K. M. P. SINGH
PRIYANKA KUMARI UJALA
K. M. K. SINHA
and
T. GOURICHARAN

Studies on the characterization of Indian coals using FE-SEM and EDS and its relevance to coal washability

Clean coal technology is a very important area of research and development as it has enormous potential to reduce harmful emissions, improves fuel efficiency which meets the present and future energy requirements. Indian coals are known for drift origin, the associated mineral matter is responsible for formation of ash in the coal, which are intimately mixed with coaly matter during the time of formation. The mineral matter present in the coal has detrimental impact on different end uses. Gradual increase in ash percentage and deterioration of good quality Indian coals have attracted the researchers to look inside the coal for its judicious utilization. Coal is extremely complex and the most heterogeneous fuel, composed of a number of distinct organic entities called macerals and inorganic entities called minerals. The term, "mineral matter", usually applies to all inorganic, non-carbonaceous material, includes those inorganic elements which may occur in organic combination. The inorganic mineral matter divided into two groups-inherent which is grown with plant life and seldom exceeds 2-3 per cent of whole mass while extraneous mineral matters generally consists of large bits and pieces of inorganic material typical of the surrounding geology. These extraneous mineral matters so finely divided and uniformly dispersed within the coal and enter into the coal matrices and behave like inherent mineral matter which cannot be removed by any means of physical washing. The coal at below -500 micron is density separated using centrifuge and studied with FE-SEM and EDS. Knowledge of the morphological relationship between the inorganic phases and organic matter is helpful to devise suitable schemes for cleaning coals containing such particles. The surface morphology, presence of pore and their sizes were carried out using scanning electron microscopy; while EDS analysis helps to determine the elemental composition of the mass of a particular area, advantage is simplicity with accuracy and speed.

Dr. KMP Singh, Scientist, Ms. Priyanka Kumari Ujala, Scientist, Mr. KMK Sinha, Principal Scientist and Dr. T. Gouri Charan, Sr. Principal Scientist & Head, of Head Research Grouop, CSIR-Central Institute of Mining & Fuel Research, Dhanbad

Introduction

The energy growth is directly linked to well-being and prosperity across the world. Meeting the growth demand for energy in a safe and environmentally responsible manner is a key challenge for researchers. The coal is abundantly available and cheapest source of energy with their vast reserves worldwide, expected to provide energy for longer duration. The Indian coals are Gondwana origin which blessed with low sulphur but high mineral matter content. The coals are having two major components – inorganic "the mineral" and organic "the macerals". The mineral matter is reported higher in Indian coal and intimately mixed with the coaly matter due to drifted origin, consider to have negative role in the energy production at the same time creates environmental issues at different levels.

Coal maceral is the organic part, used to provide energy and controls its overall behaviour. Spackman' expanded the maceral concept and made it more useful for applied studies. The macerals are smaller in size <100 micron in diameter, and well mixed together to make it difficult to separate. The macerals are suffix as 'inite' and classified into three main groups – vitrinite, exinite or liptinite and inertinite – all are having distinctive set of physical and chemical properties. The first two groups are traditionally held to be reactive and the third one is relatively less reactive. Macerals generally occur in association with each other and are known as 'microlithotype'. The maceral compositions of coals differ with ranks, for the macerals of same rank, vitrinite contains more oxygen, exinite more hydrogen and inertinite more carbon.

There are various coal properties such as ash content, sulfur content, moisture content etc. which may help to know some important fundamental coal properties such as rank, chemical structure and maceral compositions in the characteristic and kinetic behaviour of coal [4].

The inorganic mineral matter may be one of the constituents from the original plant materials called inherent mineral matter and may also be leached into coal from surrounding environment during the processes of coalification called extraneous mineral matter, responsible for ash.

Under the circumstances, inherent mineral matter has a uniform distribution within the coal and seldom exceeds 2-3 per cent of the coal ash which is imbedded with the coaly matter. Sometime the minerals are slowly filled up in the cell matrix as a slow and long-term contact with the soluble/ suspended solution and become part and parcel of the coal matrix. The extraneous mineral matter generally consists of large bits and pieces of inorganic material typical of the surrounding geology at the time of coalification. In some cases the extraneous matter in drift origin is so finely divided and uniformly dispersed within the coal, it behaves like inherent mineral matter, and hard to separate by physical means of coal washing. The extraneous ash forming mineral matter, only a part can be removed by density gradients and other physico-chemical methods of coal preparation.

Materials and methods

The coal from Eastern Coalfields, were collected and pulverized to 72 mesh (212 micron) size and the representative fraction of coal sample was used in the study. The proximate analysis of the coal were determined followed by standard IS 1350-I (1984).

A. Coating

The representative coal samples after centrifugation were dried well till constant weight. A pinch of the coal sample gravity wise were stuck on 12.7 mm stub over double sided carbon tape and coated with gold for 90 seconds at 20 mA. The uniform coatings of the sample to be analyzed were assured as the continuously rotating stage of the cotter with consistent speed. This coated sample used for FE-SEM imaging and analysis.

B. FE-SEM and EDS analysis

Scanning electron microscope (SEM) examines the microscopic structure and morphology by scanning the surface of materials. The morphology of coal samples were studied using Merlin VP Compact, (Carl ZEISS, Germany; make) with air lock chamber. The instrument is having, magnification: 12 to 20,00000 X, acceleration voltage: 20V to 30 kV, beam current: <100 nA, and the FE-SEM resolution: 0.8 nm at 15 kV, 1.6 nm at 1 kV, 2.0 nm at 30 kV.

