Alkali Leaching of Indian Coal for Ash Reduction

Singh, Jatinder Pal; Mohapatra S.K.; Singh, Gurprit
Mechanical Engineering Department, Thapar Institute of Engineering and Technology,
P. O. Box 147004 Patiala, Punjab, INDIA

Kumar, Satish*+
Mechanical Engineering Department, National Institute of Technology, Jamshedpur, Jharkhand, INDIA

Singh, Mani Kanwar
Mechanical Engineering Department, Chandigarh University, Gharuan, Punjab, INDIA

ABSTRACT: *Coal is a major source of energy. The available Indian coal quality is very poor having very high ash content and low calorific value. Indian coal generates a large quantity of ash as a by-product of combustion. The objectives of the present study were to reduce the ash content of coal to produce ultra-clean coal. The coal was treated with a dual chemical leaching process consisting of NaOH followed by HCl. During experiments, the concentration of NaOH was varied from 2.5 to 10 M with 1.4 N HCl. Effect of shaking speed and time was analysed at 0, 50, 100, 150 and 200 rpm and 1, 2, 3 and 4 hours respectively. After chemical leaching, the ash content was reduced from 35.33 to 0.98% in the ultra-clean coal. The concentration of alkali, shaking speed and time of duration were found as highly influencing parameters for the reduction of ash content in the coal. Moreover, the current study should result in a better option for the removal of ash content from low-rank Indian coals.*

KEYWORDS: *Coal; Chemical leaching; Ash content; Ultra-clean coal; Low-grade coal.*

INTRODUCTION

Coal plays a most important role in the generation of power and is used as a source of energy for society. Generally, bituminous and sub-bituminous types of coal are found in India which has high ash content 30 to 40 % [1]. Coal is a heterogeneous compound made up of inorganic and organic components. The inorganic portion is generally mineral matter. During combustion, inorganic compounds are converted into ash and cause harmful impacts like the contamination of water and soil by leaching of heavy metals [2, 3]. Low-rank coal is not suitable for use in combustion, liquefaction and gasification processes [4]. Ash handling and environmental hazards are major problems faced by thermal power plants which run on low-rank coal. The coal consists of considerable amounts of nitrogen, sulphur, and mineral matter along with significant quantities of silicates, metal sulfides, metal oxides, metal sulfates, etc. The cleaning of low-rank coal is necessary before its utilization in various applications to prevent environmental hazards. High-rank coal is depleting at a faster rate from mines, so the conversion of low-rank coal into superior coal has come into demand [5]. For this purpose, chemical and physical

* *To whom correspondence should be addressed.*
+ *E-mail: satish.kumar@thapar*.edu ; *satish.me@nitjsr.ac.in*
1021-9986/2018/6/147-155 9/$/5.09

coal beneficiation methods have been developed. Currently, physical coal cleaning methods like froth flotation, magnetic and gravity separation are most commonly employed to liberate impurities [1]. These methods have negligible effects on the removal of mineral matter from parent coal.

Chemical cleaning (beneficiation) is the technique by which high degrees of demineralization can be achieved. Acid, alkali and alkali-acid coal cleaning techniques were adopted by various researchers [5-10]. HCl and molten caustic leaching were effective in coal cleaning at high temperatures [5]. Coal cleaning with HF and HNO_3 produced low-ash coal [6]. Potassium hydroxide and HCl chemical cleaning at high temperatures were effective in the complete removal of sulphur [7]. In an investigation, it was observed that the effects of froth flotation and chemical cleaning processes provided high degrees of reduction in sulphur and ash from parent coal [8]. The treatment of coking coal with $Fe_2(SO_4)_3$, H_2O_2, CH_3OH, and $FeCl_3$ was also effective in the removal of ash as well as of sulphur content [9]. The use of kerosene-pine oil in the Froth flotation method was superior in ash removal over kerosene and pine oil individually [10]. Higher rates of decrease in sulphur and ash content were noticed in a treated coal sample with smaller particles size [11]. By treating coal samples with 0.5 N NaOH and 1.4 N HCl, 46.8% decreases in the mineral matter can occur [12]. The demand for chemically-treated coal in the future can be increased due to the large availability of low-rank coals having high ash and sulphur contents. The use of chemically-cleaned coal leads to lower environmental pollution and also decreases solid waste in the form of ash [13]. Previous studies indicate that chemical treatment can lead to the production of high-quality coal and environmentally friendly energy production systems.

