CHEMICAL DEMINERALIZATION OF HIGH VOLATILE INDIAN BITUMINOUS COAL BY CARBOXYLIC ACID AND CHARACTERIZATION OF THE PRODUCTS BY SEM/EDS

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ABSTRACT

A high Volatile Indian bituminous coal was subjected to a series of organic acid treatment at room temperature. Chemical leaching experiments were carried out using organic acids such as citric acid, oxalic acid, gluconic acid, acetic acid and EDTA. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrum (EDS) analysis of the leached sample were carried out to study the efficiency of leaching. Citric acid and EDTA leaching reduced the ash content to less than 1.94% and 1.81 wt% respectively. EDTA, acetic acid and gluconic acid leaching was able to remove Ca completely with substantial removal of Al and Si. Citric acid leaching could remove the Al completely from the coal matrix.SEM image showed that surface areas of mineral phases were reduced with leaching. The calorific value of the leached coal reported an increase of 12% with EDTA and gluconic acid leaching.

Key Words : Organic acid leaching, Bituminous coal, Minerals, SEM, EDS

INTRODUCTION

Mineral matters and sulphur in coal, place huge limitations on its use, and raises concern over the effects of excessive burning of coal on the climate. This calls for its use to be limited world-wide. The removal of mineral matters from coal has been practiced since its extraction from the earth and studies in to chemical demineralization have been conducted for several decades[1]. But the processes have not gained widespread commercialization. This is due to the fact that the methods for removing mineral matters need to have low cost and be environment friendly. Methods of removing metal ions from an ore mainly consist of physical, chemical and biological technologies. Conventional methods for removing metal ions from aqueous solution are chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, evaporation etc. However, chemical precipitation and electrochemical treatment are ineffective when the metal ion concentration is very low and also produce large quantity of sludge that is difficult to treat with. Volesky summarized the advantages and disadvantages of these conventional metal removal technologies[2-3].

In recent years, applying biotechnology in controlling and removing metal pollution has gained importance in the field of metal pollution control. It is because of its potential applications. Alternative process is biosorption, which utilizes various natural materials of biological origin, including bacteria, fungi, yeast, algae etc. These biosorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions from ppm to ppb level. It can effectively sequester dissolved metal ions out of complex molecule efficiently and quickly. Therefore, it is an ideal candidate for the treatment of high volume and low concentration complex industrial waste[4].

The microbial solubilization of some Indian bituminous coal was carried out by Sharma and Wadhwa revealed the removal of minerals by mixed culture of bacterium[5]. It is known that the micro organisms secrete acids during leaching. This lowers the pH of the solution and enhances the removal of minerals by reducing the cohesive force between minerals and coal matrix[6]. In the present study, efficiency of various carboxylic acids in demineralization of Al, Ca and Si minerals are investigated. The products are characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrum (EDS)

MATERIAL AND METHODS

Coal Sample

An Indian bituminous coal and Korba (K) coal, was used in this study. The bituminous coal was air-dried and ground to the particle size < 75μm. The elemental and proximate analysis is presented in **Table 1**, and the ash content is 08.20 wt% on a dry basis.

Demineralization

50 g of Korba bituminous coal (KX) was powdered and 10 g from that sample is demineralized using different carboxylic acids like gluconic acid (50%-KGl), oxalic acid (10%-KO) and citric acid (10%-KC), EDTA (0.1N-KE) and acetic acid (2N-KA) individually in a 500 ml Teflon beaker for 24 hours at room temperature (27^{o}C). The leached coal sample was separated from the respective organic acid solution by filtration using a polypropylene funnel and naturally dried at room temperature. The resulting samples were washed repeatedly with double distilled water to remove the acid content and finally dried in an oven at 70^{o}C and allowed to cool slowly in a dessicator.

Analysis of minerals and ash in virgin and leached coal

The observation and quantification of minerals in virgin and chemical leached coals were carried out using a Scanning Electron Microscope with an energy dispersive X-ray analyzer (SEM-EDS). Ash content in the virgin coal and its demineralized coals were analyzed by proximate analysis. The gross calorific values of all the coal samples were determined using an IKA C5000 calorimeter model JEOL model JSM-6390 LV.

