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Effect of Inorganic Matter on the Reactivity of Indian Coals

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Coal contains mineral matter as impurities. In the conversion processes, the presence of minerals is inevitably deleterious. But it is also well known that mineral matter in coal affects the reactivity by catalyzing carbon-gas reactions. In the present paper, influence of total mineral matter and major inorganic elements like Si, Al, Fe, Ca, Mg, K and Na on the reactivity of coal samples from different coal fields of India has been investigated. Major elements in the coal samples were analyzed by X-Ray fluorescence (XRF) spectrometer and non-isothermal thermogravimetric analysis was used to determine the reactivity of the coal samples. It has been observed that the reactivity of Indian coals first increases with the increasing mineral matter content, passes through maximum and then decreases. Same trends have been found in the case of alkaline earth metals. Unlike alkaline earth metals, reactivity of coal does not increase with the increasing concentration of alkali metals. This happens due to the variation in available surface area of coal samples with the total mineral matter and inorganic elements. It is also reported in this paper that the slagging and fouling rating for these Indian coal samples are low.

Key Words: Mineral matter, Major inorganic elements, Reactivity, Surface area.

INTRODUCTION

Coal being a heterogeneous material contains a diverse array of inorganic species which are predominantly found in the form of minerals. Mineral matter is normally considered as the sum of all inorganic materials and elements that are present in coal except organically bound C, H, O, N and S[1]. Minerals in coal generally include clay minerals (mainly kaolinite), sulfide minerals (mainly pyrite), quartz, calcite and trace amounts of minor minerals[2,3]. Such mineral matter originates from four principal sources during and after coal formation. These are (i) transportation/drift of detrital minerals into the organic material by water or wind; (ii) formation of vegetal minerals from the inorganic constituents of swamp plants; (iii) precipitation of minerals derived from rock weathering and marine water and (iv) hydrothermal solutions invaded into coal along fractures or cleats after coal formation[4-7]. The presence of minerals during conversion processes is inevitably deleterious. They not only reduce the heat value of coal but also create several operational problems like wear and tear, slagging, fouling, clinker formation, fire side deposition and corrosion in coal based plants. These problems are associated with the nature of the coal ash which depends upon its elemental composition. The elemental composition is generally expressed as wt % of the various inorganic oxides present in coal ash and major ash constituents are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2 and SO_3.

On the contrary, some of these inorganic components act as catalysts in coal conversion processes. It is well established[8-15] that the minerals in coal enhance the reactivity by catalyzing the carbon-gas reactions. Gasification reactivity of coal or coal char depends strongly on their inorganic constituents, perhaps even more than of their rank. Pullen, Mims and Davidson[16-18] reviewed the effect of minerals on coal reactivity in coal conversion processes. Miura *et al.*[19] showed that the gasification reactivity of char of low rank coal (C < 80 %) was controlled by the catalytic activity of coal minerals. Kyotani *et al.*[20], found that the catalytic effect of minerals controlled the reactivity of coal in the region where the rate was controlled by chemical reaction. But the effect of major inorganic elements on the reactivity of Indian coals is not well studied. However, Sharma *et al.*[21], showed the variation of reactivity of Indian lignite with the fuel ratio, oxygen and moisture content.

Indian coals being drifted in origin are high in ash[22]. Thus, the main emphasis of this paper is to investigate the influence of the total mineral matter as well as the effect of Si, Al, Fe, Ca, Mg, Na and K on the reactivity of Indian coals. Surface area of these coal samples has been measured to explain the variation of reactivity of coals with the total mineral matter content and major inorganic elements. Slagging index, fouling index and base/acid ratio have also been determined from the ash analyses of these coal samples. Therefore, this study will be helpful in understanding the effect of major inorganic elements on coal reactivity and to predict the operational problems which are important in the development of coal based technologies.

EXPERIMENTAL

Selection of coal samples: The coal samples were collected from different Indian coal fields supplying coal to the Indian thermal power plants. The samples were crushed and sieved so that the particle size lies between 0.15 and 0.21 mm. The proximate and ultimate analyses of the samples were done following the Indian standard (IS: 1350 series)[23] and have been shown in Table-1.

