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Mineralogical Composition and Ash Geochemistry of Raw and Beneficiated High Sulfur Coals

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Abstract: Coal is one of the most available energy sources on earth. The mineralogical and geo-chemical aspects of coals are of prime importance for their utilization. The mineralogical composition, ash chemistry, and ash fusion temperature (AFT) ranges of raw and beneficiated coals are investigated in this paper. Further, the mineral matter transformation during the beneficiation processes viz. by oxidative desulfurization; alkali extraction and ultrasonication along with the relationship of the ash fusion temperature (AFT) ranges with the ash components in the coal are discussed. The major oxides present in the coal and beneficiated coal ashes include Fe_2O_3, Al_2O_3, SiO_2, CaO, and MgO, which significantly affect the ash fusion temperature ranges. Initial deformation temperature (IDT) changes with the ash components and, increases with the increase in the Fe_2O_3 content in coal ash. With increasing concentrations of both Al_2O_3 and SiO_2, the initial deformation temperature (IDT) also increases. The increasing and decreasing nature of the initial deformation temperature (IDT) observed is also dependent upon the CaO and MgO contents. XRD analysis of the coal samples revealed significant changes in mineral matter contents with the types of beneficiation processes adopted for coal. The minerals like chlorite, illite, montmorillonite, pyrite, calcite, aragonite, and alumina have been removed during the beneficiation processes. The FTIR spectra also indicate the presence of minerals like gypsum (G), calcite (C) aragonite (Ar), quartz (Q) and kaolinite (K) in the raw coal and their subsequent removal after the beneficiation processes.

Keywords: Indian coal, High sulfur coal, Mineral matters in coal, Ash Fusion Temperatures, Ultrasonication, Low rank coal.

INTRODUCTION

Coal is regarded as the fossil fuel that has powered modern societies since industrial revolution and it still remains the dominant source of energy. Coal contains varieties of mineral matter which are of significant interest to the coal scientist. The mineral matters present in coal may occur as minerals, mineraloids and as organically-associated inorganic elements (Ward 2002). Elements, predominantly, carbon, hydrogen, oxygen, sulphur nitrogen and trace amount of calcium, magnesium, potassium, iron, aluminium, silicon, copper, boron, cadmium, arsenic, etc can be found in coal (Dai et al., 2005; Finkelman, 1994; Saikia et al., 2009; Singh et al., 2012; Singh et al., 2014; Saikia et al., 2014a). Chemical composition of coal ash is the important factor in fouling and slagging problems in coal-fired boilers and correlates with ash fusion temperature (AFT) of the coal ash produced. Ash fusion temperature of feed coal is also an important parameter in designing the coal fired boiler. The temperature of the gasifier or boiler should be maintained above the fusion temperature of the coal ash so as to keep the ash in the molten stage for removal during the combustion process. Thus, ash fusion temperature (AFT) ranges are considered as one of the important parameters and provide vital information on the suitability of a coal for combustion or gasification purposes. It is understood that fusion temperatures of coal ash are affected by different ash compositions. Fusion temperature of coal ash decreases with an increase in the CaO and Fe_2O_3 contents up to an optimum value of 35% (Liu et al. 2013; Vassileva and Vassileva 2002). A drastic drop in AFT was reported with decrease in the amount of kaolinite owing to the transformation of kaolinite into high melting mullite during heating at high temperatures (Li et al. 2011). Thus, it is necessary to study the mineralogy as well as the ash

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chemistry of coals and its relationship with the AFT in order to maintain the performance of a coal-fired boiler. Moreover, the information regarding the occurrence and distribution of minerals and elements in coal is also very important for coal processing, coal combustion, gasification and coking as well as for environmental implications. Minerals are the fundamental components that affect the occurrence and behaviour of a number of trace elements (Finkelman 1995). Hence, distribution of minerals as well as the concentrations of the elements is highly affected through different beneficiation methods. Numerous studies have been carried out on the variation of element characteristics in coal (Hower et al. 1998; Huggins et al. 2009; Moore and Esmaeli 2012; Wang et al. 2006; Khare and Baruah 2010; Singh et al., 2015). Vamvuka et al. (2001) and Saikia et al. (2009) studied the mode of occurrence of different elements in coal ash. Trace elements such as Pb, Cr, As, Hg, Sb, Cd, Co, Cu, Ni and Se (Sulovsky 2002; Raask 1985) present in the coals are reported to be associated either organically or inorganically. The majority of Indian coal reserves consist of non-coking variety of bituminous, sub-bituminous and lignite coals distributed almost all over the country. As on 1st April'2014, Ministry of Coal, G ovt. of India reported that the northeast region of India has around 1.597 billion tonnes of coal reserves distributed in the states of Meghalaya, Assam, Sikkim, Arunachal Pradesh and Nagaland. They possess variable petrological elements (Singh et al., 2013) and physico-chemical attributes like high sulfur, low ash, high heat value, high volatile matter and high tar yielding during carbonization. On the basis of physico-chemical analysis, Assam coals are sulphur rich and sub-bituminous (Khare and Baruah, 2010).The coals of this region contain ash ranging from 3.9 to 17.6% based on recent analysis (Baruah et al., 2013). There will be increased coal demand in near future for power generation in the world, including India, which needs continuous supply of clean coal suitable for power plants in order to meet the requirement and environmental challenges. Hence, there is worldwide interest in the beneficiation of low grade coals. It is essential to understand the mineralogy and the ash chemistry before and after the combustion of low grade coals. Considering the necessity and importance of the ash fusion temperature of low grade coals, beneficiation studies of the coal sample from Tirap colliery, Makum coalfield, Assam were carried out by four different methods. The coal ashes of raw coal and its beneficiated samples were characterized for their mineralogy and ash chemistry. The relationships between the ash fusion temperatures and the ash compositions of raw and beneficiated coals are evaluated, which would be helpful in designing the boiler for combustion of low grade and high sulfur coals.