Energy dispersive spectroscopy (EDS) spectra was obtained to know the phases and elemental composition, point analysis and mapping with liquid nitrogen free octane super SDD, having 60mm^2 sensor size and the detector resolution is 129.4 eV[44], make: EDAX (USA). Prior to analysis the detector was well calibrated with standards.

C. Centrifugation

The gravity fraction of coal was generated using Centurion Scientific C2 series 2000 of UK make centrifuge. The centrifuge having facility to run four tubes at a time each of having 100ml capacity with the resolution of ± 10RPM. The organic liquids with different specific gravity (benzol, tetrachloroethylene and bromoform) to get the required specific gravity with 10 gm of coal sample per tube was used. To separate the macerals/mineral a range of gravity fraction of coal at 72 mesh were applied at 3000 RPM for 60 mins, and similar condition followed throughout the experiment. The range of density/specific gravity was 1.40 to 2.00 with an interval of 0.10. Now the float and sink were bifurcated carefully by decanting the float. The separated float and sink were dried properly and used for further study.

Experimental

The representative fraction of coal sample at 72 mesh (212 micron) size was fractionated by coning and quartering and used in the study. The proximate analysis of the coal is determined followed by IS 1350-I (1984) standard and recorded, ash 24.5, moisture 1.80 and the volatile matter was 24.0 per cent.

The coal from 1.40 specific gravity to 2.0 with an interval of 0.10 was generated using the centrifugation process. The extraneous ash forming mineral of coal and the coaly particles of the fines is assumed to be separated efficiently. Total 09 samples (8 gravity fractions and 1 overall) were obtained which was analyzed under FE-SEM followed by EDS.

Association of individual mineral grains within coal matrix are quantitatively examined through the use of FE-SEM and EDS, provides information about:

1. Inorganic element content of bulk coal sample.
2. The inorganic element content of specific lithotypes and macerals in coal.
3. The abundance of macerals in coal.
4. The inorganic element content of specific mineral phases in coal.
5. The abundance of mineral phase in coal [12].

Result and discussion

The occurrence of coal seams in India is more or less confined to the lower Gondwana period. Except for the Damodar valley basin, coal deposited in all the basins was subjected to more unstable conditions with lesser rate of subsidence and therefore, failed to hit the complete coalification process. Due to their drifted origin, the coal is rich in mineral matter and also the depositional condition is such that the inertinite contents are usually very high and the macerals comprise bi-macerites or tri-macerites and are very much intermixed with mineral matter. Therefore, coal can by no means be regarded as a simple mixture, but a complex mixture in which macerals themselves and macerals and minerals together are intermixed. The Indian coal is well known for its difficult washing characteristics. It is attempted to visualize the coal and ash forming minerals in the coal and its association with coaly matter.

The various forms in which minerals commonly occur have been well documented by researchers. The syngenatic minerals are predominantly clays and quartz, which is found along with other relatively less abundant minerals, such as feldspar, apatite, muscovite, pyrite, carbonates, etc. In Indian Gondwana coals, kaolinite and quartz are preponderant and they found together constitute the bulk of minerals. These minerals are found to be intimately embedded within the organic matrix and are generally difficult to liberate during the process of beneficiation. The epigenetic minerals are somehow precipitated in cellular cavities and are thus 'locked' in cell structures which can be observed in many of the FE-SEM images of different gravities. Also, some of the minerals may be coarsely crystalline in different shapes like nodules. The minerals have also been found to be replaced, transformed or encapsulated the older minerals.

The minerals are not only embedded but intimately intermixed with coal matrix by virtue of their size. The clay found to be most abundant is widely and finely distributed in the coaly matrix and is often comprised up to 80% of the minerals present. Clay occurs as abundant small grains in which kaolinite is one of the most common, although illite is also known in many coalfields, ranging from 1 to 20 μm size. The second most abundant is quartz and its grain size varies from 5 to 50 μm. Sometimes kaolinite-quartz intergrowths are also reported in coal (Finkelman et. al. 1984).

The shining surface as appeared in different microphotographs of FE-SEM, indicates the presence of minerals on the surface and is finally confirmed by EDS. The devolatization holes may be observed in some of the micrograph, which might be created due to the liberation of oxygen from the surface at the time of coalification process [13].

Pyrite is the most abundant sulphide mineral in the coal samples as syngenetic pyrite and observed in combination of elements S/Mo/Fe/C/O/Si/Al, as filling pores in inertinite, cubic crystals, as cell or cavity-infilling, or as replacement of the maceral components [14].

The overall coal sample analyzed for coal minerals with the elemental composition identified by EDS mapping are presented in the 3D bar graphs (Fig.1). From the graphs it may clearly be observed that at this 212 μm size the elements dispersed is kaolinites, quartz, detritus, calcite, pyrites, ect., and not in its free state. The iron (Fe) recorded higher in combination of Fe/Si/Al/C and next in the combination of S/Mo/Fe/C/O/Si/Al, while least in the form of C/O/Al/Si.