RESULTS AND DISCUSSION

Minerals in Bituminous coal

Fig.1 shows the SEM/EDS profile for the raw coal (KX). The elemental composition as quantified by EDS is estimated as follows: Si -1.18; Al 0.95; Ca - 0.18 wt%. Except for carbon, oxygen, nitrogen and traces of sulphur, Si and Al are the major elements in the virgin coal. The bright particles with size of 10 μm are identified as minerals phase of Al and Si[7] by EDS spot analysis.

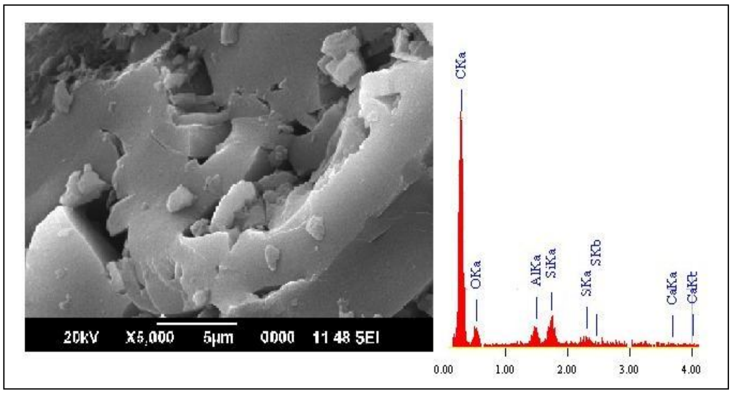

Fig. 1 : Observation and identification of minerals in virgin coal (KX) by SEM -EDS

Effect of acetic acid leaching on demineralization

Fig.2 shows the SEM/EDS profile of acetic acid leached coal sample (KA). When the bituminous coal was treated with 50 ml of 2N acetic acid for 24 hrs at 27^{o}C, the ash content decreased from 8.2 to 3.854 wt%. The elemental composition as estimated by EDS is as follows: Si -0.23 wt %; Al.0.23 wt% and Ca - Nil. Oxygen content shows an increase of 17.24% whereas carbon shows a decrease of 2.01 wt %. This might be due to the oxidation of the coal matrix as a result of leaching. The micrograph shows so many devolatization holes which are due to the liberation of oxygen from the surface[7-11]. Sulphur content also decreased to zero value. The calcites mineral is completely removed by forming calcium acetate complexes and aluminum minerals are removed partially with the formation of aluminium acetate. The expected dissolution reaction is as follows :

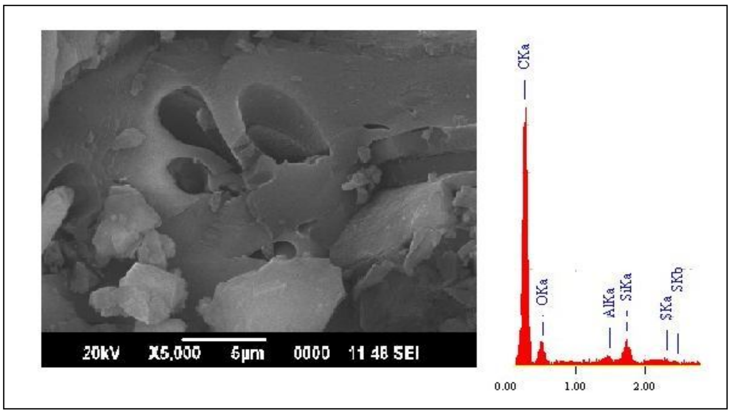

Fig. 2 : Observation and identification of minerals in acetic acid leached coal (KA) by SEM -EDS

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

$$2CH_3COO^- + Ca^{2+} \rightarrow Ca(CH_3COO)_2$$

(Calcium acetate)

EDS analysis showed that Al content was changed from an initial value of 0.95% to 0.23% with acetic acid leaching possibly by forming aluminum acetate.