EXPERIMENTALS

Coal Samples and Beneficiation Methods

The representative coal sample was obtained from coal chemistry pilot plant of CSIR-NEIST (India), which was previously collected from Tirap colliery of Makum coalfield (latitude 27°13'- 27°23'N and longitudes (95°35'-96°00'E), Assam. The geological setting of the coalfield has been described by Ahmed (1996) and Saikia et al. (2014a).

Four different types of beneficiations were performed with raw coal (TR). In a typical beneficiation study, 20 g of raw coal sample was added to a mixture of 8.8 ml 20% HCOOH and 50 ml 20% H_2O_2. The mixture was refluxed at its boiling point for one hour. It was then filtered and washed with de-ionized water until the pH becomes neutral. The oxidized sample (TOX) obtained was dried and preserved for further analysis. About 10 g of TOX was mixed with 100 ml of 1M NaOH solution and refluxed for one hour. The mixture was then filtered and washed with dilute HCl solution until the pH became neutral and then with de-ionized water to remove the chloride ions. The resultant sample (TOXA5H) was air dried and preserved for further analysis. In another beneficiation method, 20g of raw coal sample was mixed with 200 ml of 1M NaOH solution and refluxed for one hour. The mixture was filtered and washed with dilute HCl to neutralize and then with de-ionized water to make the sample chloride free. The obtained sample (TA5H) was air dried and preserved for further analysis. In the fourth beneficiation process, 20g of raw coal sample was mixed in an alkali solution (NaOH: KOH in 1:1 ratio) and subjected to ultrasonication (Model: Sonapros PR-1000 M) for 3 hours at 20 KHz energy under atmospheric pressure. The resultant mixture was filtered and washed with de-ionized water until the solution became neutral. The beneficiated coal sample (TAU) was air dried and preserved for further analysis. The ashes of the raw and beneficiated coal samples were obtained by heating the coal samples in a muffle furnace at around 815 °C under static air with a heating rate of 3°C/min and holding at this temperature for 1 hour.

Chemical Analysis of Coals

The proximate and sulfur analysis of the coal samples were performed in proximate (TGA 701, Leco, USA) and sulfur (S-144DR, Leco, USA) analyzers, respectively, using standard methods (ASTM, 2002; ASTM 2011a, b, c).

Elemental analysis (C/H/N) was performed using a Perkin- Elmer (Model 2400) elemental analyzer (ASTM, 1991). The calorific values were determined using a bomb calorimeter (ASTM, 2006). The ash analysis of coal samples was carried out using standard methods (Himus, 1954).

Ash Fusion Temperatures (AFT) Analysis of Coal Ash

Ash fusion temperature (AFT) measurements were carried out using an ash fusion point determination apparatus (Leitz Wetzlar). The measurements were performed following standard procedure (Indian Standard, 1990). It was carried out by heating a little amount of coal ash sample (~2 mg) at a rate of 10 °C/min up to 1000 °C, and then changing the heating rate to 5 °C/min up to 1600°C in absence of air. During the process, the initial deformation temperature (IDT), hemispherical temperature (HT) and final fusion temperature (FT) were recorded according to the specific shapes of the ash cylinder formed. The ash fusion temperature (AFT) ranges of the individual coal samples were also determined.

XRD, FTIR and SEM Analyses of Coals

The XRD analysis of the coal ashes was performed in X-ray Diffractometer (Rigako, ULTIMA IV). X-ray diffraction data of raw and beneficiated coal samples were obtained with the start angle 5.00, stop angle 100.00 and step angle 0.02^o with a scanning rate of 4^o per minute and target Cu Kα (θ =1. 54056 Å). The program 'XG operation RINT 2200' associated with the XRD was used to process the diffractogram and the library database 'Rigaku PDXL 1.2.0.1' was used for identification of the peaks. The SEM images of the coal samples were obtained by a Scanning Electron Microscope (JSM-6360; JEOL). The samples were prepared by sprinkling powdered samples onto a carbon coated metallic holder followed by gold coating. The FTIR spectra of the coal ashes of the raw and beneficiated coals were recorded using a Perkin-Elmer system (Spectrum 100). The pellets were made by mixing same weight of dried samples and KBr during recording of each FTIR spectrum. The spectra were recorded in a wavelength range of 400-4000 cm^{-1}, with an accuracy of 0.3.

Trace Element Analysis in the Coals

Both the coal and ash samples were digested in a mixture of acids. About 0.2 g of each sample was taken and a mixture of HCl, HF, HNO_3 (3 ml of 37% con. HCl, 3 ml of 40% con. HF, and 9 ml of 65 % con. HNO_3) added. Each sample mixture was then digested in a microwave digester (Milestone: Start-D). After digestion, each sample was cooled, filtered using a Whatman-42 filter paper and diluted with de-ionized water to 50 ml. Filtrates were analyzed for the presence of the trace elements using Atomic Absorption Spectrophotometer (AAS, Perkin Elmer, model Analyst- 700).

