I. AHMAD
M. NABIULLAH
and
R. S. PRASAD

Role of oxygen functional groups and fuel ratio in self heating of coal

A number of methods are in practice at different places throughout the world to determine susceptibility of coal towards spontaneous heating. Among these, crossing point temperature (CPT) method is very simple and gives a good idea of the propensity of coal towards heating. Liability index calculated using CPT is also useful for studying the propensity of coal towards spontaneous heating. However, determination of CPT in lab requires extra precaution for repeatable results.

To overcome the difficulties, attempts were made to study the relationship between peripheral oxygen groups or the functional oxygen groups in coals and their correlation with proneness to auto-oxidation using liability index (LI). Also the correlation between liability index and crossing point temperature have been presented in this paper.

Introduction

Coal mine fire is well known since inception of coal mining. Among the various causes [1] of mine fire, spontaneous combustion/self heating or auto oxidation of coal is predominant. Heating in mines is accompanied by haze, sweating, gob stink, fire stink, and eventually fire [2]. It has however been observed in actual situation that often some of the above indications may or may not occur before initiation of the fire. It is, therefore always not possible to get information in advance about impending fire to take precautionary measures. In present day scenario with increasing depth of mines, enhanced production targets, need for increased mine water gauge and mechanization, the problem has become more serious and may occurs in all types of mines. It is therefore required to study the causative factors contributing essentially towards auto oxidation in coal.

It is an established fact that coals of different ranks and origin have different capacities for absorption of oxygen. It has also been observed that higher the oxygen absorption capacity of the coal, higher will be its susceptibility to spontaneous combustion. The rate of oxygen absorption has been proposed by some investigators [3, 4, 5] as a reliable measure to determine the susceptibility of coals to auto-oxidation. Some workers determined the susceptibility of coals to auto-oxidation by measuring the heat evolved during coal oxidation in the laboratory using micro colorimeter [6]. Per-oxy complex formation capacity of coals during oxidation has also been used for measuring proneness to auto-oxidation [7-11]. Nature of humic acid [12] formed during oxidation was also used as one of the parameters for classifying coals as regards its proneness to spontaneous combustion. In India however, the most popular method for determining the proneness to auto-oxidation is the crossing-point temperature (CPT) method of Ganguly et al [13]. CPT method is used widely for determining the proneness to auto-oxidation. However, the experimental conditions viz. rate of oxygen flow, rate of heating, particle size of coal, etc. meticulously is required to be maintained during determination of CPT for repeatable results. Also an uninterrupted power supply during the experiments is essentially required. Hence the present work was undertaken to study other properties of coal, which can be used to determine comparative proneness to auto-oxidation.

Messrs. I. Ahmad and M. Nabiullah, Scientists, Central Institute of Mining and Fuel Research, Dhanbad (Jharkhand) and Mr. R. S. Prasad, Reader, Deptt. of Chemistry, V B University, Hazaribagh (Jharkhand)

The methods discussed above for classification of coal with regard to their proneness to auto-oxidation are based on the oxidation characteristics of coal. Not much work has been done to find a relationship between proneness of spontaneous combustion and chemical constitution of coal. Mazumdar et al [14] have found out that formation of peroxides and hydro-peroxides under low temperature oxidation of coal is due to the initial attack by oxygen on the methylene groups constituting the hydro-aromatic structure of coal. Some others [15 - 16] are of opinion that low rank coals have high oxygen sorption capacity and prone to auto-oxidation. It may be due to high proportion of oxygen functional groups, particularly the hydroxyl, carbonyl and carboxyl groups in such coals.

In addition to oxygen functional groups in coal, fixed carbon, volatile matter, ash, moisture and sulphur also play an important role in determining the liability of coal towards spontaneous heating. The knowledge of correlation of the above factors may be very useful for development of liability index for prediction of spontaneous heating.

A number of techniques are practiced at different places throughout the world to determine susceptibility of coal. Among these, crossing point temperature method though have limitations mentioned above is being used for determination of propensity of coal towards heating. Liability index calculated using crossing point temperature [17] is useful for studying the propensity of coal towards heating.

Feng.et.al. [17] suggested the following formula for determination of liability index (LI) of coal towards spontaneous heating

$$\text{Liability index} = \frac{\text{Average heating rate} \times 1000}{\text{Crossing point temperature}}.$$

Attempts have also been made to study the relationship between peripheral oxygen groups or the functional oxygen groups in coals and their correlation with liability index to assess proneness to auto-oxidation. The other properties of coal which are easy to determine are the volatile matter and fuel ratio. Comparative studies of liability of coal with CPT and fuel ratio have also been presented in this paper.