The SEM image at higher-resolution of the coal (down to nm scales can be probed) and allowed more definitive identification of pore-filling material, better evaluation of micro-porous regions, and investigation of variations in maceral type. In Fig.4b the different minerals matter like kaolinite, platy kaolinite, quartz, mineral detritus filled in cells, fibrous calcite, etc. can be seen. The cleat fractures are confined to the organic matter and occur within the thicker vitrinite bands within the coal sample, and are filled mainly by kaolinite [14].

Fig.1a EDS mapping of the overall sample shows that associated kaolinite is liberated and exposed on the surface which led to the shift of local surface property from hydrophobicity to hydrophilicity [15].

The syngenetic minerals are generally intermixed with the organic constituents and deeply inter-grown in nature and the epigenetic minerals, however, occupy the micro-pores, cleats, cracks, tissues [16]. It is evident from the microphotographs of FE-SEM that in the physical appearance itself different minerals matter is increasing as the specific gravity increases. Now FE-SEM images and the EDS are indicative of kaolinite and occupy the micro-pores, cleats, cracks, tissues of the coaly matter. In Fig.4a and b kaolinite on the matrix surface can be seen in FE-SEM images which appears as pore filing mineral at specific gravity 1.60. The lower gravity fraction 1.40

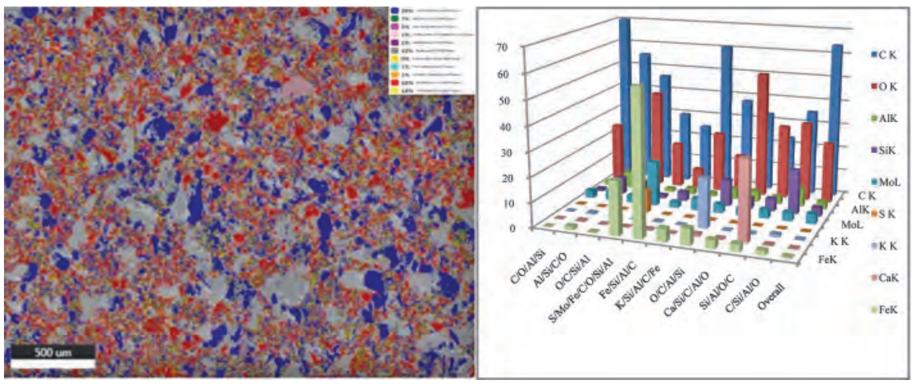

Fig.1 EDS mapping of the overall coal and 3D bar graphs showing elemental composition

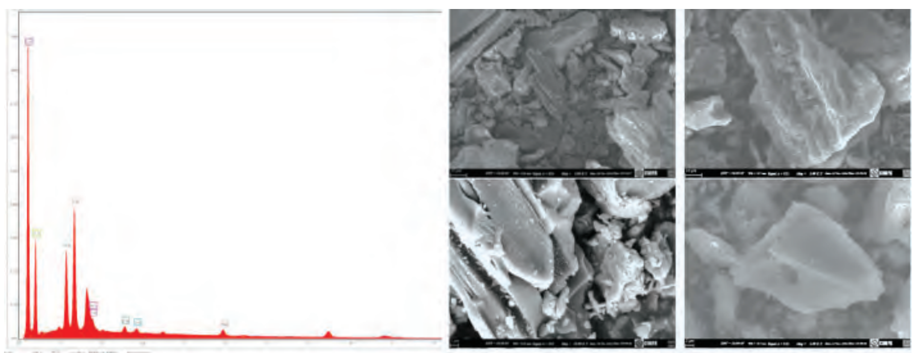

Fig.1a EDS spectraof minerals identifiedof overall coal and microphotographs showing particles with mineral matters

and 1.50 the mineral matter appears very less which is also indicated in the EDS graphs 2a and 3a.

At a slightly higher specific gravity 1.70 the mineral detritus filled in cells can be seen in the microphotographs 5b, which is further indicated in their corresponding EDS 5a.

The microphotographs of specific gravity 1.80 (Figs.6a and 6b) quartz on the matrix can be observed as the Si percentage has increased in their EDS graphs (Fig.6a).

The platy kaolinite on the matrix surface at specific gravity 1.90 with other mineral may be observed in Fig.7a and b.

In Fig.8b some fibrous calcite on the matrix surface with specific gravity fraction 2.00 appears with other minerals. The