Thermogravimetric analysis: Non-isothermal thermogravimetric analysis was carried out using Netzsch STA 409 C thermal analyzer. 20 mg of coal sample was taken for each experiment in the alumina crucible. Ultra pure dried air (99.999 % of purity) was chosen as oxidizing gas. The flow rate of the air was fixed at 50 cc/min and the sample was heated in air with a heating rate of 10 K/min up to the temperature of 1073 K. The thermogravimetric analyzer was calibrated and repeatability of the instrument was checked by several experiments taking calcium oxalate. Blank run was carried out under the same experimental conditions and to minimize the Buoyancy effect each experiment was corrected with the blank run. K-type thermo couple was used to measure the reaction temperature with accuracy level of ± 2 °C.

Ash composition analysis: Coal ash was prepared following Indian standard method (IS: 1350 series) and chemical analysis of the ashes was carried out using wavelength-dispersive PW 2424 MagiX X-ray fluorescence (XRF, Philips) spectrometer (ASTM D3682-78). For quantitative measurement by XRF, substantial sample preparation is necessary, particularly for solids and powdered samples, where analyte line intensity depends on surface roughness, particle size and packing density. Therefore, reference samples and unknown samples were prepared under same conditions. Suitable grain size reduction was achieved by automatic grinder (Mini Mill, Fritsch). Subsequently, the sample was pressed with stearic acid as binder using TP 20 P Herzog hydraulic equipment applying 150 KN forces for 5 min to form a stable pellet of 40 mm of diameter keeping sample and binder ratio of 10:1. Calibration for XRF spectrometer is the process of setting up regression lines used to convert the measured count rates into concentrations. To accomplish this, reference samples of known concentrations were measured. In the calibration, the count rates measured at the peak position were plotted against the concentrations of the associated reference samples. The regression line in the plot was calculated by the instrument software in such a way that the minimal error was obtained over the whole regression line by minimizing the RMS or K value. The RMS error is the root of the mean square of the sum of the differences between the given and calculated values of the reference samples. K can be considered as a weighted standard deviation and had a value in the range of 0.03-0.1. Matrix effect for each element was corrected by the mathematical method using software supplied with the instrument. Therefore, considering the above facts, best fitted regression line for each element was obtained during calibration and chemical analysis of the ash samples was performed. The precision of the measurement was between 0.1 and 0.3 % and the accuracy lied between $0.01c^{1/2}$ and $0.05c^{1/2}$, where c is the analyte concentration.

Surface area measurement: Surface area of the coal samples was measured by Tristar 3000 surface area analyzer (Micromeritics, USA) using BET equation. The adsorbate was nitrogen gas (purity 99.999 %) and isotherm was measured at the boiling temperature of liquid nitrogen, *i.e.*, at 77 K. Five points of the isotherm were taken in the relative pressure range

TABLE-1
PROXIMATE (DRY BASIS) AND ULTIMATE ANALYSES (DAF* BASIS)

Sample	Ash (wt %)	VM* (wt %)	FC* (wt %)	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O (wt %)
C1	37.03	29.82	33.15	78.80	5.85	1.88	1.06	12.41
C2	37.24	28.87	33.89	75.83	5.42	1.52	1.03	16.20
C3	41.61	26.73	31.66	72.17	5.55	1.69	1.11	19.48
C4	37.29	29.83	32.88	77.22	5.41	1.66	0.80	14.91
C5	30.40	24.42	45.18	80.27	4.52	1.51	1.51	12.20
C6	38.76	26.52	34.72	76.35	4.52	0.35	1.57	17.22
C7	47.31	21.22	31.47	75.15	3.61	1.20	0.94	19.10
C8	43.70	23.42	32.88	74.07	4.10	1.68	1.12	19.03
C9	41.67	30.84	27.49	73.28	6.51	1.76	0.76	17.68
C10	29.96	29.21	40.83	77.63	5.45	1.45	0.59	14.89
C11	41.99	24.04	33.97	75.69	5.06	1.51	0.81	16.92
C12	37.07	27.26	35.67	77.57	5.34	0.98	0.67	15.45
C13	38.33	27.44	34.22	74.23	5.44	1.15	0.79	18.38
C14	31.71	31.08	37.21	75.54	5.85	1.32	0.57	16.72
C15	41.23	26.52	32.25	75.87	4.60	1.66	0.74	17.13
C16	36.03	27.08	36.89	73.36	4.38	1.69	1.85	18.72
C17	36.84	25.78	37.38	75.00	4.42	1.70	2.38	16.50
C18	31.18	31.72	37.10	77.97	5.16	1.56	1.88	13.44
C19	31.22	30.25	38.54	78.87	4.85	1.72	2.35	12.21
C20	49.00	21.92	29.08	73.55	4.13	1.65	1.03	19.63

*DAF = Dry ash free, VM = Volatile matter and FC = Fixed carbon.

of 0.05-0.3. Straight lines were obtained and the correlation coefficients for all the measurements were greater than 0.99. From the slope and intercept of straight line, surface area was calculated. Before conducting experiments, surface of the coal samples was cleaned by flowing nitrogen gas at 150 ºC for 3 h in a separate unit.