Experimental

Coals from Jharia, Raniganj and some high sulphur coals from the tertiary fields of Assam were selected for the study. Their proneness to auto-oxidation was determined by the crossing-point method of Ganguly [13]. Proximate and ultimate analysis was done by the I.S.I. method. Hydroxyl group was estimated by the method of Mazumdar et al [18, 19]. The carboxyl group was estimated by the Base Exchange method [20]. The carbonyl group was estimated by a modified Kerulen's method. For this purpose one gram coal was taken in 30 ml (approximately) absolute alcohol with one gram hydroxyl amine hydrochloride and one gram sodium acetate. This was refluxed for three hours, filtered and washed. From the gain in nitrogen per cent in the sample due to oxidation, the carbonyl oxygen group was calculated.

Results

The proximate and ultimate analysis of the coal samples of various fields are given in Table 1. In Table 2 values of fuel ratio, CPT and LI of different coal samples are furnished. In Table 3 results of the oxygen functional groups are given. Co-relation of different parameters of coal samples with liability index are depicted in Figs.1-5.

Discussion of results

From Table 1 it can be seen that the coal of BCCL (Jharia coalfield) are having low moisture, low VM and high fixed carbon where as in coal from ECL (Raniganj coalfield) are high moisture, high VM and low fixed carbon. The coal samples of Assam coalfield have low moisture but high VM and sulphur content.

TABLE 1: RESULTS OF PROXIMATE AND ULTIMATE ANALYSIS OF COAL (D.M.F.)

	Name of the colliery	Moisture %	Ash %	Volatile matter %	Fixed carbon %	Carbon %	H2 %	N2 %	Sulphur %
1.	Amlabad XIV seam, BCCL	1.4	9.6	26.0	63.0	89.4	5.0	1.9	0.6
2.	Loyabad X seam, BCCL	0.5	18.2	27.8	53.5	90.0	4.9	2.0	0.7
3.	Khas Jairampur VII seam, BCCL	1.66	9.87	31.32	57.15	85.5	5.1	2.41	0.6
4.	Khas Khajora, Jambad seam, ECL	6.5	13.8	43.2	36.5	80.4	5.6	2.0	0.42
5.	Jambad-Khajora Jambad top seam, ECL	7.8	14.6	43.0	34.6	81.2	5.8	2.0	0.5
6.	Khas Jambad, Jambad seam, ECL	7.9	14.8	42.5	34.8	80.9	5.5	1.9	0.46
7.	Baragolai, NECL	2.47	3.04	48.26	46.23	81.07	2.76	1.76	2.47
8.	Tipong-Khashi seam (Margerita), NECL	2.24	1.62	50.64	45.5	82.9	6.2		
9.	Makum, NECL	2.37	4.8	48.98	43.85	75.4	5.4	1.82	5.87
10.	Raniganj Colliery Raniganj seam, ECL	6.5	18.8	42.3	32.4	81.2	5.5	1.8	0.5
11.	Central and Lower Jambad Jambad bottom seam, ECL	7.2	16.0	41.1	35.7	81.0	5.5	1.7	0.58
12.	Darula Samla Darula seam, ECL	9.7	13.8	40.4	36.1	81.2	5.3	2.1	0.5

Table 2: Fuel ratio, CPT and liability index (LI) of different coal samples

	Name of colliery and seam	Fuel ratio	C.P.T, °C	LI
1	Amlabad XIV seam, BCCL	2.42	176	5.68
2	Loyabad X seam, BCCL	1.92	163	6.13
3	Khas Jairampur, Jharia field VII Seam, BCCL	1.82	161	6.21
4	Khas Kajora, Jambad seam, ECL	0.84	109	9.17
5	Jambad Kajora, Jambad top seam, ECL	0.80	109	9.17
6	Khas Jambad, Jambad seam, ECL	0.82	110	9.09
7	Baragolai, NECL	0.96	135	7.41
8	Tipong-Khasi seam (Margerita), NECL	0.90	153	6.54
9	Makum, NECL	0.90	156	6.41
10	Raniganj, Raniganj seam, ECL	0.77	111	9.01
11	Central and Lower Jambad, Jambad bottom seam, ECL	0.87	113	8.85
12	Darula, Samla Darula seam, ECL	0.89	115	8.7