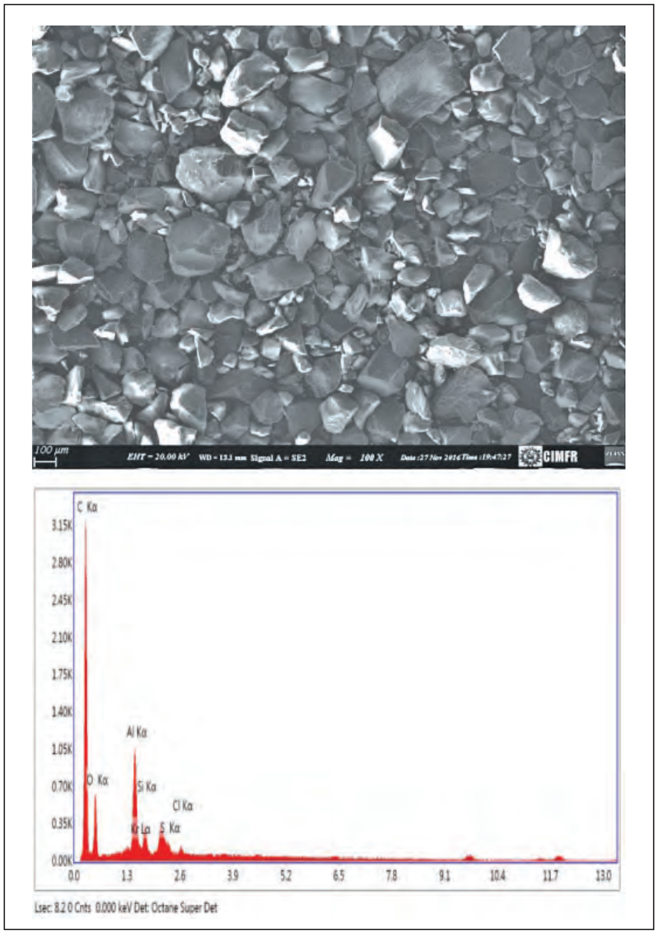

Fig.2a FE-SEM microphotographs of sp.gr. 1.40 and EDS spectra of minerals identified

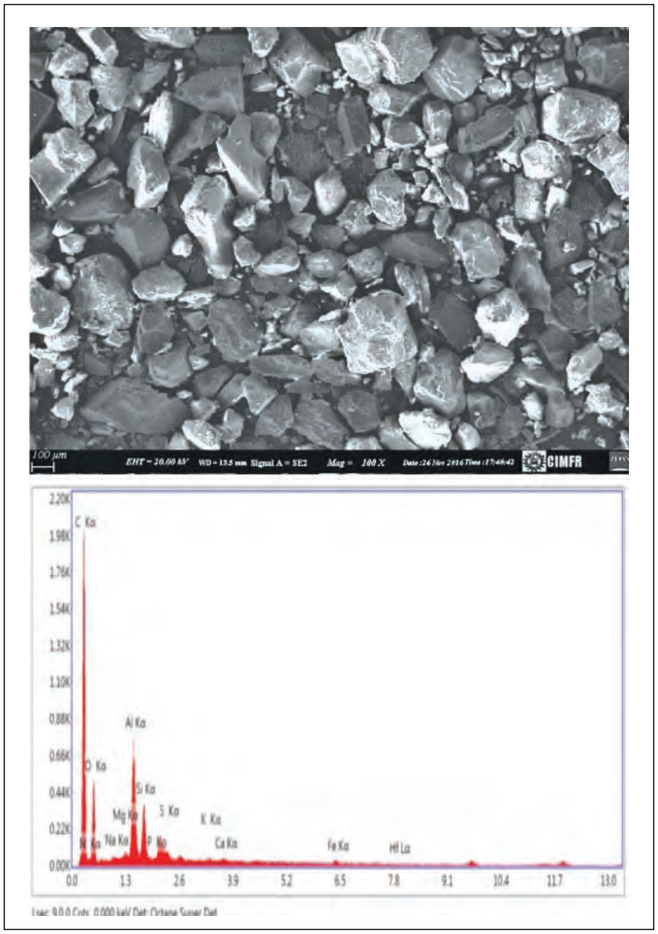

Fig.3a FE-SEM microphotographs of sp.gr. 1.50 and EDS spectra of minerals identified

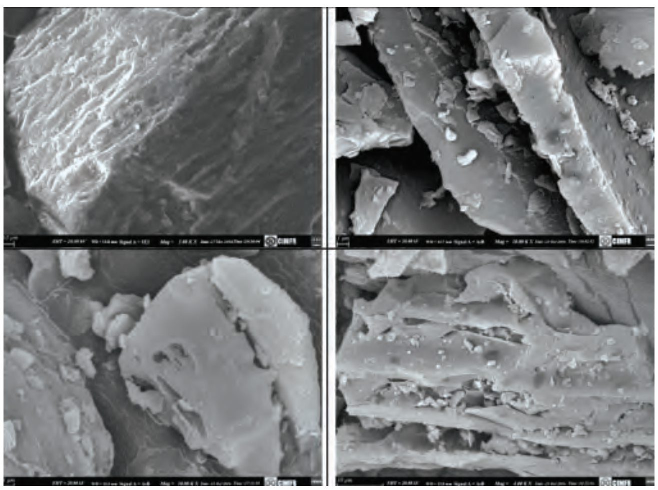

Fig.2b: Microphotographs showing particles of the coal at 1.40 sp.gr.

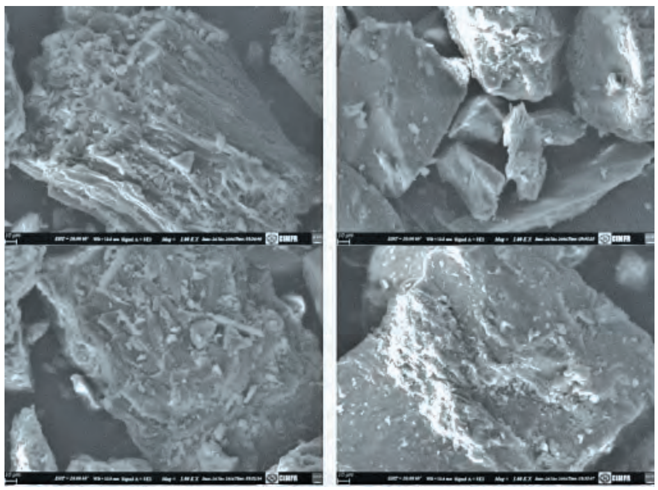

Fig.3b Microphotographs showing particles of the coal at 1.50 sp.gr.

sink material of the specific gravity 2.00 i.e. >2.00 fraction carbon content is not higher than 18 per cent in association with different mineral matter. The highest iron content is in the form of Fe/Si/O/Al while the pyrite form S/Fe/O/Si/Al account for about 18 per cent at this gravity level (Fig.9, 9a).