RESULTS AND DISCUSSION

The concentrations (wt %) of the elements (Si, Al, Fe, Ca, Mg, Na and K) in ash samples and total mineral matter content of coals on dry basis are presented in Table-2. Total mineral matter content on dry basis was calculated from the Parr formula[24,25] and the concentrations (wt %) of the above mentioned elements of the coal ash samples were calculated using the ash analysis results. Non-isothermal thermogravimetry as described earlier was used to determine the reactivity of the coal samples. Here, the term reactivity means the maximum rate of reaction under the experimental conditions. Table-3 shows the reactivity values of the coal samples considered for this study[26]. These values have ranged from 5.28 to 8.45 %/min. Since coal is a diverse array of inorganic constituents, variation of the coal reactivity with the total mineral matter content (wt %), calculated on dry basis as well as with the content (wt %) of Si, Al, Fe, Ca, Mg, Na and K has been discussed.

TABLE-2
TOTAL MINERAL MATTER CONTENT (wt %, DRY BASIS) OF THE COAL SAMPLES AND ELEMENTAL COMPOSITION OF COAL ASHES (wt %)

Sample	Si (wt %)	Al (wt %)	Fe (wt %)	Ca (wt %)	Mg (wt %)	Na (wt %)	K (wt %)	Total mineral matter (wt %)
C1	28.65	14.14	4.47	1.00	0.13	0.18	0.70	40.4
C2	28.21	15.47	3.35	0.95	0.21	0.18	0.95	40.6
C3	29.22	13.49	4.19	0.76	0.14	0.18	1.15	45.3
C4	28.09	15.71	3.35	1.28	0.19	0.13	0.70	40.6
C5	28.98	13.66	3.77	0.12	0.04	0.35	2.17	33.4
C6	29.49	14.39	3.91	0.30	0.05	0.13	0.65	42.4
C7	28.35	13.09	3.85	1.80	0.55	0.62	1.50	51.4
C8	28.5	13.50	4.20	1.60	0.35	0.51	1.20	47.5
C9	28.79	13.28	4.59	1.45	0.20	0.18	0.62	45.2
C10	28.99	12.41	4.19	1.62	0.29	0.75	1.00	32.6
C11	30.06	13.66	2.79	0.65	0.11	0.22	0.90	45.6
C12	29.12	12.81	4.19	1.57	0.33	0.25	1.12	40.3
C13	28.00	12.82	5.59	1.73	0.38	1.00	0.9	41.7
C14	29.53	12.74	3.35	1.51	0.27	1.34	0.85	34.5
C15	30.80	13.08	2.51	1.35	0.15	0.18	0.87	44.8
C16	29.17	12.72	4.75	1.63	0.42	0.20	0.62	39.6
C17	28.38	15.21	2.93	1.57	0.25	0.27	0.67	40.6
C18	29.65	12.00	3.91	2.03	0.47	0.30	1.63	34.4
C19	27.51	11.27	5.87	2.97	0.66	0.67	1.60	34.6
C20	28.16	12.10	3.63	3.57	0.68	0.75	1.70	53.2

TABLE-3
REACTIVITY, SURFACE AREA OF THE COAL SAMPLES AND SLAGGING INDEX, FOULING INDEX AND BASE/ACID RATIO OF THE COAL ASHES

