aluminosilicates, the latter precipitates out in the form of a gel,²⁹ as per the reaction shown below schematically:



The gel on heating may convert either to zeolite or feldspathoid such as sodalite, nosalite, etc., depending on the alkali concentration. Borthakur et al.³² observed formation of hydroxy sodalite $[\text{Na}_6(\text{AlO}_2)_6(\text{SiO}_2)_6 \cdot x\text{NaOH} \cdot (8-2x)\text{H}_2\text{O}]$ on treatment of kaolinite and illite type clay with sodium hydroxide solution. Yang et al.²⁰ obtained a desilicated product which could be either

$3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ or $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{SO}_4$ (nosalite) or probably both by digesting coal with caustic soda solution at 300 °C. The effect of alkali treatment on ash reduction being less with Boragolai coal, this coal is likely to contain a larger amount of alkali-soluble silica and alumina. Continuous decrease in ash removal or gain in ash with alkali concentration and reaction time is therefore attributed to progressive precipitation of alkali aluminosilicates which accumulates with the coal. This can happen when more and more silica and alumina from the coal dissolves out.

The CEC (cation exchange capacity) of the samples presented in Table 5, continuously increases with alkali concentration. This suggests that formation and accumulation of sodium and potassium aluminosilicates gel increase with increase in concentration of the alkali. Alkali aluminosilicates gel can entrap water molecules, alkali and soluble salts.

Alkali extracts of the coal samples (not shown in Table) contain SiO_2 , Al_2O_3 , Fe_2O_3 , Ca^{2+} , Mg^{2+} , SO_4^- , etc., constituents. This is attributed to dissolution of water-soluble materials such as sulfates of calcium and magnesium present in the coal or conversion of some water-insoluble component to soluble salts due to reaction with the alkali. Alkali reacts with sulfides and materials containing SiO_2 , Al_2O_3 , Fe_2O_3 , etc. and acidic oxides (such as amorphous silica, quartz, clay minerals, etc.), forming soluble sulfates, alkali silicates, aluminates, ferrates, etc. The solubility of these constituents changes with the nature and composition of the parent material. Amorphous silica dissolves more than crystalline silica and the solubility of the clay minerals are also different. Dissolved silicates and aluminates may interact and form sparingly soluble alkali aluminosilicates hydrogel. Potassium aluminosilicates gel may precipitate when the concentration of the dissolved potassium silicate and potassium aluminate ion exceed the solubility product of potassium aluminosilicates.³²

Hydrochloric acid treatment of the alkali-treated coal results in significant reduction of mineral matter. The ash reduction is more than that achieved with the nontreated coal and is obviously due to formation of additional acid-soluble components during alkali treatment. Alkali aluminosilicate gel formed during alkali treatment undergoes decomposition in the presence of the acid-forming soluble salts. The reduction in ash content on acid treatment of the alkali-treated coal was found to increase with increase in concentration of the alkali. This is attributed to increase in dissolution of silica and alumina and consequently the amount of aluminosilicate formation with increase in alkali concentration. The degree of demineralization of Boragolai and Ledo coals by successive treatments with sodium hydroxide and acid solution increases from 40.9 and 40.0 wt % to around 50 and 44 wt %, respectively, with an increase in concentration of the alkali from 2 to 16%. Demineralization with potassium hydroxide and acid solution increases from 33 and 28 wt % to around 43 and 45 wt % on increasing the alkali concentration from 2 to 16%. Similarly a mixture of sodium and potassium hydroxide solution (1:1) also increases demineralization of Boragolai and Ledo coal from 45 and 43 wt % to around 54 and 50 wt % on increasing the alkali concentration from 2 to 16%.