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

$$3CH_3COOH \rightarrow 3CH_3COO^- + 3H^+$$

$$3CH_3COO^- + Al^{3+} \rightarrow Al(CH_3COO)_3$$

(Aluminum acetate)

Effect of Oxalic acid leaching on demineralization

SEM-EDS analysis of demineralized coal treated with 2N Oxalic acid (KO) reveals that large particles of kaolinite and bassanite were extensively removed; however, a lot of particles are still remaining **Fig. 3**. Estimation of the elemental composition (Si - 1.11; Al - 0.94; Ca - Nil wt %) analyzed by EDS also shows total removal of Ca and partial removal of Al. However, Si shows little change comparing with the elemental composition of virgin coal. The oxygen content is increased by 46%.The SEM image of the demineralized coal also shows small devolatization in the surface. The possible mechanism of organic acid in mineral extraction is by forming calcium oxalate complexes[12-13].

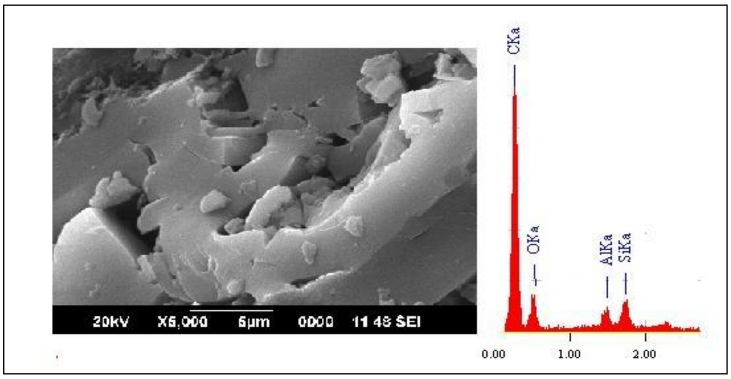

Fig. 3: Observation and identification of minerals in oxalic acid leached coal (KO) by SEM -EDS

$$C_2H_2O_4 \rightarrow (C_2O_4)^{2-} + 2H^+$$
$$(C_2O_4)^{2-} + Ca^{2+} \rightarrow CaC_2O_4$$
(Calcium oxalate)

Effect of Citric acid leaching on demineralization

Leaching was also performed with citric acid. The SEM image of the residual coal (KC) from this treatment is provided in **Fig. 4.** It can be seen that this leachant caused morphological change in the particle and did enormous harm to the surface by leaching many inorganic elements. Estimation of the elemental composition (Si^- 0.61 wt%, Al = nil, Ca = nil, S = nil) analyzed by EDS also shows remarkable decrease of silicates and total removal of aluminum and calcites by forming their respective complexes.

The efficiency of citric acid and oxalic acid in the demineralization of aluminum was reported[11-12]. Citric acid is a tricarboxylic acid and contains three carboxylic groups and one hydroxyl group as possible donor of protons (H^+) at 25^{o}C. When alumina cation (Al^{3+}) are present in the coal and citric acid is fully dissociated in aqueous solution, a complexation reaction may take place.

$$C_6H_8O_7 \rightarrow (C_6H_5O_7)^{3-} + 3H^+$$
$$(C_6H_5O_7)^{3-} + Al^{3+} \rightarrow Al\,(C_6H_5O_7)$$
(Aluminium citrate)

$$2\,(C_6H_8O_7) \rightarrow 2(C_6H_5O_7)^{6-} + 6H^+$$
$$2(C_6H_5O_7)^{6-} + 3Ca^{2+} \rightarrow Ca_3\,(C_6H_8O_7)_2$$
(Calcium citrate)

The aluminum and calcium citrate complexes are precipitated as white precipitate and removed

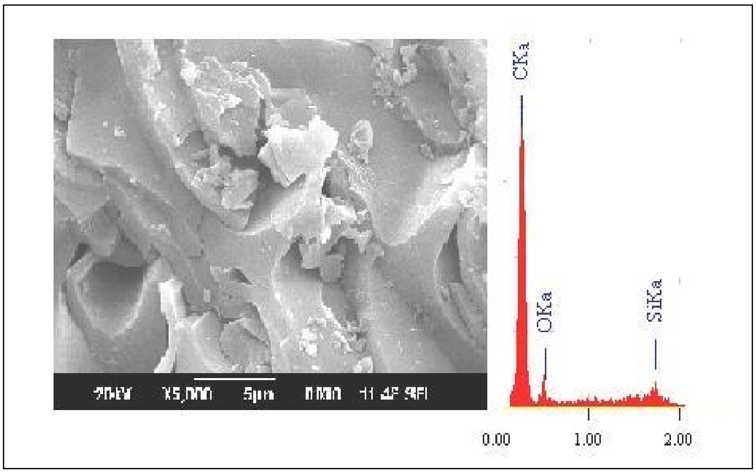

Fig. 4 : Observation and identification of minerals in citric acid leached coal (KC) by SEM -EDS

from the sample by washing with water and filtration. Sulphur is totally removed when leached with this reagent.