Sample	Reactivity (%/ min)	Surface area (m^2/g)	Slagging index	Fouling index	Base/acid ratio
C1	7.48	32.26	0.07	0.02	0.10
C2	7.23	31.74	0.06	0.02	0.09
C3	7.77	25.75	0.06	0.02	0.10
C4	7.68	35.99	0.04	0.02	0.09
C5	5.66	10.47	0.10	0.05	0.10
C6	6.93	25.89	0.07	0.01	0.08
C7	6.01	10.01	0.07	0.11	0.13
C8	6.33	11.50	0.08	0.09	0.12
C9	8.45	30.12	0.05	0.03	0.11
C10	6.27	13.10	0.05	0.13	0.13
C11	7.39	18.50	0.03	0.02	0.07
C12	6.76	28.11	0.05	0.04	0.12
C13	6.78	25.20	0.08	0.21	0.16
C14	6.51	11.65	0.04	0.21	0.12
C15	7.94	29.25	0.03	0.02	0.08
C16	6.91	30.01	0.15	0.03	0.12
C17	7.13	25.62	0.13	0.03	0.09
C18	6.19	6.07	0.17	0.05	0.13
C19	5.50	10.49	0.32	0.18	0.20
C20	5.28	8.08	0.09	0.17	0.17

Fig. 1 reflects the variation of reactivity (%/min) of the coal samples with the total mineral matter content (wt %), calculated on dry basis. It is clear that the reactivity increases with the increasing amount of total mineral matter content, passes through a maximum and then decreases. Here, reactivity attains maximum value of 8.45 (%/min) at 45.2 (wt %) of mineral matter and then decreases with increasing amount of mineral matter. The correlation coefficients of increasing and decreasing trends are 0.87 and 0.95, respectively. This type of variation of reactivity with mineral matter content has been found by other researchers also[27,28]. The increase in reactivity is due to the catalytic effect of mineral matter and decreasing of the coal reactivity is caused by the decreasing of exposed surface area of the coal samples. In Fig. 2, total mineral matter (wt %), calculated on dry basis, has been plotted against surface area. It clearly shows that the surface area of coal samples first increases up to 45.2 (wt %) of mineral matter and then it decreases with the increasing amount of mineral matter. Though, in the present study, both reactivity and surface area of coals follow the same trend with mineral matter content, the increase in reactivity in Fig. 1 is mainly due to the catalytic effect of mineral matter. This is evident from Fig. 3, where reactivity increases with increasing mineral matter content of coals of almost same surface area values (vary from 28.11 to 32.26 m^2/g). Therefore, it is confirmed from the above discussion that in Fig. 1, increase in reactivity with mineral matter content is due to its catalytic effect and decrease is caused by the decrease in surface area. Now decrease in surface area with mineral matter content will be discussed. Surface area values (BET) of the coal samples are presented in Table-3. The decrease in surface area with mineral matter content is a result of two factors.

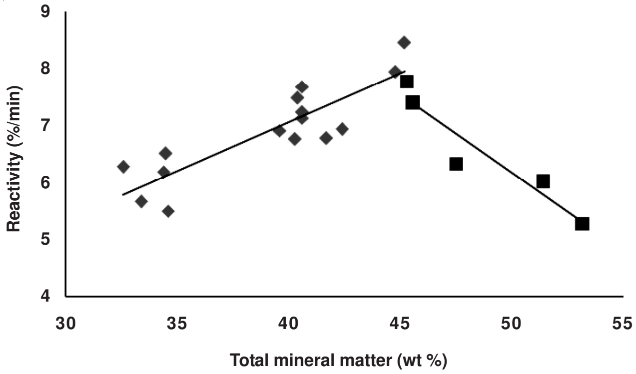

Fig. 1. Variation of reactivity with total mineral matter content (dry basis)

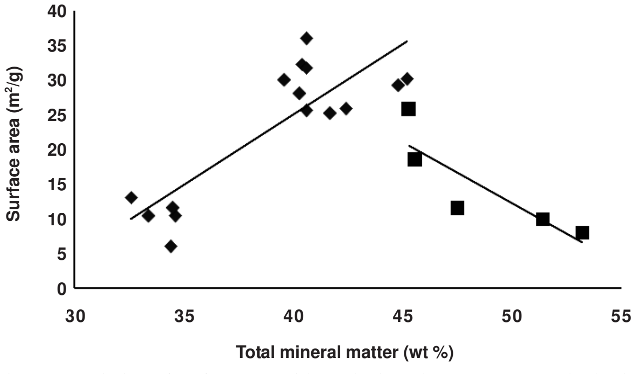

Fig. 2. Variation of surface area with total mineral matter content (dry basis)