The maceral part of the coal are very difficult to identify using the FE-SEM images, but as it appears from the FE-SEM images even at 1.40 specific gravity and at 72 mesh size it is hard to observe in its clean form. It is very difficult to differentiate between liptinite and resin due to similarity in grey level. The Indian coals are reported with presence of very less liptinite group maceral [17].

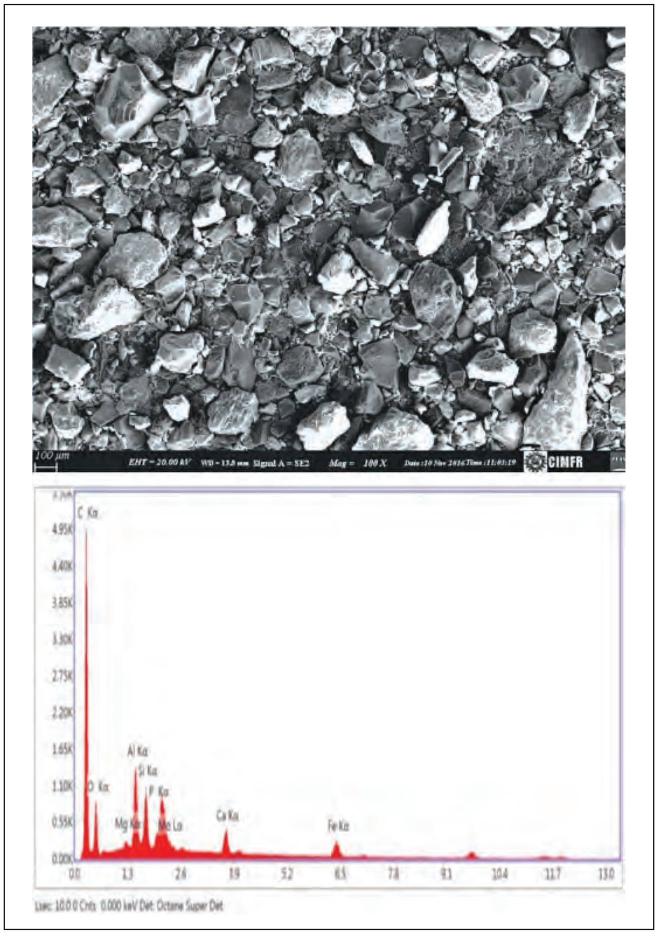

Fig.4a FE-SEM microphotographs of sp.gr. 1.60 and EDS spectra of minerals identified

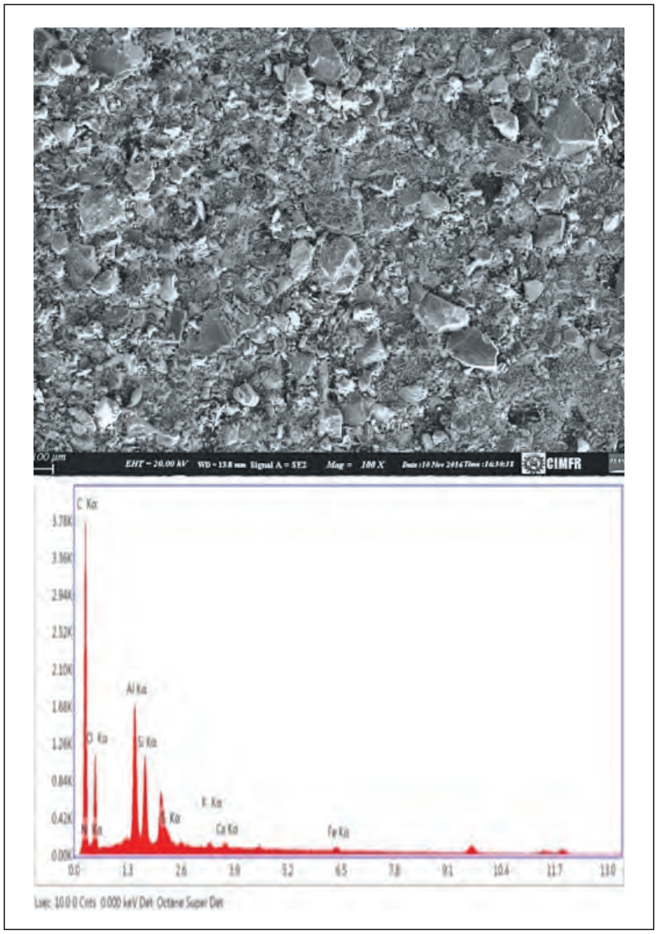

Fig.5a FE-SEM microphotographs of sp.gr. 1.70 and EDS spectra of minerals identified