RESULTS AND DISCUSSION

Proximate and Ultimate Analyses

Proximate and ultimate analyses of raw and beneficiated coals are presented in Table 1. It is observed that moisture content (M) of the beneficiated coals is marginally reduced, which is expected due to chemical treatment and subsequent drying. Hardly any changes are observed in the volatile matter (VM), fixed carbon (FC), carbon (C) and hydrogen (H) contents after the beneficiation processes. However, ash and total sulfur (TS) in the beneficiated coals are reduced considerably, as compared to the raw coal. Maximum reduction of mineral matter and consequently ash (~65%) was achieved, when coal samples were subjected to ultrasonication in alkali solution, whereas treatment with in-situ generated per-acid and alkali followed by acid washing results in removal of ~54% and ~52% respectively. Total sulfur removal is comparatively less when subjected to ultrasonication in presence of alkali solution (~17%) than that of per-acid oxidation (~24%). This is due to the fact that per-acid generated insitu is one of the strong oxidant, which is capable to oxidize sulfur functionalities in coal to make them extractable in the alkaline/acidic medium (Baruah et al. 2007).

Mineral Transformations

Based on the association with the coal matrix, minerals

Table 1. Proximate and ultimate analyses of the raw and beneficiated coals (dry basis, wt %)

Coal samples	M	VM	Ash	FC	C	H	N	O	TS	Deashing	Desulfurization
TR	2.07	44.00	3.58	52.43	82.30	6.62	1.0	3.34	3.16	—	—
TOX	1.74	43.70	2.66	55.41	82.03	6.59	0.91	4.97	2.84	25.70	10.12
TOXA5H	1.99	45.21	1.65	53.21	81.93	6.40	0.89	6.73	2.40	53.91	24.05
TA5H	1.89	44.92	1.72	53.36	82.46	6.58	0.90	5.83	2.51	51.96	20.56
TAU	1.74	47.36	1.27	51.36	81.46	6.29	1.0	7.36	2.62	64.52	17.08

M- Moisture, A- Ash, VM- Volatile Matter, FC- Fixed Carbon, TS: Total Sulphur are classified as included or excluded (Liu at al. 2007). Some of the excluded minerals can be removed by flotation, while water or acid soluble minerals (included type) can be removed from coal through leaching. During the alkali extraction, a marginal increase in ash content from oxidized coals was observed due to the formation of sodium aluminosilicates. Alkali dissolves the alumina and silica present in the coal samples as quartz, kaolinite and montmorillonite, which are acidic in nature and can react with alkali to form soluble silicate and alumina-silicate (Baruah and Khare, 2007). Sharma et al. (1961) studied the effect of alkali treatment on coal and associated minerals. They found that new hydroxyl groups were formed during the process due to hydrolysis of un-reactive oxygen. Under mild conditions, treatment of alkali and acid resulted upto 75% demineralization of Indian coals (Sharma and Gihar, 1991). Wang et al. (1986) also observed that the alkali treatment of coals results in the formation of either $3Na_2O.3Al_2O_3.6SiO_2$ or $3Na_2O.3Al_2O_3.6SiO_2$ Na_2SO_4.

Thus, four different beneficiation processes can alter the mineral compositions of the beneficiated coals. This difference may also cause variations in the AFTs of the coals as shown in Table 1. Some of the minerals present in raw and beneficiated coal ashes are investigated through XRD and FTIR analyse and are shown in Figs. 1 and 2 respectively. Deashing of the samples treated with alkali (TOXA5H and TA5H) are higher compared to that of oxidized samples (TOX). This may be due to the presence of higher amounts of acid insoluble silicates, alumina-silicate and pyrites in the oxidized sample. These minerals can easily react with alkali rather than acid (Shivaprasad et al. 2010; Wang et al. 1986) as per the following reactions:

$$2\,NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$
$$30\,NaOH + 8FeS_2 \rightarrow 4Fe_2O_3 + 14Na_2S_2O_3 + 15H_2O$$

During ash formation, the minerals in coal decompose to various products. The abundance of hematite in the beneficiated samples (Fig. 1) probably reflects a greater degree of oxidation of pyrite. Oxidation of pyrite to hematite would also contribute to the reduction of total sulfur content of the beneficiated coals. Some of the possible mineral decomposition reactions during ashing (Li et al. 2011; Mitchell and Gluskoter 1976; Baruah and Khare 2007; Sulovsky 2002) are as follows:

$$\text{Anhydrite or Gypsum } (CaSO_4) \rightarrow CaO + SO_2 \qquad (1)$$

$$\text{Pyrite } (FeS_2) \rightarrow Fe_2O_3 \qquad (2)$$

$$\text{Kaolinite } (Al_2O_3.2SiO_2.2H_2O) \rightarrow \text{Metakaolin } (Al_2O_3.2SiO_2) \qquad (3)$$

$$\text{Metakaolin}(Al_2O_3.2SiO_2) \rightarrow \text{Mullite } (3Al_2O_3.2SiO_2) \qquad (4)$$

$$\text{Boehmite } (Al_2O_3.H_2O) \rightarrow \gamma\text{-}Al_2O_3 + H_2O \qquad (5)$$

$$\left.\begin{array}{l}\text{Calcite}\\ \\ \text{Dolomite}\end{array}\right] (CaCO_3) \rightarrow \text{lime } (CaO) + \text{Periclase } (MgO) \qquad (6)$$

$$\begin{array}{ccc} \text{Pyrite} \rightarrow \text{Pyrrhotite } (Fe_{0.877}S) & \rightarrow & \text{Sulfideoxide mixture (molten)} \\ & & \downarrow \qquad (7) \\ \text{Hematite } (Fe_2O_3) & \leftarrow & \text{Crystallization of Magnetite } (Fe_3O_4) \end{array}$$

Sodium aluminium silicate hydroxide can be formed because of the partial dissolution of the minerals in the coal samples. Kaolinite forms sodium aluminium silicate hydroxide with alkali as per the following reaction:

$$3Al_2Si_2O_5(OH)_4 + 8NaOH \rightarrow [Na_8(Al_6Si_6O_{24})(OH)_2] \qquad (8)$$