A literature review reveals that coal cleaning methods improve the quality of coal and help to reduce the ash content of coal. Limited work has been reported on the multi stage chemical cleaning of low-rank Indian coals with aqueous solutions of alkali or acid chemical agents. In the present study, an attempt has been made to investigate chemical leaching characteristics of low-grade Indian coal with NaOH and HCl at different concentrations. The experimentation was extended to a three-stage chemical cleaning of coal in order to observe optimum conditions.

EXPERIMENTAL SECTION

A coal sample was collected from the Guru Gobind Singh Super Thermal Power Plant, Ropar (Punjab), India. The collected sample was present in lump form. These lumps were crushed into small sizes (less than 5 cm) with the help of a hammer type coal crusher and then pulverised by a rotary ball mill. The pulverized coal sample was dried in an electric oven (manufactured by Narang Scientific work Pvt. Ltd., New Delhi, India) for three hours at 120°C to remove moisture from the coal. The sample was further processed for dry sieving using a mechanical sieve shaker (manufactured by Mody testing instruments corporation, Vadodara, India). The sieve analysis was carried out on BS-410 sieves (British Standard) to study the particle size distribution of pulverized coal. The sample of 75-106μm mesh size was collected from the respective sieves and used for further experimentation. The leaching experiments were conducted with changing the NaOH concentration from 2.5 to 10 M and further treated with 1.4 N HCl. The particle of the coal sample was taken in the range of 75-106 μm due to the enrichment of this particle size range in the pulverized coal sample. The coal was mixed with an aqueous solution at a ratio of 1:10 (gram/ml). As coal is hydrophobic in nature, to ensure the proper mixing the slurry was stirred with the help of a magnetic stirrer (manufactured by IKA, Bangalore, India) for 10 minutes. The detailed procedure of the investigation is represented in Fig. 1. After mixing, a shaking operation was performed using an orbital shaker (manufactured by Remi Elektrotechnik Ltd., Vasai, India) at 150 rpm, 50°C for two hours. The coal sample was filtered with 11μm Whatman disc filter paper and dried in an oven at 120°C to scrub out coal from filter paper. The treated coal samples were repeatedly washed with distilled warm water until a natural pH value wasn't achieved. The demineralized coal was again treated with 1.4 N HCl (Hydrochloric acid) for one hour. After the filtration of treated coal, the percentage of ash in the coal sample was determined using a muffle furnace (manufactured by Macro Scientific Works Pvt. Ltd. Delhi, India). In the second stage, the first-stage processed coal sample was again treated with respective concentrations of NaOH and 1.4 N HCl for durations of two and one hours respectively; again, the suspension was filtered at room temperature and the percentage of ash content was analysed.