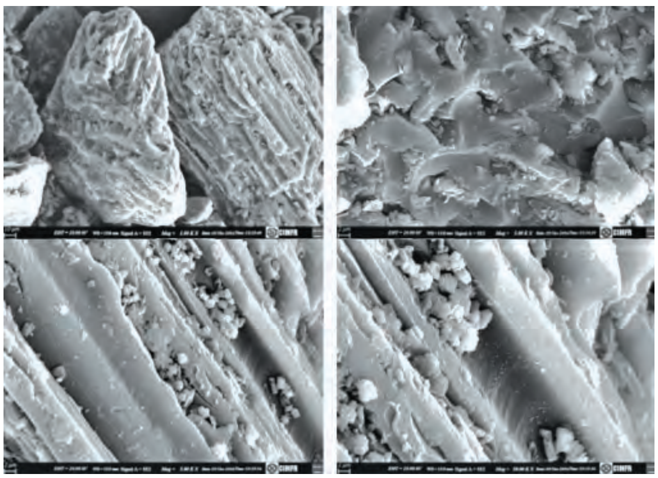

Fig.4b Microphotographs showing particles at 1.60 sp.gr. kaolinite on matrix surface

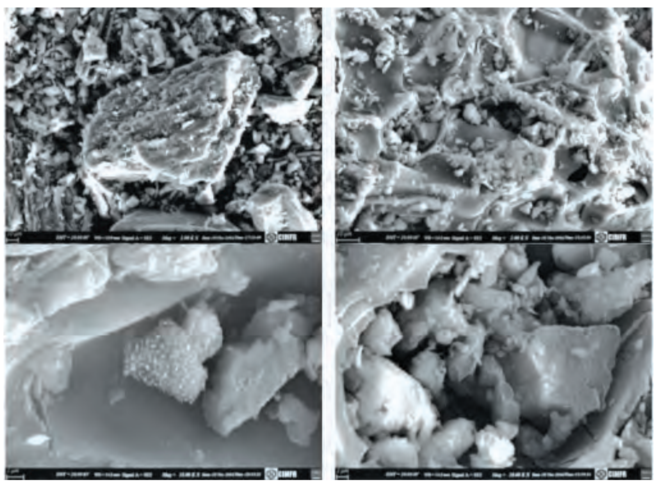

Fig.5b Microphotographs showing particles at 1.70 sp.gr. mineral detritus filled in cells

There is considerable variation in the relative abundance of mineral components for coals of different specific (e.g., relatively more quartz, clay may clearly be observed with the investigated coals). The aim of the study is to know the effects of mineral matter in coal and to obtain a characteristic surface morphology of the sample and the disclosure of a carbon porous structure using the field emission scanning electron microscope (FE-SEM). Techniques employing scanning electron microscopy (FE-SEM) EDS are emerging as useful tools for the characterization of coal and its associated mineral matter to be used in conjunction with advanced coal conversion and coal cleaning processes. The methodology

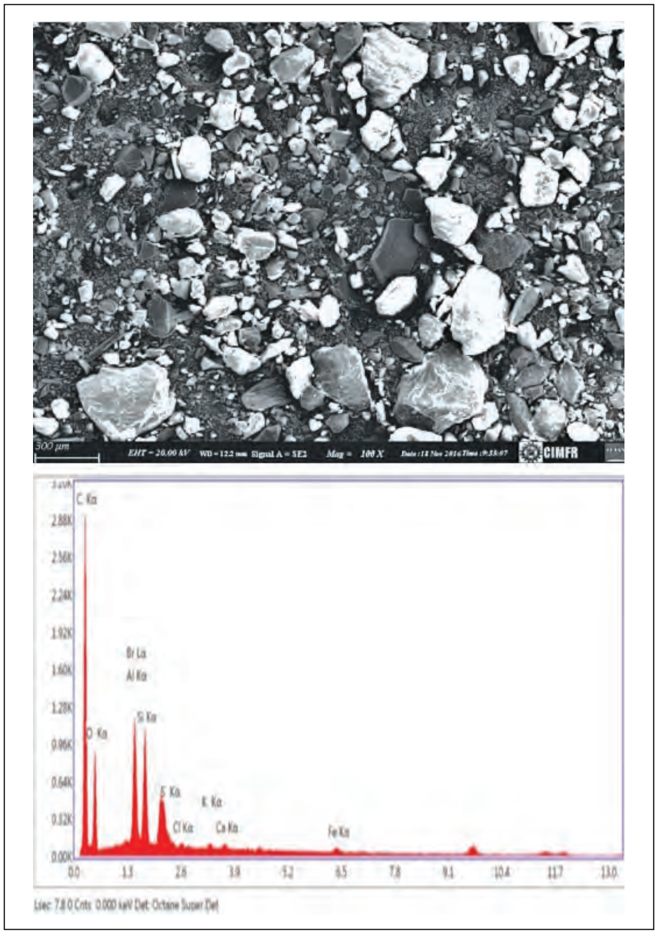

Fig.6a FE-SEM microphotographs of sp.gr. 1.80 and EDS spectra of minerals identified