XRD Analysis of Raw and Beneficiated Coal Ashes

Some of the minerals are qualitatively identified in the raw and beneficiated coal ashes based on the d-spacing values (Table 3). The comparative examination of minerals in the samples was made through their intensities. It was observed that the peak intensities of mineral changes with the types of beneficiation methods or treatments. The minerals like montmorillonite (M), illite (I), kaolinite (K), calcite (C) are present in most of the samples. However, hematite (H) peak is more intense in the beneficiated samples than in the raw sample. Chlorite (Cl) was absent in the beneficiated samples, which was present in the raw sample. On extraction with NaOH, some of the minerals (e.g. hematite) become less abundant compared to those in the oxidized sample. The minerals, whose intensities were reduced during all the beneficiation processes includes calcite (C), hematite (H), illite (I), montmorillonite (M), gypsum (G), rutile (R), kaolinite (K). The peak intensities of the minerals e.g. quartz (Q), illite (I), montmorillonite (M), kaolinite (K) were reduced in TA5H compared to those in TOXA5H. However, peak intensities of the minerals such as hematite (H), calcite (C), gypsum (G), rutile (R) were slightly increased in TOXA5H than that of TA5H. In the ultrasonicated sample (TAU), some of the peaks, such as illite (I), montmorillonite (M), pyrite (P), aragonite (Ar), alumina (A) are not observed, which have been removed during ultrasonication. However, some of the mineral peaks were intense in the ultrasonicated sample compared to those in raw sample. It is observed that the peaks assigned

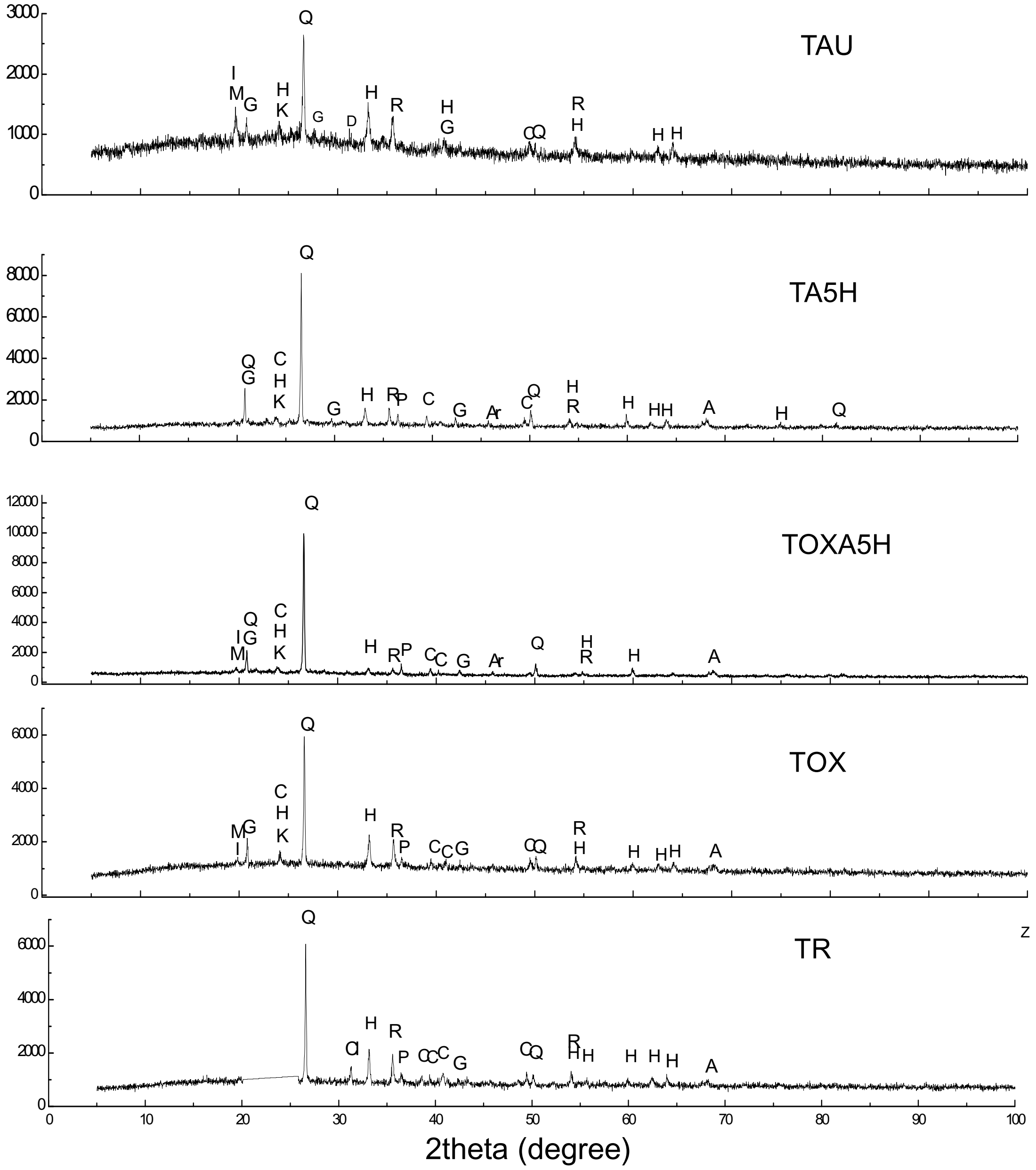

Fig.1. XRD patterns of raw and beneficiated coal ashes (Q= Quartz; M= Montmorillonite; H= Hematite; P= Pyrite; C=Calcite; Cl= Chlorite; R= Rutile G= Gypsum; I= Illite; Ar= Aragonite; A= Alumina; D=Dolomite; K= Kaolinite)

for illite (I), montmorillonite (M), quartz (Q), calcite (C), gypsum (G), hematite (H), kaolinite (K), dolomite are more prominent in the ultrasonicated sample than that of the raw coal. This is attributed to the transformation of minerals during the ultrasonication of coal (Saikia et al. 2014b). However, chlorite (Cl), pyrite (P) and alumina (A) are not observed in the ultrasonicated sample (TAU), which are removed during the process.