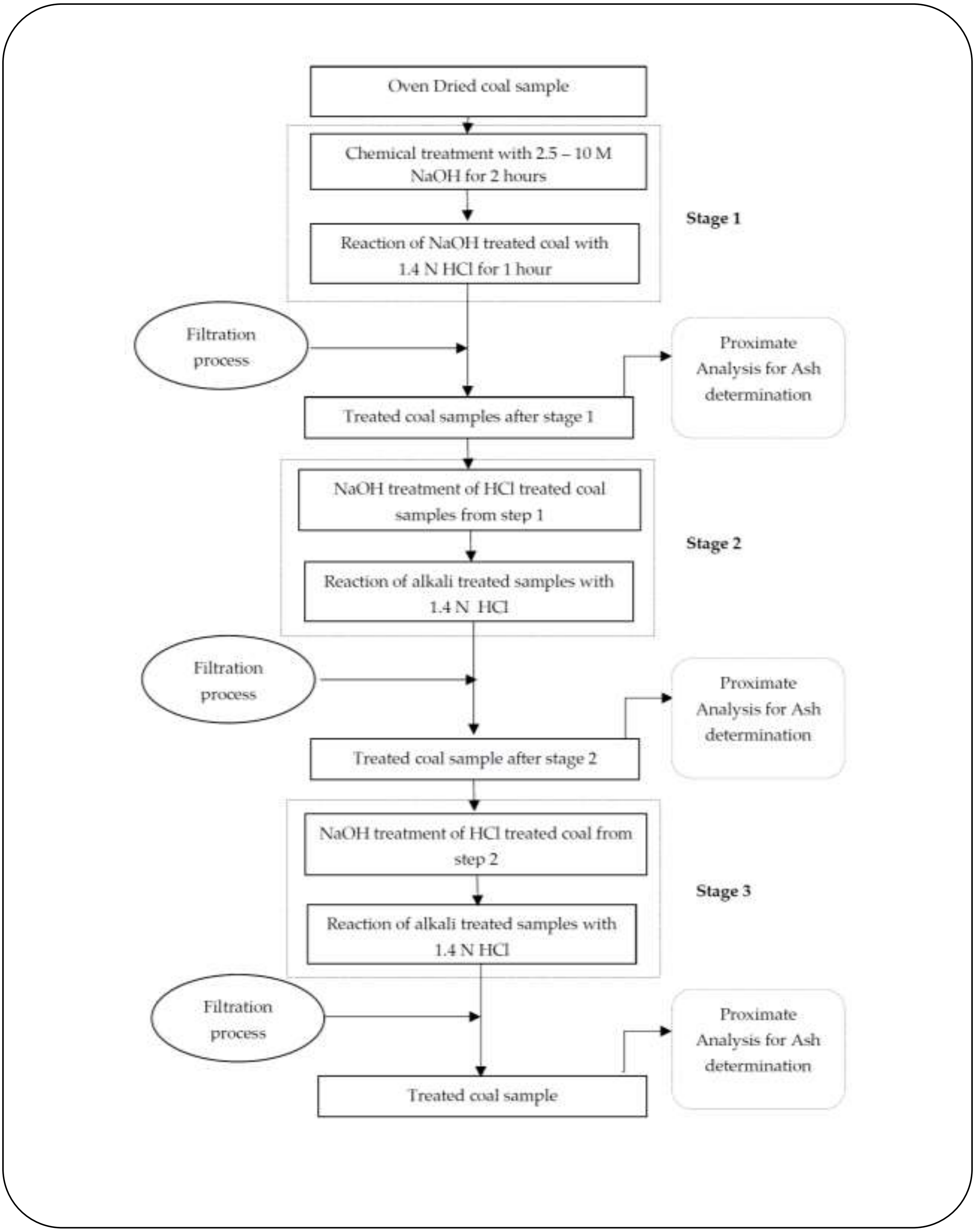

Fig. 1: Schematic representation of procedure followed in experimentation.

Table 1: Proximate Analysis of untreated coal sample.

S. No.	Parameters	Weight %
1	Moisture	5.52
2	Ash	35.33
3	Volatile matter	19.09
4	Fixed carbon	40.06

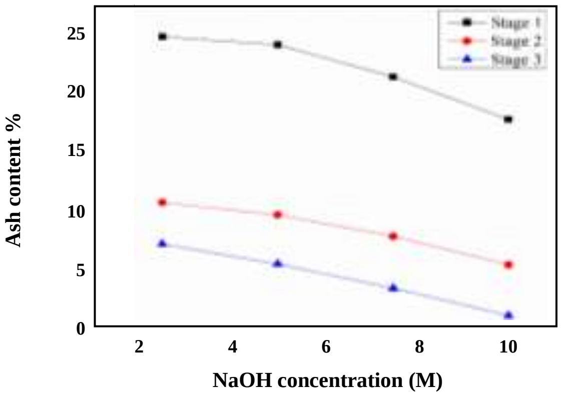

Fig. 2: Effect of NaOH concentration on ash removal.