Effect of EDTA on demineralization

Chelating agents like Ethylene Diamine Tetra Acetic acid (EDTA) has the ability to chelate or bind metals such as calcium. The kinetics of calcite dissolution using chelating agents is not as fast as those using strong mineral acids. Chelating agents can increase calcite dissolution rates through ligand promoted dissolution[14]. Leaching of the coal is performed with EDTA and then the mineralogical study of the residual coal is done. SEM micrograph and EDS spectra of the sample leached with EDTA (KE) is illustrated in **Fig. 5**. Numerous aggregated particles can be seen on the surface. The porosity has been increased and provides strong evidence that significant amount of inorganic elements especially calcites are removed. However, the surface coverage is still bright and luminous indicating the presence of mineral phases. The EDS analysis (Al = 0.28 wt%; Si = 0.29 wt%; Ca = Nil.) confirms that calcites are removed along with significant removal Al and Si. The possible reaction mechanism is as follows:

In the calcite chelating process, one EDTA molecule will associate with two Ca^{2+} ions allowing the dissolution of two moles of calcites per one mole of EDTA.

$$EDTA^{4-} + 2\,Ca^{2+} \rightarrow Ca_2\,EDTA$$

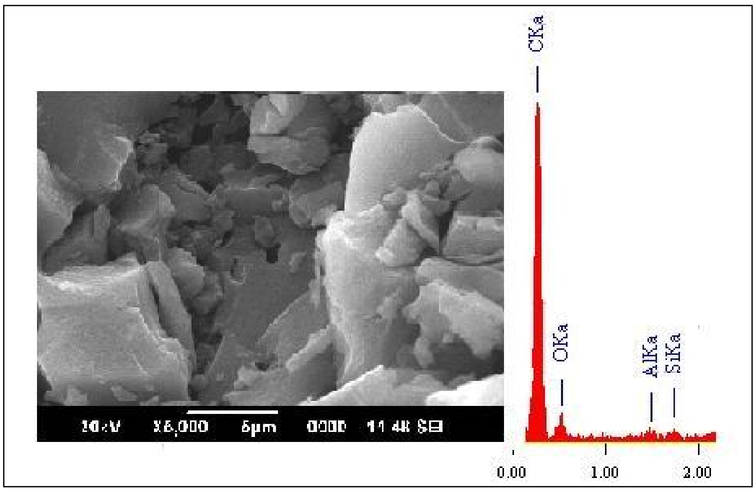

Fig. 5 : Observation and identification of minerals in EDTA leached coal (KE) by SEM -EDS

Effect of gluconic acid on demineralization

SEM-EDS analysis of the bituminous coal treated with gluconic acid is (KGl) shown in **Fig. 6**.The EDS analysis showed that there is 53% reduction in Al and Si minerals (Al^- 0.37 wt%; Si^- 0.66 wt%; Ca^- Nil) . SEM micrograph revealed the shining surface, an indication of presence of minerals still on the surface. With gluconic acid total reduction of calcium minerals are observed with the possible formation of calcium gluconate.