Table 3: Results of oxygen functional groups

	Name of the colliery	Hydroxyl group%	Carbonyl group%	Carboxyl group%
1	Amlabad XIV seam, BCCL	1.04	0.045	0.03
2	Layabad X seam, BCCL	1.53	0.057	0.05
3	Khas Jairampur VII seam, BCCL	1.5	0.11	0.06
4	Khas Khajora Jambad seam, ECL	4.3	4.76	0.72
5	Jambad Khajora Jambad top seam, ECL	4.63	4.86	0.81
6	Khas Jambad, ECL	4.7	4.9	0.8
7	Baragolai, NECL	2.20	0.26	0.07
8	Tipong-Khasi seam (Mrgerita), NECL	2.82	0.37	0.028
9	Makum, NECL	3.3	0.175	0.118

From Tables 1 and 2 it can be seen that the low ranks coal which have high moisture content and low carbon per cent, the CPT and LI do not change in a regular pattern with increase in carbon and moisture percentage. It is worth mentioning here that there is good co-relation between CPT and LI (Fig.1). The coals of high rank have higher CPT and lower LI. It may be due to the fact that oxidation largely affects the ali-cyclic and aliphatic systems around the aromatic rings of coal [21] at lower temperature of oxidation. Also the rate of oxidation is less in higher rank coals and hence the heat build-up is less and crossing point is higher thus LI is less. In the same rank of coal, some coals may have higher per cent carbon but the aromatic, aliphatic, ali-cyclic structure do not vary with increase in per cent carbon, hence the crossing point do not vary much, but do vary in irregular way with the per cent carbon; so per cent carbon cannot be taken as guide to proneness to auto-oxidation. The tertiary coal of Assam (NECL) which is of very high per cent of sulphur, the proneness to auto-oxidation decreases with the increase in carbon per cent. More work has to be done to substantiate this.

Mazumdar et al have stated when coal is oxidized at lower temperature, i.e. below 170°C, oxidation is only restricted to the peripheral structure of coal leaving the aromatic skeleton unaffected. From the results of the study of oxygen functional groups, it can be seen from Table 3 and Figs. 2-4 that there is a relationship with the hydroxyl group, carbonyl groups and carboxyl groups with the liability index. Thus, it is clear from the results that higher is the oxygen functional groups more is the proneness towards spontaneous heating. It is well known that the carbonyl and hydroxyl groups in organic compounds are easily oxidized to carboxyl and carbonyl groups respectively. In coals too these are easily attacked and till about 170°C oxygen functional groups and alicyclic structure are attacked on oxidation. The more the number of hydroxyl and carbonyl groups in coal, more number of sites will be available for attack by oxygen; hence rapid oxidation takes place resulting in increasing the liability index or lowering the crossing point. The functional group, therefore, can be used as an index to proneness to auto-oxidation. In Assam coals they do not follow the same pattern as the Jharia and Raniganj coals; this may be due to the high per cent sulphur in these coals in the form of groups like SH, S=S etc.

Table 2 gives a relationship of fuel ratio to liability index. Fuel ratio is a very important parameter as it takes into account both the aromatic, alicyclic and aliphatic structure of coal. From the study it is found that proneness to oxidation decreases with increase in fuel ratio as seen in Fig.5. The fuel ratio is defined as ratio of fixed carbon to volatile matter. As mentioned earlier volatile matter is mostly the aliphatic and alicyclic part of coal while fixed carbon is the aromatic part; hence a high fuel ratio means more aromatic structure than aliphatic and alicyclic structures, hence less prone to oxidation. This could, therefore, be used as a measure for determining proneness of coal to auto-oxidation.