The same procedure was followed in the third stage of chemical leaching. The second-stage processed coal sample was further treated with NaOH and HCl. The final coal suspension was filtered, dried, and preceded for ash content analysis. To analyse the effect of shaking speed, the leaching experiments were performed at different shaking speeds namely, 0, 50, 100, 150, and 200 rpm for two hours. Further analyses were carried out to test the effect of reaction time at a constant speed of 150 rpm at a temperature of 50ºC for one, two, three and four hours.

RESULTS AND DISCUSSIONS

Effects of NaOH concentration on ash content

Three-Stage chemical treatment of coal has been carried out to investigate the effect of alkali NaOH concentration on ash content in the coal sample, which is shown in Fig. 2. Proximate analysis of untreated coal is represented in Table 1. During the experiments, the concentration of NaOH was varied from 2.5 to 10 M with a fixed concentration of HCl (1.4 N) at 150 rpm shaking speed for the duration of two hours. The ash content was determined by a proximate analysis using a muffle furnace (IS-1350). The percentage decrease in ash content was calculated by using equation 1:

$$\text{Percentage decrease in ash content} = \frac{a-b}{a} \times 100 \qquad (1)$$

Where *a* represents ash content in the parent coal sample, and *b* is the reduced ash content percentage in chemically-treated coal. From Fig. 2, it is observed that the ash content present in the coal sample decreases with an increase in NaOH concentration. In the coal sample, initially, ash content was found to be 35.33% (by weight). After the first stage of the experimentation, ash content in the coal, sample was reduced to 24.71, 24.02, 21.28 and 17.665% with 2.5, 5, 7.5 and 10 M NaOH solution respectively. The first-stage processed samples were not sufficient to produce ultra-clean coal (having an ash content of less than 1%), so further experiments were carried out while the value of ash content was reduced to 10.59, 9.54, 7.71 and 5.29 % after the second stage. After the third stage, ash content was reduced to 7.06, 5.36, 3.29 and 0.98%. Results show that ultra-clean coal was produced with 10 M NaOH and 1.4 N HCl solutions after the third stage of the chemical leaching process. Alumina and silica present in coal react with NaOH to form soluble compounds namely, silicates and aluminates as represented in the following chemical equations [7]:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (2)$$

$$Al_2O_3 + 2NaOH \rightarrow Na_2AlO_2 + H_2O \qquad (3)$$

As NaOH concentration increases, the concentration of silicate and aluminate ions also gradually increases in the solution until alumina silicate does not start accumulating. The mineral matter present in the form of alumina and silica in coal was dissolving out from the coal. Similar observations were also drawn by researchers [14-16] with KOH-HCl, HCl-HF, $Ca(OH)_2$-HCl and HNO_3-HCl respectively, to produce ultra-clean coal.

Effect of shaking speed on ash content

The chemical leaching experimentation was also performed to investigate the effect of shaking speed on ash content in the coal sample. Experiments were performed at different shaking speeds (0, 50, 100, 150 and 200 rpm) with 10 M NaOH and 1.4 N HCl solutions. Samples were shaken in an orbital shaker for two hours at a temperature of 50ºC. Variation of ash reduction with shaking speed is shown in Fig. 3. The decrease in the ash content was observed with an increase in shaking speed. In the initial stage, the ash content in the coal was reduced to 30.23, 25.67, 21.59, 17.66 and 15.852% (by weight) with shaking speeds of 0, 50, 100, 150 and 200 rpm respectively. Similarly, ash content was reduced to 20.43, 15.54, 10.32, 5.29 and 3.72% after the second stage. However, the values of ash content were reduced to 16.45, 11.32, 6.65, 0.98 and 0.62% after the third stage. Results show that ultra-clean coal was produced with 10 M NaOH solution at shaking speeds of 150 and 200 rpm. The gradual decrease in ash content at the higher rpm was due to an increase in the mass transfer rate between coal and leaching agents. The results obtained were aggregated with results discussed by other researchers [8].