FTIR Analysis of Coal Ashes

The presence of minerals in raw and beneficiated coal ashes was also assessed through FTIR spectroscopy. The assignments of the minerals in the raw and beneficiated coals are depicted in Fig. 2. FTIR spectroscopy also supports the presence of minerals like gypsum (G), calcite (C), aragonite (Ar) quartz (Q), kaolinite (K) in the raw and beneficiated coals. However, the peak intensities of the minerals in the FTIR spectra vary due to the type of beneficiation processes. The peak intensities of the minerals, as seen in the treated samples were, more intense than that of the raw sample. The peak intensities of the minerals in TAU sample were more intense than the rest of the beneficiated samples. This

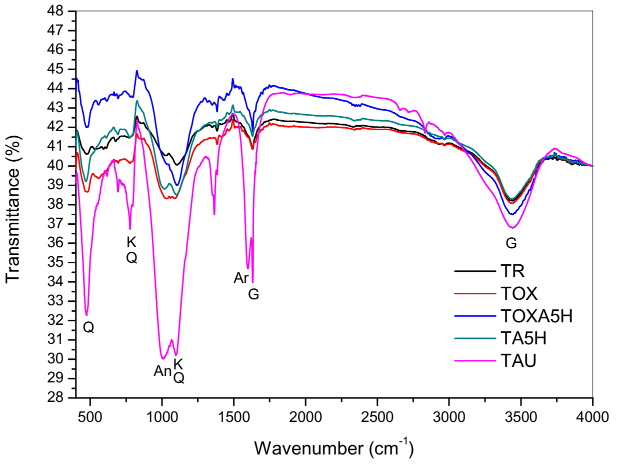

Fig.2. FT-IR spectra of raw and beneficiated coal ashes. (G= Gypsum; C = Calcite; Ar = Aragonite; Q = Quartz; K=Kaolinite)

may be due to the transformation and conversion of the minerals in the coal matrix during the beneficiation process. However, this is to be further studied with more samples at different temperatures for understanding the mineral transformation in the ultrasonication process.

Kaolinite undergoes dehydration at approximately 400-525 °C (Falcone et al. 1984). Due to dehydration, the kaolinite structure can collapse and form metakaoline. But due to the poorly defined crystalline structure, metakaolin could not be detected in the XRD. In coal ash samples, calcium reacts primarily with dehydrated kaolinite forming alumino-silicates (Falcone et al. 1984). The aluminosilicate minerals e.g. montmorillonite, chlorite, illite are detected in XRD and FTIR analyses (Figs. 1 and 2). The highest intensity peak in all the XRD is of quartz, because of its abundance and stability throughout the ashing process (Falcone et al. 1984).

SEM Analysis of Coals

The SEM analysis of raw and beneficiated coals is also carried out to see the effect of the beneficiation process. Fig. 3 shows the SEM photomicrographs of raw and treated coals. Fig. 3(A) represents the SEM image of raw coal with a homogeneous distribution of crystals of different minerals. Both luminous and non-luminous features are seen on their surfaces; however, the majority is non-luminous (Manoj et al., 2009). The luminous features indicate the presence of mineral phases. The surface of the coal is rough containing micro-cracks. Because of the beneficiation processes, the surface of coal becomes spongy, which can be seen in the Figs. 3B-E. Fig. 3B which is due to leaching of coal by oxidation in in-situ generated per-acid. The alkali treatment and subsequent extraction processes lead to cavity formation after the removal of oxidized soluble mineral matters as seen in Figs. 3C-D. Silicate and alumina-silicate minerals are acidic in nature and have a high affinity towards OH^{-} ions. These minerals are partially dissolved in alkali solution and can be removed via solvent extraction leading to cavity formation. Formation of cavity also facilitates the breakage of coal particles, which can be observed in the SEM image of alkali treated samples (Fig. 3E). The maximum amount of minerals removed from all the beneficiated coals, resulted in the formation of cavities and hence decreases the ash yield (see Table 1).

Ash Fusion Characteristics of Raw and Beneficiated Coals

The coal ashes are normally classified as low melting (<1300 °C), medium melting (1300-1450 °C) and high melting (>1450 °C) (Vassilev et al. 1995). Table 2 represents some of the oxides present in the coal ashes along with AFTs of the ashes. AFTs of coal ashes are found to vary considerably among the raw and beneficiated coals. initial deformation temperature (IDT) is in range of 1040-1210 °C, hemispherical temperature (HT) is found to be in the range of 1300-1360 °C and final temperature (FT) is in range of 1460- 1500 °C. Thus, these high sulfur coal samples can be considered as medium melting AFT types. The effects of the oxides present in the ash on the ash fusion temperature (AFT) are shown in Figs. 4-8.