Table 4. Effect of Alkali Followed by Acid Treatment on Deminerlization of Coal Leached for 8 h at 95 °C (all results on dry basis)

treatments	Boragolai coal		Ledo coal	
	ash (%)	degree of deminerlization (%)	ash (%)	degree of deminerlization (%)
Nil	8.8		11.0	
10% HCl	6.3	28.4	8.8	20.0
2% NaOH + 10% HCl	5.2	40.9	6.6	40.0
4% NaOH + 10% HCl	5.1	42.0	6.5	40.9
8% NaOH + 10% HCl	4.8	45.4	6.3	42.7
16% NaOH + 10% HCl	4.4	50.0	6.2	43.6
2% KOH + 10% HCl	5.9	32.9	7.9	28.2
4% KOH + 10% HCl	5.5	37.5	7.4	32.7
8% KOH + 10% HCl	5.3	39.8	6.8	38.2
16% KOH + 10% HCl	5.0	43.2	6.0	45.4
2% NaOH + KOH (1:1) + 10% HCl	4.8	45.4	6.3	42.7
4% NaOH + KOH (1:1) + 10% HCl	4.5	48.9	6.1	44.5
8% NaOH + KOH (1:1) + 10% HCl	4.3	51.1	5.9	46.4
16% NaOH + KOH (1:1) + 10% HCl	4.0	54.5	5.5	50.0

Table 5. Cation-Exchange Capacities of Treated Coal Leached for 8 h at 95 °C

concentration (%)	Boragolai coal	Ledo coal
	CEC value (mequiv/g)	CEC value (mequiv/g)
<i>a</i>	0.20	0.27
NaOH		
2	0.32	0.40
4	0.59	0.60
8	0.65	0.68
16	0.73	0.76
KOH		
2	0.45	0.53
4	0.64	0.65
8	0.75	0.83
16	0.95	0.98
NaOH + KOH (1:1)		
2	0.51	0.58
4	0.68	0.70
8	0.82	0.89
16	1.02	1.13

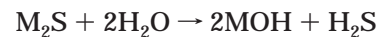
^a Values for unleached coal.**Table 6. Effect of Alkali Treatment on Desulfurization of Coal Leached for 8 h at 95 °C (all results on dry basis)**

treatments	Boragolai coal		Ledo coal	
	total sulfur (%)	degree of desulfurization (%)	total sulfur (%)	degree of desulfurization (%)
Nil	4.27		4.31	
NaOH				
2%	3.49	18.3	3.72	13.7
4%	3.46	19.0	3.68	14.6
8%	3.44	19.4	3.64	15.5
16%	3.39	20.6	3.48	19.2
KOH				
2%	3.22	24.6	3.61	16.2
4%	3.16	26.0	3.52	18.3
8%	3.05	28.6	3.45	20.0
16%	2.98	30.2	3.23	25.1
NaOH + KOH (1:1)				
2%	3.18	25.5	3.50	18.8
4%	3.13	26.7	3.41	20.9
8%	3.01	29.5	3.22	25.3
16%	2.94	31.1	3.13	27.4

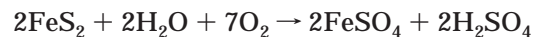
Desulfurization of the coal samples by treatment with alkali of different concentrations followed by 10% hydrochloric acid, compared to the acid and alkali alone are presented in Tables 6 and 7. Desulfurization by successive treatments of the coal samples with the alkali and acid is much higher than by treatment with the acid or alkali alone and it increases with increase in alkali

concentration. The results shows that around 33 and 30 wt % of the total sulfur present in Boragolai and Ledo coal, respectively, may be removed by treating the coal samples with 16% sodium hydroxide solution followed by 10% hydrochloric acid. Around 35 and 34 wt % of total sulfur present in Boragolai and Ledo coal may be removed by treating the coal samples with 16% potassium hydroxide solution followed by 10% hydrochloric acid. But 45 and 41 wt % of total sulfur present in Boragolai and Ledo coal, respectively, may be removed by treating the coal samples with a 16% sodium and potassium hydroxide mixture (1:1) followed by 10% hydrochloric acid.

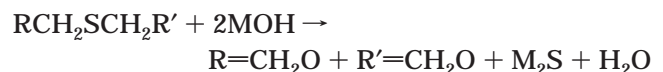
The distribution of sulfur in the coal samples is presented in Table 8. The alkali removes different forms of sulfur, sulfate, pyritic, as well as organic sulfur. Alkali may react with pyritic sulfur forming soluble sulfates as per the following reactions:



where M = Na or K. Oxidation of pyritic sulfur to soluble salts may also take place through air oxidation in aqueous medium:



Alkali may also convert some of the organic functional groups such as thiols, disulfide, etc., present in the coal to soluble salts:



where M = Na or K, and R = alkyl or aryl group.