Effect of reaction time on ash content

The effect of time duration on chemical washing of coal is investigated in this section. Coal particles of 75-106 µm were treated with 10 M NaOH and 1.4 N HCl solutions for durations of 1, 2, 3 and 4 hours. Details of the reduction of ash content with variations of time are represented in Fig. 4. The decrease in the ash content was noticed with an increase in reaction time. The ash content of the parent coal was reduced to 19.96, 17.66, 15.84 and 13.32% after the first stage with reaction time periods of 1, 2, 3 and 4 hours respectively. Similarly, the weight percentage of ash content was reduced to 8.32, 5.29, 4.53 and 3.52% after the second stage of chemical leaching. Subsequently, ash content was reduced to 5.64, 0.98, 0.45 and 0.3% after the final stage. The ultra-clean coal was produced with 10 M NaOH and 1.4 N HCl solutions while treated for durations of 2, 3 and 4 hours. The decrease in ash content for coal cleaning at higher time duration was due to increases in reaction time. Present results were quite close to investigations previously carried out by a few researchers [17-20].

Effect of Temperature on Ash Content

The effect of temperature on ash content in coal was also investigated at different temperatures namely 25, 40, 50 and 60˚C. Coal samples of particle size 75-106 µm were treated with 10 M NaOH and 1.4 N HCl solutions. The decrease in ash content was noticed with an increase in temperature as shown in Fig. 5. In the first stage, ash content

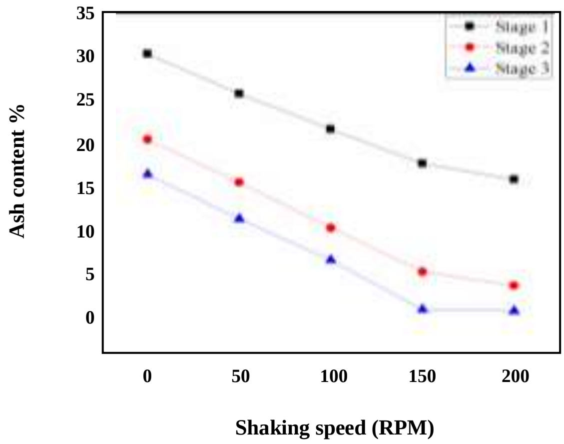

Fig. 3: Effect of shaking speed on ash reduction.

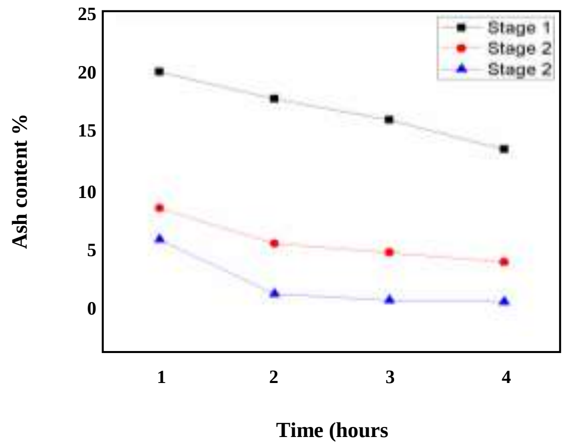

Fig. 4: Effect of reaction time on ash removal.

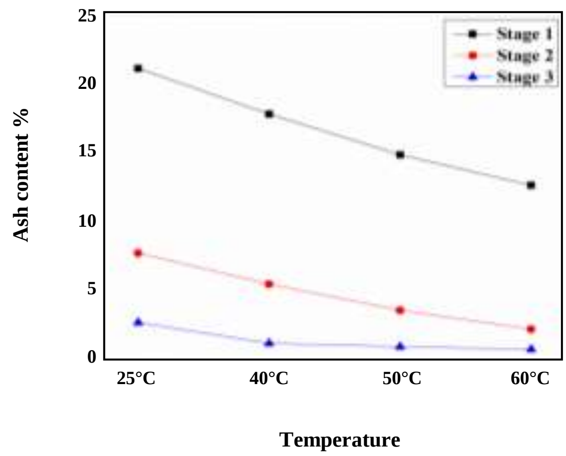

Fig. 5: Effect of temperature on ash removal.