It is observed that CaO significantly influences the AFTs (Fig. 5). With an increase in CaO content, IDT is increased gradually. This may be due to the presence of a monomeric

Table 2. Ash analysis of the coals (wt %)

Ash samples	Ash	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Others	AFT(°C)			GCV (kcal/kg)
								IDT	HT	FT	
TR	3.51	47.8	28.8	15.7	0.92	0.13	6.65	1210	1360	1460	7810
TOX	2.61	39.07	26.10	12.03	0.15	0.15	22.5	1120	1300	1500	7870
TOXA5H	1.62	37.9	9.08	11.4	0.04	0.12	41.46	1040	1320	1500	8015
TA5H	2.02	35.2	20.36	13.5	0.11	0.08	30.75	1120	1340	1500	796
TAU	1.25	34.5	10.71	11.9	0.09	0.11	42.69	1060	1300	1480	7560

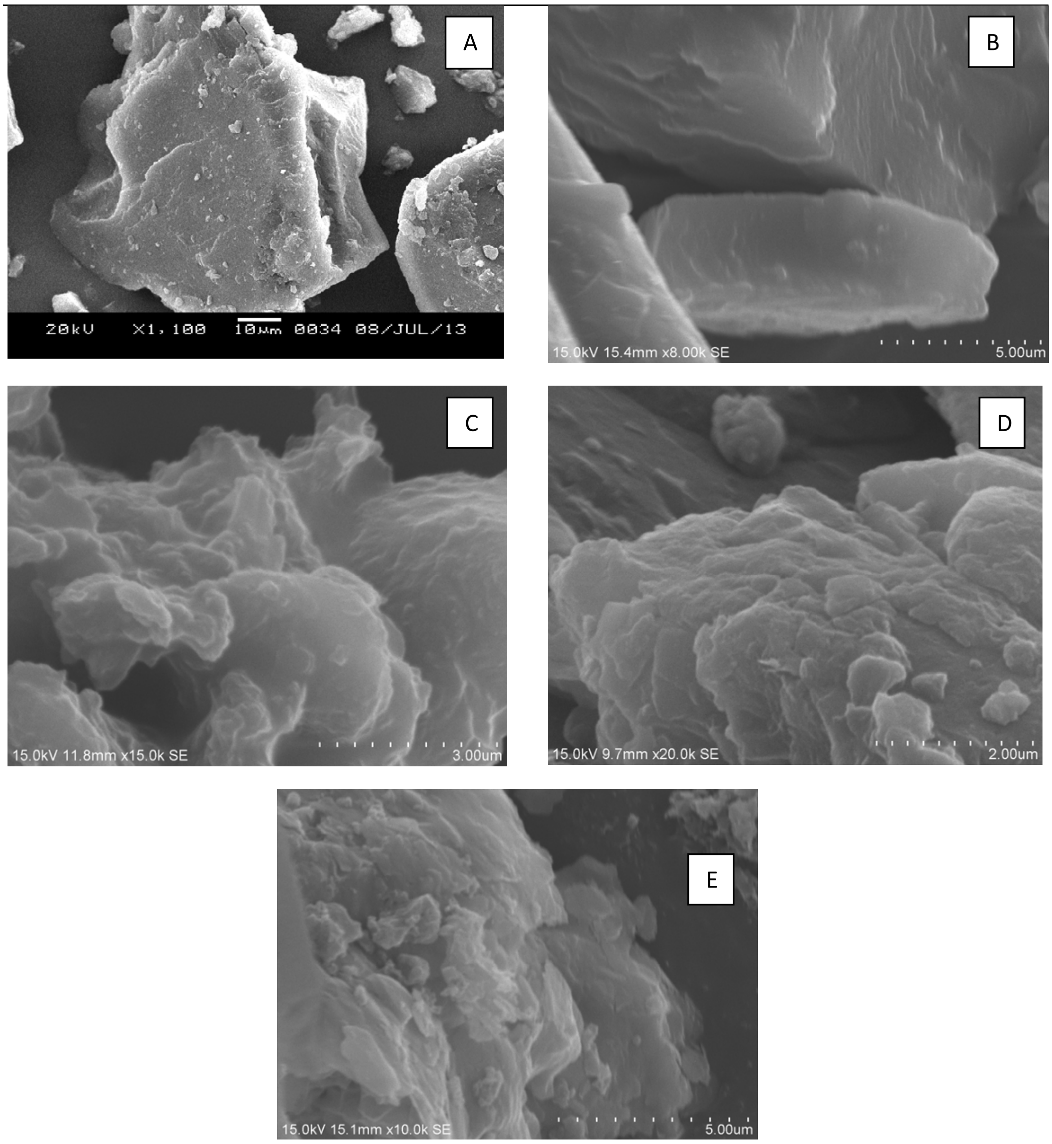

Fig.3. SEM images (SE) of raw and beneficiated coals; [**A** (TR)-rough surface with microcracks; **B** (TOX)-spongy surface; **C** (TOXA5H)-Cavity formation; **D** (TA5H)- cavity formation, breakage of coal particles; **E** (TAUS)- breakage of coal particles]

form of CaO, which has a high melting point (Liu et al. 2013). However, no significant change is observed in case of HT and FT due to CaO. Vassileva and Vassileva (2002) reported that CaO has a property of fluxing action at higher temperature, which leads to decrease in the AFTs with increasing in its amounts. However, the samples under investigation contain very low amount of CaO as compared to other coals (CaO >5%), which may reduce the effect of CaO (Song et al. 2010). The reverse change of IDT with CaO contents may be due to the occurrence of non-mineral Ca in coal with organic sulfur during ashing (Saikia et al. 2014). On the other hand, CaO is a refractory oxide (Quann and Sarofim, 1982) and its slight increase in concentration increases the AFTs (Vassileva and Vassilev 2002).