$$2(C_6H_{12}O_7) \rightarrow (C_{12}H_{22}O_{14})^{2-} + 2H^+$$

$$(C_{12}H_{22}O_{14})^{2-} + Ca^{2+} \rightarrow C_{12}H_{22}O_{14}$$

Calcium gluconate

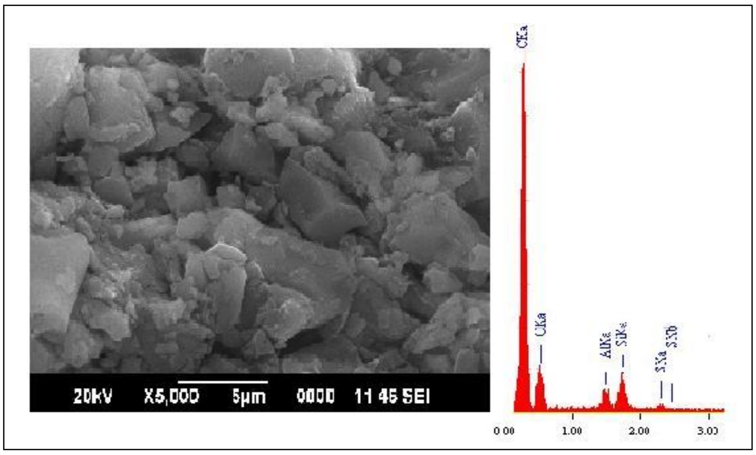

Fig. 6: Observation and identification of minerals in gluconic acid leached coal (KGl) by SEM -EDS

Characterization of the demineralized coal

Table. 1 shows the C, O, S and mineral content in Indian bituminous coal and its demineralized products. When the coal was leached with acetic acid, oxalic acid, citric acid and EDTA individually, the sulphur content was nil. Other elements such as Ca are removed completely where as Si and Al content reduced considerably. Carbon content showed an increase with from an initial value of 80.91 to 82 wt% and 82.22 wt% with EDTA and gluconic acid leaching respectively. **Table 1** also shows the change of calorific value of bituminous coal (KX) after leaching with different leachants on an ash free basis. Acetic acid and oxalic leaching did not improve the calorific value of coal, suggesting that oxidation has happened to the organic structure of coal with leaching. Calorific value decreased slightly with an increase in oxygen content by 46% with oxalic acid leaching. It is noticeable that ctric acid and EDTA leaching could decrease the ash content to 1.94 wt% and 1.81 wt% respectively. Citric acid leaching totally removed the aluminates without the appreciable loss of calorific value of the coal. EDTA and gluconic acid leaching removed the mineral content to an appreciable amount without much oxidation to the coal matrix. Calorific value of the sample also reported an increase of ~12% with EDTA and gluconic acid leaching.

Table.1. Elemental and Proximate analysis of bituminous coal before and after demineralization

	KX	KA	KO	KC	KE	KGl
Proximate Analysis (wt %)						
Ash (db)	8.20	5.99	4.18	1.94	1.81	3.90
Volatile Matter(daf)	32.40	32.72	33.23	33.93	32.30	31.93
Fixed Carbon	52.30	54.25	56.57	59.03	60.33	58.42
Moisture	7.10	7.04	6.02	5.10	5.56	5.75
Elemental Analysis						
C	80.89	79.28	73.70	79.85	82.40	82.22
O	16.53	19.38	24.23	19.54	17.03	16.55
Si	1.18	1.10	1.17	0.61	0.29	0.66
Al	0.95	0.23	0.90	-	0.28	0.37
Ca	0.18	-	-		-	-
S	0.27	0.01	-	-	-	0.20
Calorific Value (MJ/kg)	24.09	24.43	25.35	26.48	26.97	26.85

CONCLUSION

The effect of demineralization on an Indian bituminous coal has been studied using organic acid chemical leaching method by acetic acid, oxalic acid, citric acid, EDTA and gluconic acid. The following conclusions are summarized

1. The Citric acid leaching removes the Ca and Al containing minerals and majority of Si containing minerals. The ash content also decreases remarkably from 8.2 wt% to 1.94 wt% with citric acid leaching where as EDTA and gluconic acid leaching reduced the ash content to 1.81 wt% and 3.90 wt% respectively mainly by removing Si and Al minerals.
2. The analysis result of calorific value for the raw coal and the demineralized coal suggests that no oxidation to the coal organic structure occurs during leaching by EDTA and gluconic acid. Calorific value showed an increase of 12% with gluconic acid and EDTA leaching. However the oxygen content does not appreciably increase.
3. The sulphur content is completely removed with citric acid, acetic acid, EDTA and oxalic acid leaching for the particular coal.
4. SEM micrograph indicates that acetic acid, citric acid and EDTA acid treatment procedure have measurable effect on the coal surface.

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