Table 2: Effect of chemical leaching on ash constituents (by EDS) and calorific value (by Bomb Calorimeter).

Stages	Coal samples	Ash constituents (wt. %)							Calorific Value (MJ/kg)
		Al_2O_3	SiO_2	CaO	FeO	K_2O	Na_2O	Unburnt Carbon	
Initial	Untreated coal	18.43	48.13	5.43	9.65	2.86	2.58	7.56	21.17
First	2.5 M NaOH + 1.4 N HCl	15.34	40.56	5.34	7.56	2.32	2.12	6.8	25.19
	5 M NaOH + 1.4 N HCl	14.02	36.28	4.32	6.08	1.94	1.93	4.98	25.41
	7.5 M NaOH + 1.4 N HCl	12.38	28.56	3.45	5.23	1.50	1.67	3.54	25.88
	10 M NaOH + 1.4 N HCl	9.98	10.98	2.65	3.98	1.28	1.51	1.56	26.55
Second	2.5 M NaOH + 1.4 N HCl	12.56	32.65	4.54	5.78	1.96	1.95	5.22	25.78
	5 M NaOH + 1.4 N HCl	9.87	28.54	3.95	4.65	1.21	1.53	3.10	25.94
	7.5 M NaOH + 1.4 N HCl	7.23	20.95	2.45	3.45	1.08	1.26	2.56	26.36
	10 M NaOH + 1.4 N HCl	5.90	4.95	1.54	2.43	0.89	0.98	0.92	27.03
Third	2.5 M NaOH + 1.4 N HCl	10.54	22.45	3.46	3.56	1.42	1.34	3.54	25.99
	5 M NaOH + 1.4 N HCl	8.65	16.54	2.75	2.13	1.02	1.20	2.86	26.24
	7.5 M NaOH + 1.4 N HCl	5.46	7.86	1.90	1.56	0.78	0.97	1.4	26.72
	10 M NaOH + 1.4 N HCl	1.56	1.25	0.98	0.45	0.35	0.67	0.56	27.38

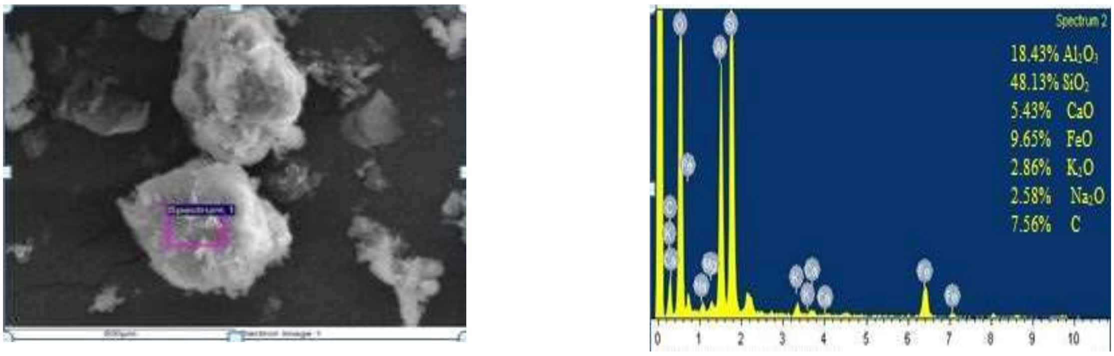

Fig. 6: EDS image of ash retained from untreated coal.

from coal was reduced to 20.98, 17.66, 14.69 and 12.48% with temperature 25, 40, 50 and 60°C respectively while ash content in coal was reduced to 7.54, 5.29, 3.38 and 2.12% respectively after the second stage. However the values of ash content were reduced to 4.54, 0.98, 0.73 and 0.65% after the final stage. Decrease in ash content was observed at higher temperatures due to increase in reaction kinetics with temperature [5, 17, 21].