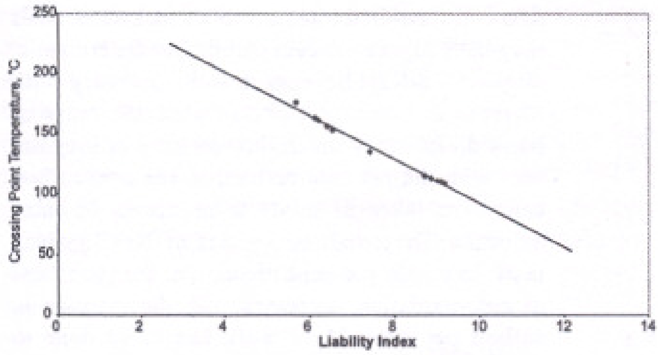

Fig.1: Variation of liability index with CPT

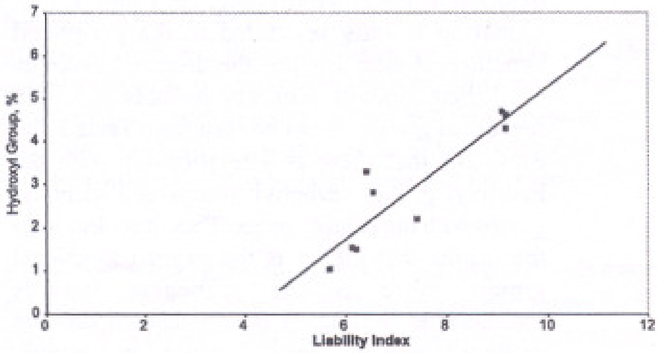

Fig.2: Variation of liability index with hydroxyl group

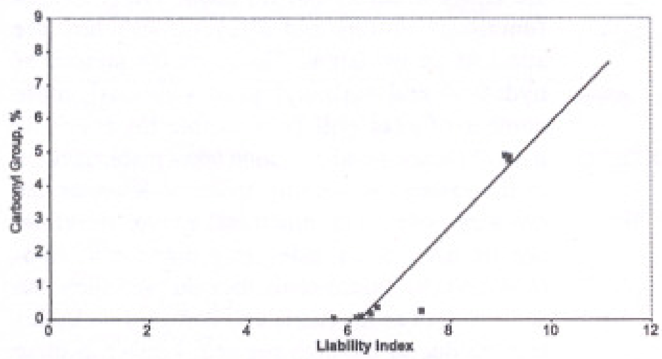

Fig.3: Variation of liability index with carbonyl group

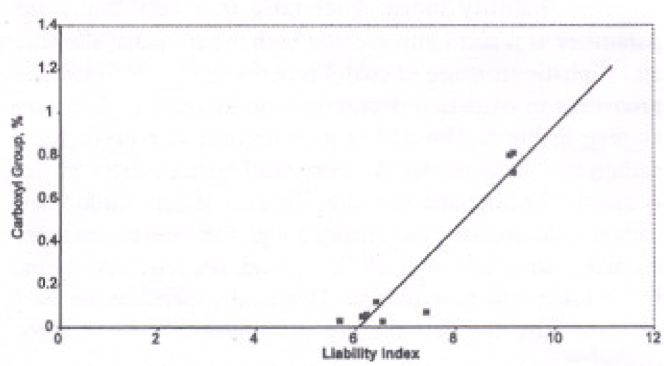

Fig.4: Variation of liability index with carboxyl group

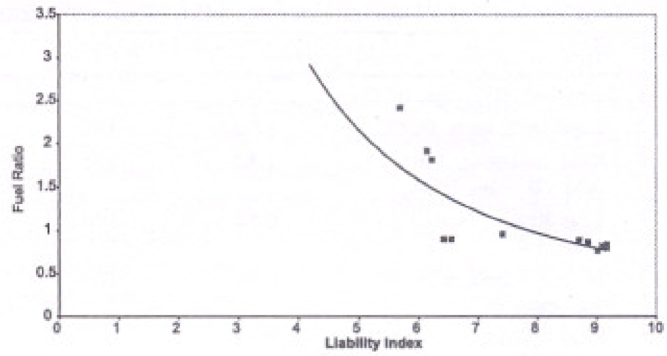

Fig.5: Variation of liability index with fuel ratio

Conclusion

From the study of the constitution of coal and the proneness to oxidation it is found that the functional group and fuel ratio has a definite relation with proneness to oxidation and could be used as a parameter for classifying coals for susceptibility to oxidation.

The liability index calculated using crossing point also indicates good correlation with oxygen functional groups in coal.

Acknowledgement

The authors express their gratitude to Director CIMFR for permission to publish this paper. The views expressed in the paper are of the authors and not of CIMFR.

References

1. Banerjee, S. C. (1985): "Spontaneous combustion of coal and mine fires", Oxford and IBM publication.
2. Mukherjee, S. K, Singh, P. K. and Bhattacharjee, B. (1988): "Critical analysis of some occurrences of underground fire in Raniganj Coalfield" *Journal of Mines, Metals and Fuels*, September, pp 428-433.
3. Coward, H.F. (1957): "Research on spontaneous combustion of coal", S.M.R.E Research Report, No.142
4. Winmill, T.F (1915-16): "Absorption of oxygen by coal. VIII. Effect of the absorption of the size of the coal particles and the percentage of oxygen in the air", *Trans. Instn. Min. Engrs*; Lond, Vol.51, p.510.
5. Graham, I. J. (1929-30): "The gaseous products resulting from fires and underground heating", *Trans. Instn. Min. Engrs*; Lond, Vol.79, p.92.
6. Hodges, D. J. and Acharjee B. (1965): "An isothermal Micro calorimeter", *Lab Pract.*, 40, 842-850.
7. Cudmore, J. F. (1969): Australian Coal Industries Research Laboratories Ltd., P-R 69.
8. Yohe, G. R. and Wilt, M. H.(1942): "Oxidising power of Illionis coal. II. Effect of extended time", *J. Amer. Chem. Soc.*, Vol.64 pp 1809.