Both the inorganic and organic sulfur in the coal may be removed to various levels depending on the alkali concentration. Almost complete removal of pyritic and sulfate sulfur and around 9–11% organic sulfur from Boragolai and Ledo coal is possible by using 16% sodium hydroxide solution followed by using 10% hydrochloric

Table 7. Effect of Alkali Followed by Acid Treatment on Desulfurization of Coal Leached for 8 h at 95 °C (all results on dry basis)

treatments	Boragolai coal		Ledo coal	
	total sulfur (%)	degree of desulfurization (%)	total sulfur (%)	degree of desulfurization (%)
Nil	4.27		4.31	
10% HCl	3.43	19.7	3.85	10.7
2% NaOH + 10% HCl	3.20	25.1	3.42	20.6
4% NaOH + 10% HCl	3.15	26.2	3.28	23.9
8% NaOH + 10% HCl	3.02	29.3	3.16	26.7
16% NaOH + 10% HCl	2.85	33.2	3.02	29.9
2% KOH + 10% HCl	3.12	26.9	3.35	22.3
4% KOH + 10% HCl	3.04	28.8	3.20	25.7
8% KOH + 10% HCl	2.93	31.4	3.12	27.6
16% KOH + 10% HCl	2.76	35.4	2.86	33.6
2% NaOH + KOH (1:1) + 10% HCl	3.03	29.0	3.10	28.1
4% NaOH + KOH (1:1) + 10% HCl	2.81	34.2	2.92	32.2
8% NaOH + KOH (1:1) + 10% HCl	2.52	41.0	2.71	37.1
16% NaOH + KOH (1:1) + 10% HCl	2.34	45.2	2.53	41.3

Table 8. Effect of Alkali Followed by Acid (10% HCl) on Distribution of Sulfur in Coal

alkali concentration (%)	sulfur distribution					
	Boragolai coal			Ledo coal		
	pyritic	sulfate	organic	pyritic	sulfate	organic
NaOH						
<i>a</i>	0.64	0.52	3.11	0.52	0.41	3.38
2	0.10	0.05	3.05	0.05	0.03	3.34
4	0.08	0.03	3.04	0.03	0.01	3.24
8	0.06	0.01	2.95	0.02	0.01	3.13
16	0.02	0.00	2.83	0.00	0.00	3.02
KOH						
2	0.04	0.03	3.05	0.03	0.02	3.30
4	0.02	0.01	3.01	0.02	0.01	3.17
8	0.00	0.00	2.93	0.01	0.00	3.11
16	0.00	0.00	2.76	0.00	0.00	2.86
NaOH+KOH (1:1)						
2	0.02	0.01	3.00	0.02	0.01	3.07
4	0.01	0.00	2.80	0.01	0.00	2.91
8	0.00	0.00	2.52	0.00	0.00	2.71
16	0.00	0.00	2.34	0.00	0.00	2.53

^a Values for unleached coal.

acid. A 16% potassium hydroxide solution removes around 11–15% organic sulfur at 95 °C which increases to around 25% using NaOH and KOH (1:1).

The removal of a large amount of organic sulfur is possibly due to low coalification rank of the coal.^{33–35} These coals contain more of the organic sulfur in aliphatic or labile form, mainly as thioethers (sulfides) and disulfides.³⁶ Sulfur distribution in Assam coal revealed the presence of mercaptan, disulfide, thiol, sulfide, and simple thiophene as the major functional-

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ities.³⁷ The strong alkali probably removes the aliphatic sulfur and some simple heterocyclic compounds present in the coal.

Conclusions

Assam coal (Boragolai and Ledo) may be conveniently demineralized and desulfurized by treating successively with aqueous solutions of sodium hydroxide, potassium hydroxide, sodium hydroxide and potassium hydroxide mixture (1:1), and hydrochloric acid. The method allows removal of 28–54% of the ash, total inorganic sulfur, and around 25% organic sulfur. Demineralization and desulfurization by alkali and acid treatment is promising for adoption as the alkali may be regenerated by various chemical means and the acid by distillation. The removal of a relatively large amount of organic sulfur is attributed to low coalification rank of the coal where most of the sulfur exists as the aliphatic or labile form.

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