Effect of chemical leaching on Calorific Value and ash constituents of coal sample

Chemical characterizations of parent coal and chemically-treated coal ash were studied using EDS (energy dispersion x-ray spectrography). The chemical composition of ash obtained after every stage is represented in Table 2. Results obtained from EDS of parent coal ash (Fig. 6) shows that aluminum oxide and silica oxide were present in major proportions. However, other compounds, like calcium oxide, iron oxide, potassium oxide, and sodium oxide were present in minor proportions. In the parent coal, Al_2O_3, SiO_2, Na_2O, FeO and CaO were present in percentages of 18.43, 48.13, 2.58, 9.65 and 5.43% (by weight) respectively. However, the percentage of all ash constituents decreased with an increase in NaOH concentration, as represented in Table 2.

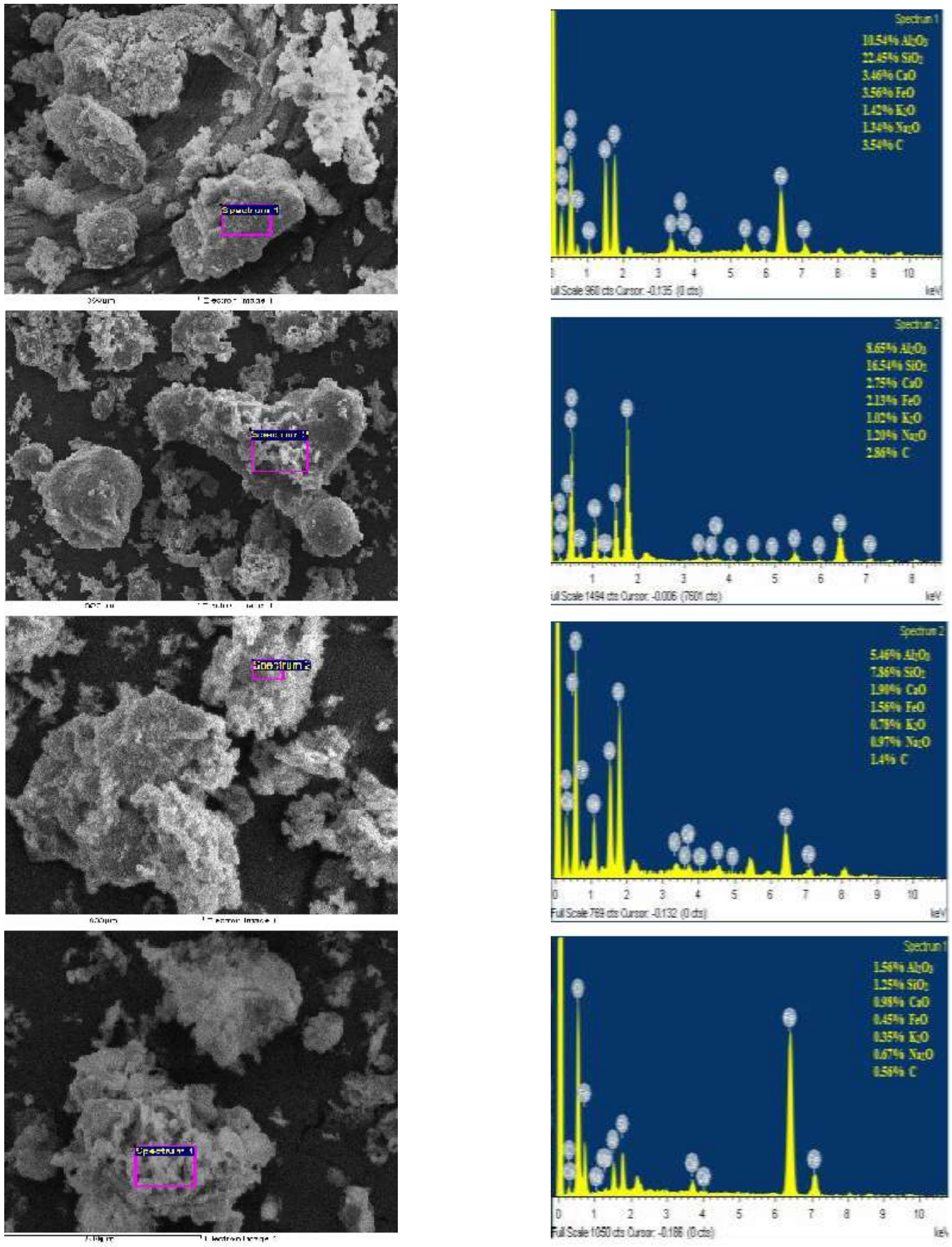

Fig. 7: EDS of ash retained from coal treated by 1.4 N HCl and NaOH of (a)2.5 M , (b)5 M , (c)7.5 M and (d)10 M.

The chemical leaching treatment was successfully completed at the end of the third stage. An EDS image of 2.5 M NaOH and 1.4 N HCl treated coal is represented in Fig. 7(a), which reveals that percentages of Al_2O_3, SiO_2, CaO, FeO, K_2O and Na_2O were reduced to 10.54, 22.45, 3.46, 3.56, 1.42 and 1.34% respectively. From Fig. 7(b), it is noticed that ash constituents further undergo decrease to 8.65, 16.54, 2.75, 2.13, 1.02 and 1.20% when treated on treating with 5 M NaOH and 1.4 N HCl. Previous trends show that the NaOH concentration significantly contributes to the reduction of ash constituents, which can also be found in Figs. 7(c) and 7(d). After treating the coal samples with 7.5 M NaOH and 1.4 N HCl, percentages of ash constituents were found at percentages of 5.46, 7.86, 1.90, 1.56, 0.78 and 0.97%. Ultra-clean coal was produced with 10 M NaOH and 1.4 N HCl; percentages of ash constituents were 1.56, 1.25, 0.98, 0.45, 0.35 and 0.67%. The significant decrease in the percentage of unburnt carbon from 7.56 to 0.56% was observed after the chemical treatment.