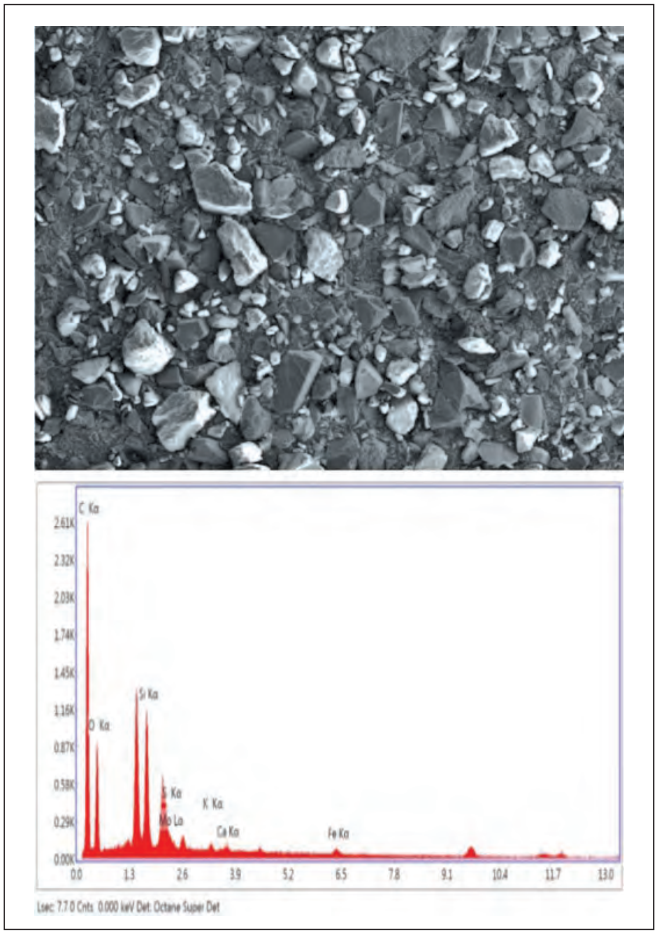

Fig.7a FE-SEM microphotographs of sp.gr. 1.90 and EDS spectra of minerals identified

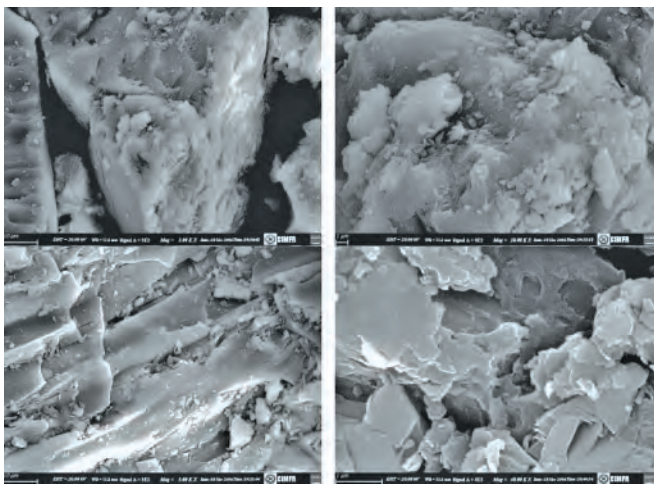

Fig.6b Microphotographs showing particles at 1.80 sp.gr. quartz on matrix surface

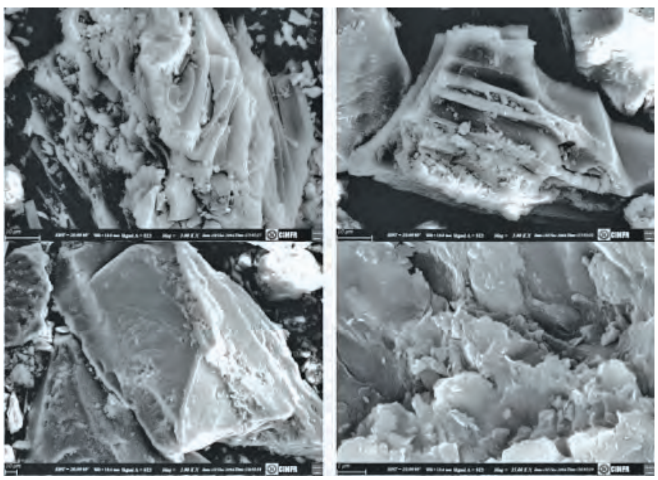

Fig.7b Microphotographs showing particles at 1.90 sp.gr. platy kaolinite on matrix surface

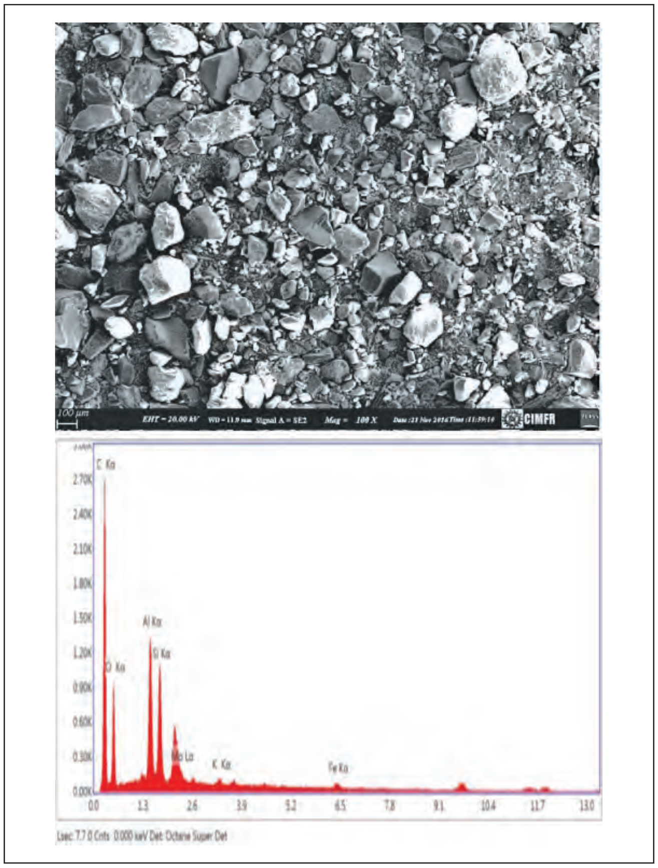

Fig.8a FE-SEM microphotographs of sp.gr. 2.00 and EDS spectra of minerals identified