9. Yohe, G. R. and Harman, C. A. (1941): "Oxidising power of Illionis coal.I. Reaction with titanous chloride", *J. Amer. Chem. Soc.*, Vol.63, p.555.

10. Jones, R. E. and Towned. D. T. A. (1949): "Oxidation of coal", *J. Sc. Chem. Ind.*, Vol.68, p.197.

11. Chakraborty, S. L. (1960): "Auto-oxidation of Indian coal, Part I, Influence of variables on the formation of peroxide bodies", *J. Mines, Metals and Fuels*, Vol.8, No.9

12. Kreulen, D. J. W.(1948): "Elements of Coal Chemistry", Nijgh & Van Ditmar, N.V., Rotterdam.

13. Ganguly, M. L. and Banerjee, N. G. (1953): "Critical Oxidation & Ignition Temperature of Coal", *The Imma Review*, Vol.2, No.4.

14. Majumdar, B. K., Banerjee, A. and Nandi, H. C. (1983): *Fuel Science & Technology India*, Vol.2, No.3, July, p.97.

15. Yohe, G. R. and Blodgett, E. O. (1947): *J. Am. Chem. Soc.*, Vol.69, p.2644..

16. Nandi, S. P., Kini, K. A. and Lahiri, A. (1957): *J. Ind. Chem. Soc., Ind & News Ed*, Vol.20, No.2, p.91.

17. Feng, K. K., Chakrabotry, R. N and Cochrain, T. S. (1973): "Spontaneous Combustion – A Coal Mining Hazard" *The Canadian Mining & Metallurgical Journal* 75-84.

18. Mazumdar, B. K., Bhangle, P. H. and Lahiri, A. (1956): *J, Sc. Ind. Res.*, 1956; 15 B, p.44.

19. Mazumdar, B. K., Bhangle, P. H. and Lahiri, A. (1959): *Fuel*, 1959; p.212.

20. Bhowmick, J. N., Mukherjee, P. N. and Lahiri, A. (1959): "Studies on oxidation of coal at lower temperature", *Fuel*, Vol.38, p.211.

21. Mazumdar, B. K., Chakravarty, S. K., (Mrs.) Saha, M., Anand, K. S. and Lahiri, A. (1959): "Further studies on the mechanism of the oxidation of coal" *Fuel*, Vol.38, p.469.

COAL EXPLORATION – EXPANDED REQUIREMENT IN INDIA

(Continued from page 7)

Conclusions

Many fold increase in the demand of coal in the coming years, particularly, to meet the energy needs of the country puts onerous responsibility on coal sector to meet country's requirement. About 61.5% of total resources of India remain to be upgraded to 'proved' category for project planning and mining, there is an urgent need to 'prove' such resources through detail exploration.

The pace of exploration of coal, so far, has been dictated by the need of the time and as such the capacity of exploration in the country has been limited. Exploratory drilling, mostly coring, is the traditional and still the most common method used in coal exploration in the country. The drilling rigs deployed are normally the conventional wire line rigs which are, in general, smaller in size and have achievable productivity ranging from 300 to 400m/month. The choice of the traditional methods of detailed coal exploration in India as evolved over the years with normally smaller drilling rigs has largely been dictated by the limitations imposed by ground conditions.

Introduction of 'state of the art technology' in detailed exploration need to be pursued to enhance the confidence level of the data generated for planning of more and more mechanized, large and efficient mines. This will also result in acceleration in the pace of exploration to a considerable extent. The thrust on technology should, however, take into consideration the limitations imposed by the ground conditions in which the coal bearing areas occur in the country.

Since the present capacity of the existing exploration agencies and the associated services with respect to all the elements of coal exploration is limited to the current requirement only, the capacities need to be expanded to meet the demand for desired level of production. Outsourcing of exploration services to both national and international agencies is considered to be a necessity to meet the increased requirement of exploration of coal.