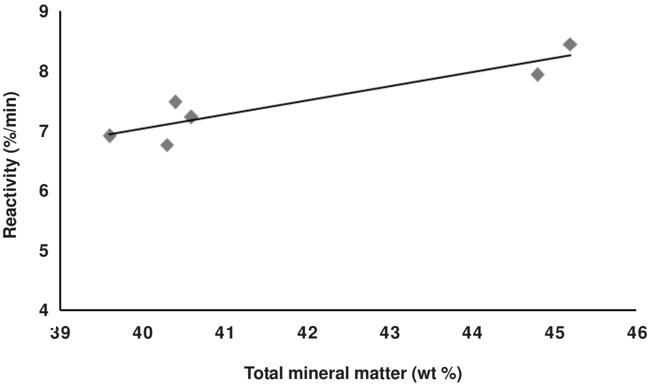

Fig. 3. Variation of reactivity with total mineral matter content (dry basis) of the coal sampes of almost same surface area

First, as the mineral matter content increases after a limiting amount, the available surface gets covered with the excess amount of mineral matter[27,28]. Therefore, the decrease in available surface area is due to the association of excess mineral impurities with the coal matrix.

Second possibility is attributed to the formation of low melting eutectic[4,29] due to the presence of basic oxides and acidic oxides in certain proportions under the experimental conditions. This low melting eutectic may form semi fused type materials which cover the available surface causing a decrease in surface area and porosity. As a result, reactivity of coal decreases.

It has been observed that the individual effect of Si and Al on the reactivity of coal is not strong. This is due to the inert behaviour of quartz and kaolinite[27]. It is generally accepted that iron oxides are not good catalysts for carbon gas reactions[30,31]. No correlation has been found between coal reactivity and Fe content. As Fe would be oxidized to Fe_3O_4 under the experimental conditions, lack of correlation between coal reactivity and Fe content is justified. However, some relationship has been found between coal reactivity and sum of Si, Al and Fe content. Fig. 4 shows the variation of reactivity of coal with the sum of Si, Al and Fe content. The trend is same like variation of reactivity with the mineral matter content. The possible reason has already been explained in the variation of reactivity with mineral matter content.

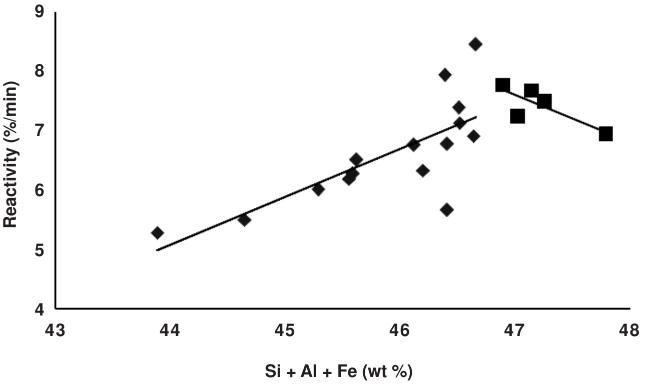

Fig. 4. Variation of reactivity with Si + Al + Fe content

Influence of Ca and Mg content on reactivity of coal has been shown in Figs. 5 and 6, respectively. It clearly indicates that the reactivity first increases with the increasing concen-