The abundance of Fe in coal ash is basically related to the Fe-based minerals such as pyrite, hematite, chlorite etc. The content of Fe_2O_3 is plotted against AFTs (see Fig.4). IDT shows a significant change with respect to the different percentages of Fe_2O_3, which is less significant in the case of HT and FT. IDT increases gradually with an increase in the Fe_2O_3 content in coal ash of raw as well as beneficiated samples. However, Liu et al. (2013) have reported a decrease in AFT with increasing Fe_2O_3 content in coal ash. Saikia et al. (2014) have reported through XRD study, a significant proportion of Fe in coals in non-mineral form. This includes Fe in solution in pore water, amorphous Fe oxides or hydroxides within the mineral matter, or Fe attached in some way (e.g. by adsorption) to the organic matter.

Table 3. d-values in the XRD of the coal ashes and their assignments

d-spacing values (Å)	Possible minerals	Chemical formulae
4.44	Illite (I)	$K_{1.5}Al_4(Si6.5Al_{1.5})O_{20}(OH)_4$
4.44	Montmorillonite(M)	$(Na,Mg,Al)Si_4O_{10}(OH)_2$
4.29, 3.35, 1.81	Quartz (Q)	SiO_2
4.29, 2.96, 2.85, 2.67, 2.19	Gypsum (G)	$CaSO_4.2H_2O$
3.67, 2.23,1.83	Calcite (C)	$CaCO_3$
3.67,2.69,2.51,2.19, 1.83,1.69, 1.59,1.45	Hematite (H)	Fe_2O_3
3.67, 2.69	Kaolinite (K)	$Al_2Si_2O_5(OH)_4$
2.85, 2.86	Dolomite (D)	$CaMg(CO_3)_2$
2.85	Chlorite (Cl)	$(Mg,Fe,Al)_6(AlSi)_4O_{10}(OH)_8$
2.69,2.45,1.98	Aragonite (Ar)	$CaCO_3$
2.45	Pyrite (P)	FeS_2
2.45	Rutile (R)	TiO_2
1.37	Alumina (A)	Al_2O_3

Such Fe may be relatively reactive, compared to Fe in discrete minerals such as pyrite, and could therefore be involved in this abnormality in ash fusion temperature observed in this study.

Fig. 6 illustrates the relationship between SiO_2 contents and AFT of raw and beneficiated coals. There is no significant change in HT and FT with the changes in SiO_2 content in the samples. However, a gradual increase in IDT is observed with higher SiO_2 content. This increase in IDT is possibly due to refractory nature of SiO_2 (Quann and Sarofim 1982).

The greater abundance of Al_2O_3 is related to the occurrence of kaolinite in coals. The variation of Al_2O_3 content with the AFTs is shown in Fig. 7. With the increase in Al_2O_3 content, a gradual increase in the IDT is observed. However, no change is observed in case of HT and FT. The increase in AFTs with increasing amount of Al_2O_3 is also due the refractory nature of this oxide (Vassileva and Vassilev 2002).

Table 4. Some of the Trace elemental in the raw and treated coal ashes (ash basis; ppm)

Elements	Coal ash samples				
	TR (ash: 3.51%)	TOX (ash: 2.61%)	TOXA5H (ash: 1.62%)	TA5H (ash: 2.02%)	TAU (ash: 1.25%)
Ca	29	1.9	0.50	0.60	0.40
Cu	0.10	0.30	0.10	0.10	0.10
Fe	270	252	122	230	147
Cr	0.40	0.10	0.10	0.50	0.50
Mn	1.7	0.60	0.40	1.6	1.1
Mg	40	21.0	5.0	6.0	5.2
Pb	0.11	0.12	0.13	0.11	0.11
Ni	1.8	1.3	1.2	1.8	1.5
Na	41	43	65	47	43
As	0.07	0.12	0.05	0.06	0.04

The changes of AFTs to MgO content have also been studied and depicted in Fig. 8. It is observed that IDT decreases with increasing MgO content in coal ash. It is reported that a basic oxide can also decrease the AFTs of coal ash (Gul and Uner 2007). But, HT and FT show no variation with change in MgO content in raw and beneficiated coals.

Trace Element in Raw and Beneficiated Coal Ashes

Some of major and trace elements are determined in raw and beneficiated coal ash samples and are summarized in Table 4. The concentration of elements like Fe, Cu, Ca, Cr, Mn, Mg, Pb, Ni, Na and As were considerably reduced in the coal ashes after beneficiation processes. During beneficiation, the maximum decrease in the elemental concentrations has been observed in the ultrasonicated coal ash sample (TAU). This may be due to breaking of coal particles by the ultrasonic energy, which leads to the removal of elements embedded within the coal matrix. Fe content is significantly reduced in the sample after beneficiation processes. Kukier et al. (2003) reported that iron in coal ash is mainly present as magnetite mixed in various proportions with hematite and a minor proportion can be assimilated in the glassy matrix. In the oxidized coal sample (TOX), the iron content is reduced as compared to raw sample (TR). It is due to the oxidation of pyrite to iron oxide, which is acid-soluble and hence can be leached out easily. The iron concentrations in the samples (TOXA5H, TA5H) are again reduced as compared to the oxidized sample (TOX) due to alkali extraction followed by acid treatment. There is no significant change in the concentration of Cr after beneficiation. It indicates the presence of organically associated Cr in coals, which is hard to remove by such beneficiation processes. The concentration of Cu was slightly reduced after beneficiation. This implies that Cu may be either shielded by the organic matrix, or may be present as insoluble minerals or as organometallic complexes (Swaine, 1990; Goodarzi, 2002; Finkelman, 1995; Prachiti et al., 2011). Mn is also found to be reduced after the beneficiation processes. Swaine and Goodarzi (1990; 1995) also suggested Mn can be present in coal as carbonates, which is not so hard to remove. Calcium is significantly reduced in the beneficiated samples. Calcium has multiple modes of occurrence such as anhydrite, calcite or within the glassy matrix. Calcium is largely released as cation regardless of the extractant used in beneficiation processes (Kim et al. 2003). Thus, the all the elements studied in coal ashes have shown reduction after beneficiation. However, the extent of

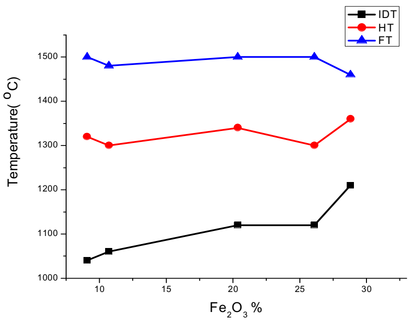

Fig.4. Effect of Fe_2O_3 on AFTs.