The calorific value of treated (as well as of parent) coal was determined by using a bomb calorimeter (manufactured by Widsons Scientific Works, New Delhi, India). Calorific value (CV) was calculated by the formula below:

$$\text{Calorific value} = \left[\frac{(2334.2\times\Delta T)-A-B}{X}\right] \quad (4)$$

Where *ΔT* is temperature change, *X* is the weight of the coal sample (in grams), *A* is the weight of nichrome wire (in grams), and *B* is the weight of cotton thread (in grams).

The CV of parent coal was found to be 21.17 MJ/kg. The CV of the coal was increased with an increase in alkali concentration. After the chemical leaching treatment in the last stage, the calorific values of the coal sample were 25.99, 26.24, 26.72, and 27.38 MJ/kg with 2.5, 5, 7.5 and 10 M NaOH concentrated solution, respectively. This increase in calorific value shows that chemicals used for cleaning did not react with the carbonaceous matter present in coal [21-24].

CONCLUSIONS

The experiments were performed to reduce ash content from pulverized coal. NaOH and HCl reacted with inorganic matter that was present in the coal. Ultra-clean coal was produced after three stages of chemical treatments and led to reductions in ash content from 35.33 to 0.98% with 10 M NaOH solution. The concentration of alkali, shaking speed and time duration were found as highly-influencing parameters for the reduction of ash content in coal. Ultra-clean coal was obtained after chemical treatments with 10 M NaOH and 1.4 N HCl. The calorific value of the ultra-clean coal was 27.38 MJ/kg. Moreover, the current study should result in better options for the removal of ash content from low-rank Indian coals. Future aspects of this study are not only limited to coal cleaning, however; they can be extended to investigations of the chemical extraction from salts obtained after chemical treatments.

ETHICAL ASPECTS

There were no violations of people's rights.

Received : Jun. 27, 2016 ; Accepted : Nov. 20, 2017

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