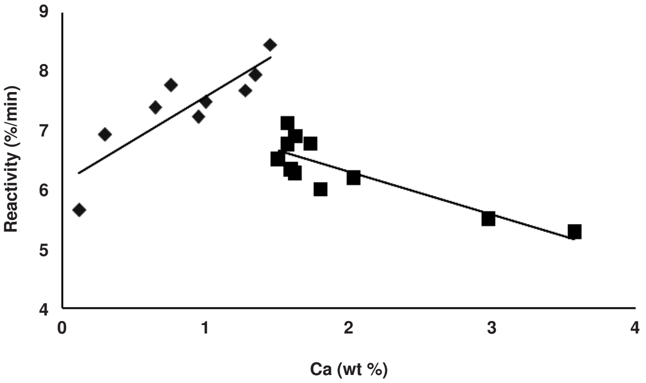

Fig. 5. Variation of reactivity with Ca content

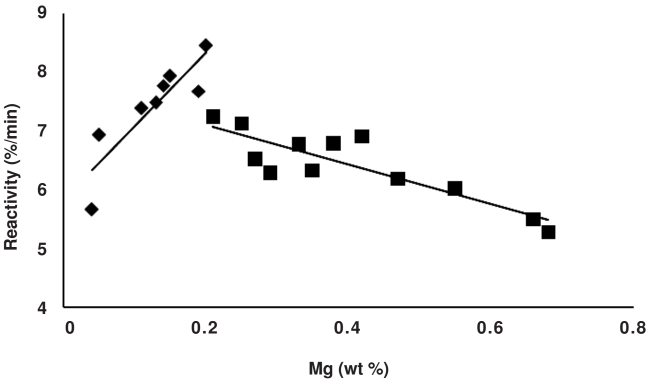

Fig. 6. Variation of reactivity with Mg content

trations of alkaline earth metals, passes through the maximum and then decreases. The trend is same as that of the variation of reactivity with mineral matter content. In Fig. 5, reactivity increases up to the value of 1.45 of Ca content (wt %) and then decreases with the increasing concentration of Ca. Correlation coefficients of increasing and decreasing trends are 0.87 and 0.85, respectively. In Fig. 6, reactivity attains maximum value of 8.45 (%/min) at 0.2 (wt %) of Mg content and then decreases. Here, the correlation coefficients of increasing and decreasing trends are 0.88 and 0.87, respectively. This observation is a result of the possible reason mentioned in the effect of total mineral matter content on coal reactivity.

Fig. 7 shows the influence of (Na + K) content on coal reactivity. It has been found that the reactivity decreases with the increasing amount of (Na + K). The decreasing trend of reactivity with alkali metal concentrations is due to the following reasons:

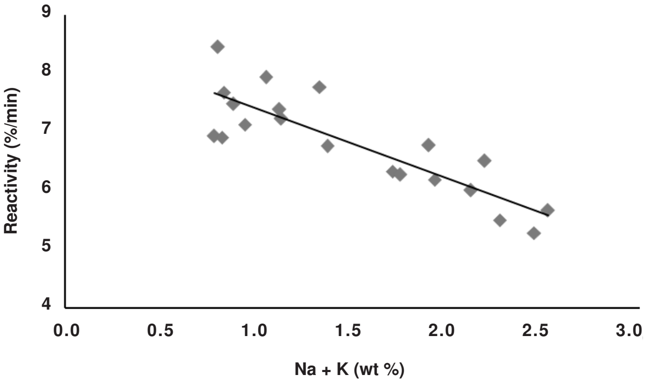

Fig. 7. Variation of reactivity with Na + K content

Alkali metal compounds are of low melting temperature and form semi fused type masses with the refractory materials such as SiO_2 and Al compounds which are already present in coal. This semi fused masses cover the available surface causing a decrease in surface area and porosity which results in the decrease in reactivity of coal. Variation of surface area with (Na + K) content has been plotted in Fig. 8 and it reflects that the surface area decreases with increasing amount of (Na + K). Increase in propensity of formation of semi fused type masses is also evident from the base/acid ratio of these coal ash samples which have been shown in Table-3. It is the ratio of the sum of the wt % of basic oxides (Fe_2O_3 + CaO + MgO + Na_2O + K_2O) and sum of the wt % of acidic oxides (SiO_2 + Al_2O_3 + TiO_2) and is used as an indication of the tendency of the ash to form a low melting point eutectic. Fig. 9 shows that the reactivity of coal decreases with the increase in base/acid ratio.