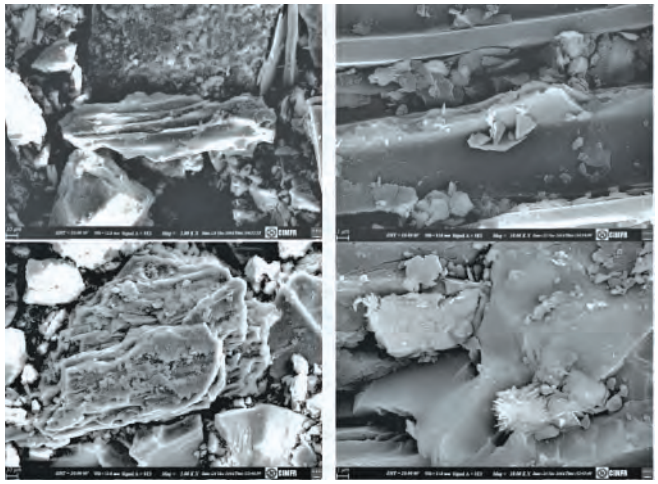

Fig.8b Microphotographs showing particles at 2.00 sp.gr. fibrous calcite on matrix surface

of FE-SEM is described along with several illustrative applications related to coal beneficiation. These distributions can be related to processing behaviour and may be used to explain, and possibly even predict, the recovery and quality of product under various cleaning conditions.

Conclusion

The observation shows that the lower gravity fraction of coal consists of less extraneous mineral matter relatively to their parent coal. With the increase of specific gravity of the fractions kaolinite, platy kaolinite, quartz, mineral detritus filled in cells, fibrous calcite, etc. increased as appeared in the microphotographs.

The results are specially useful for detecting differences between coal and mineral matter in respective gravity fractions and finding the reasons for unusual processing behaviour. Since the mineral content and composition may vary widely from coal to coal, the detailed characterization provided by FE-SEM and EDS techniques is quite helpful by visualizing and details of different phases of mineral matter and their compositions for strategic purpose. The study may be a path for the planning, design, testing, and evaluation of coal beneficiation and conversion processes. FE-SEM-based is uniquely capable of characterizing coal and mineral particles for these important properties, and thus to aid in coal beneficiation.

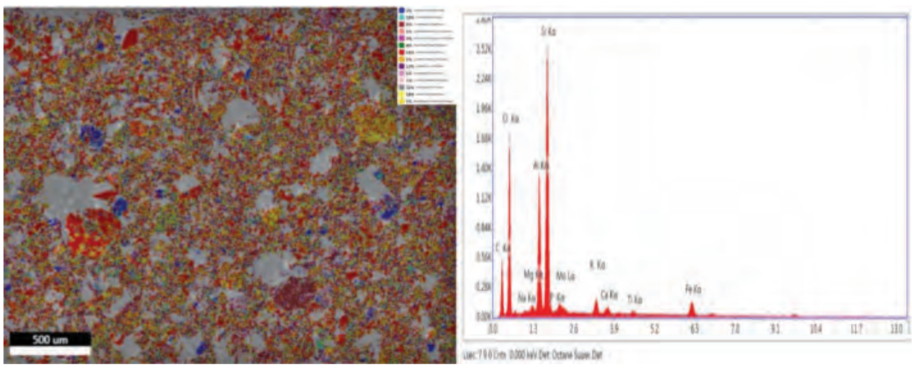

Fig.9 EDS mapping of the >2.00 sp.gr fraction coal sample and EDS spectra of minerals identified

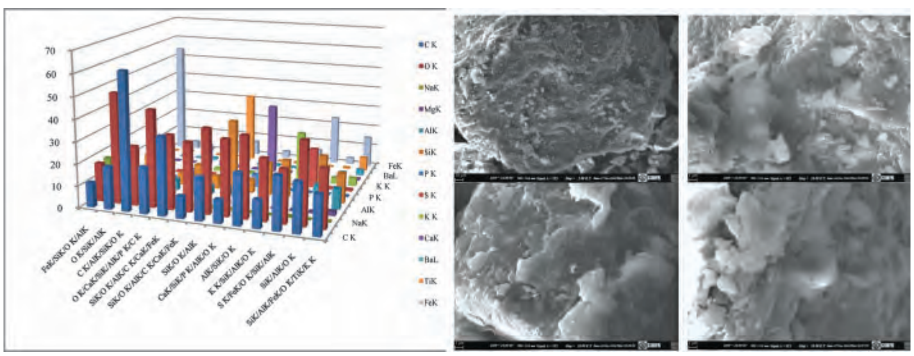

Fig.9a 3D bar graphs showing coal minerals with the elemental composition of identified minerals for > 2.00 sp.gr fraction and the micrographs of coal with mineral matters

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