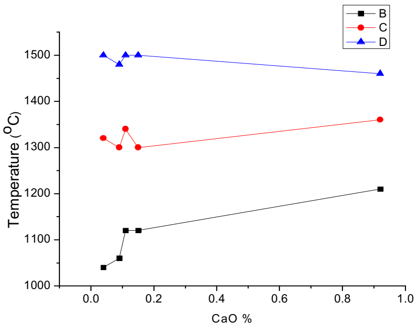

Fig.5. Effect of CaO content on AFTs.

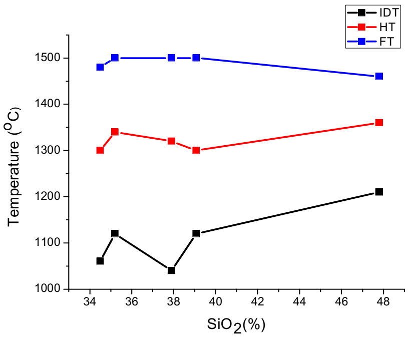

Fig.6. Effect of SiO_2 on AFTs.

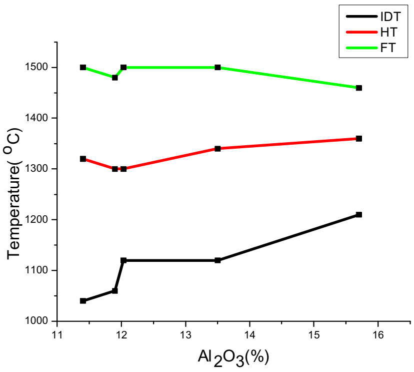

Fig.7. Effect of Al_2O_3 on AFTs

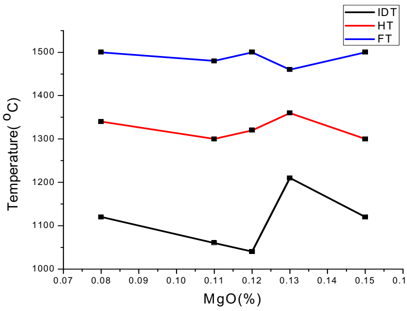

Fig.8. Effect of MgO on AFTs

removal of the elements depends on the methods used for beneficiations. Solubility of the elements in the solvent used is also a factor for their removal. Mg content is decreased during all the beneficiation methods adopted. Maximum Mg removal is found in TAU sample, which was subjected to ultrasonication in the presence of alkali. Magnesium in coal mainly occurs in association with dolomite and chlorite minerals. In our study, Ni content is also reduced in clean coal by these beneficiation processes.

Arsenic mainly occurs with iron disulfides in coal and a minor part is bonded directly to organic matter (Sulovsky 2002). Some researchers (Kryukova et al. 1985; Goodarzi 1987) also reported that As is organically associated with coal. Belkin et al. (1997a, b) reported arsenopyrite-rich coals. Studies also have shown that As occurs as arsenate in coals (Ren et al. 1999). In present study, As content is slightly reduced after beneficiation. The oxidized samples (TOXA5H) have shown higher As content than raw coal. This may be because of arseno-pyrites, which is not oxidized with per-acids. The As content is significantly reduced in two samples (TA5H and TAU) during the processes like alkali extraction and ultrasonication. In low-rank coals, significant content of ion-exchangeable sodium is present associated wth the coal matrix in salt form of carboxylic groups (Schafer, 1970). On heating coal, these groups containing alkali species decompose and react with other ash components such as silica (Kosminski et al. 2006). Sodium also present in the form of sodium chloride in coals (Kosminski et al. 2006). In present study, sodium content is found to be increased in the beneficiated samples as compared to raw sample. This may be due to the formation of gel type insoluble sodium aluminosilicates due to the reaction of sodium with kaoline (Mukherjee et al. 2001). Among all the beneficiation processes studied, the ultrasonication is the best process for removal of the unwanted elements of the coal occurring as impurities.

CONCLUSIONS

The XRD analysis revealed the presence of minerals, like illite (I), montmorillonite (M), quartz (Q), calcite (C), gypsum (G), hematite (H), kaolinite (K), dolomite in the high sulfur Assam (Indian) coals. The FTIR analysis also supports the presence of the minerals like gypsum (G), calcite (C), aragonite (Ar), quartz (Q), kaolinite (K) in raw and beneficiated coals. The mineral transformations occurred during the beneficiation processes such as oxidation, alkali treatments, and ultrasonication affect the AFTs of the coals. The SEM analysis reveals the formation of cavity due to removal of minerals embedded in coal matrix during beneficiation processes. The Ash Fusion Temperature ranges (AFTs) of high sulfur coal (India) generally increases with increase in Fe_2O_3 and CaO contents in coal ashes. It could be due to the non-mineral forms of Ca and Fe in coals. The results obtained in this paper bear a significant importance to the thermal-based industries using high sulfur coals. Trace elemental analysis reveals that the elements are also reduced to a considerable extent after beneficiation. The ultrasonication is one of the best processes for removal of these unwanted elements from coals.

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