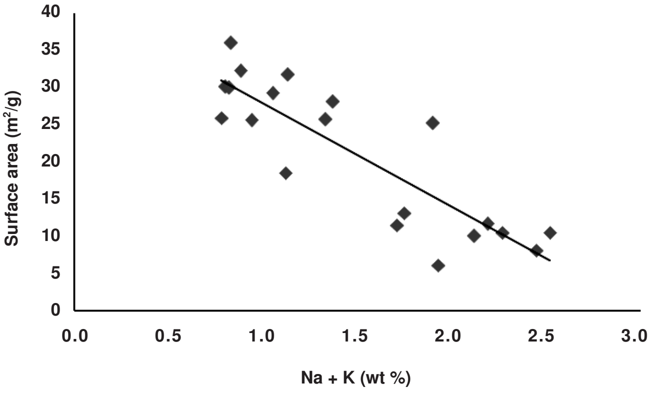

Fig. 8. Variation of surface area with Na + K content

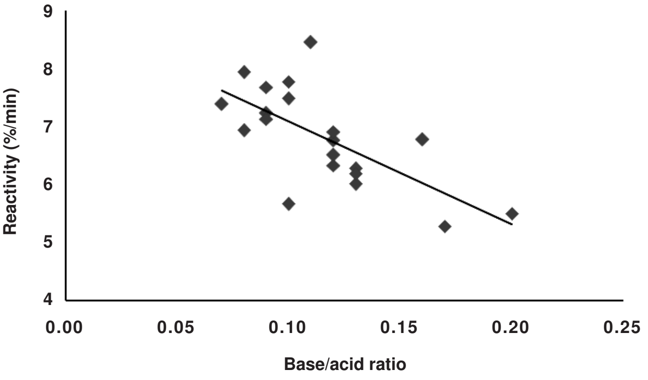

Fig. 9. Variation of reactivity with base/acid ratio

Second possibility is that the mineral distribution in coal is as important as concentration. Survey of literatures[8,32] suggests that the very little amount of catalyst is required to produce a large effect only when the catalytic impurity is well dispersed through out the carbon. It is also reported that the well distributed catalyst can only increase the activity. Therefore, it will be justified to state here that the gradual decrease in reactivity with the increasing amount of alkali metals is linked with the non-uniform distribution of the minerals rich in alkali metals through out the complex coal matrix. These minerals get agglomerate under the reaction conditions and catalytic activity of alkali metals is deactivated.

Third reason[9,33] is the presence of small amount of Na and K compared to the other elements. The catalytic activity of alkali metals is suppressed by the greater catalytic activity of alkaline earth metals. It is evident from Fig. 10, where variation of reactivity has been plotted against (Na + K + Ca + Mg) content. It clearly shows that the trend is similar to that of Ca and Mg content, *i.e.*, increasing and decreasing trend. Chemical form of the alkali metals within the complex coal matrix may also be responsible for gradual decrease of reactivity with (Na + K) content. Some amount of Na and K may be attached to aluminosilicate lattice in an unexchangeable form and are believed to be catalytically inactive.

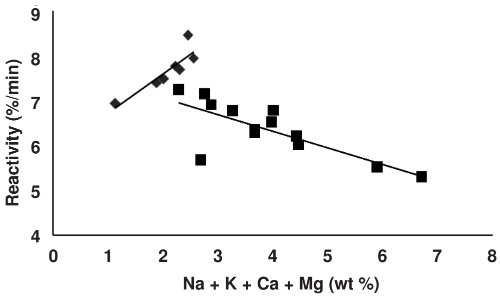

Fig. 10. Variation of reactivity with Na + K + Ca + Mg content

Therefore, influence of total mineral matter and major inorganic elements like Si, Al, Fe, Ca, Mg, K and Na on the reactivity of Indian coal samples has been discussed. It has been already mentioned that the presence of minerals in coal is inevitably deleterious and creates several operational problems like slagging, fouling, clinker formation and fire side deposition during coal conversion processes. These are the major problems which lead to the frequent shut down of coal based plants. These problems are associated with the nature of different constituents present in the coal ash. So, slagging and fouling indices have been determined in the present paper to predict operational problems. Basic oxides, acidic oxides and S influence the slagging and Na_2O, K_2O and S are mainly responsible for fouling phenomena. Slagging index is the product of the base/acid ratio and the wt % of sulphur (dry basis) in the coal and fouling index is the product of the base/acid ratio and the wt % of Na_2O. In this paper, slagging and fouling indices of the ashes have been presented in Table-3. As these values for most of the samples are less than 0.2, slagging and fouling rating for these coal samples are low and will not create any such operational problems.

Conclusion

In the present study, influence of total mineral matter and major inorganic elements like Si, Al, Fe, Ca, Mg, K and Na on the reactivity of Indian coal samples has been discussed. It may be concluded that the (i) total mineral matter has definite effect on the reactivity of Indian coals. Reactivity of coal increases with the increasing amount of the mineral matter, reaches maximum and then decreases. It can be explained from the catalytic activity of mineral matter and exposed surface area of coal. (ii) Variation of reactivity of coal with alkaline earth metals shows the same trend as that was found with the total mineral matter content of coal. (iii) The lack of correlation between individual content of Si, Al and Fe and coal reactivity is attributed to the chemical states of these elements within the complex coal matrix. (iv) Gradual decrease in coal reactivity with increasing concentrations of alkali metals is due to the formation of semi fused type mass, chemical form of alkali metals in coal matrix and non uniform distribution of minerals rich in alkali metals. (v) Surface area plays an important role in variation of coal reactivity with mineral matter and major inorganic elements and (vi) finally, slagging and fouling ratings of these Indian coal samples are low and will not create any operational problems.

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