ASSESSMENT OF SPONTANEOUS HEATING SUSCEPTIBILITY OF COALS USING WET OXIDATION POTENTIAL DIFFERENCE TECHNIQUE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING

BY

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NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA – 769008

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CERTIFICATE

This is to certify that the thesis entitled **"Assessment of Spontaneous Heating Susceptibility of Coals using Wet Oxidation Potential Difference Technique"** submitted by **Kumar Abhishek (Roll no. 112MN0605) in** partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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Kumar Abhishek
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DECLARATION OF ORIGINALITY

I, **Kumar Abhishek**, **Roll Number 112MN0605** hereby declare that this thesis entitled **"Assessment of Spontaneous Heating Susceptibility of Coals using Wet Oxidation Potential Difference Technique"** represents my original work carried out as a student of NIT Rourkela and so, to the best of my knowledge contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked with at NIT Rourkela or elsewhere, is explicitly acknowledged in the thesis. Works of other authors cited in this thesis have been duly acknowledged under the sections "References". I have also submitted my original research records to the scrutiny committee for evaluation of my thesis.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present thesis.

Date : **Kumar Abhishek**

NIT Rourkela

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ABSTRACT

The main reason behind the spontaneous heating of coal is auto-oxidation. The after effect of spontaneous heating is a major setback in the production of coal. The prevention of spontaneous heating can only be predicted through experimental findings and results through different types of experiments. The spontaneous heating depends on many intrinsic factors such as, Ash content, moisture content, volatile matter content and fixed carbon. Apart from all the above mentioned parameters, wet oxidation potential difference method can also be correlated so as to predict its spontaneity for heat. The spontaneous heating susceptibility varies over a large span, thus the experiments become an important tool in predicting the vulnerability to spontaneous heating of a coal sample.

In this project, the wet oxidation potential difference experiment was conducted for 20 different coal samples from different mines across India. The coal samples were collected by channel sampling and then they were prepared according to the Indian Standards. The calorific value of all the samples was also measured using the Bomb Calorimeter along with that proximate analysis was also conducted so as to obtain the different parameters about the coal samples such as calorific value, ash, moisture, volatile matter, fixed carbon content. Correlation study was carried out to find out the suitability of the method to assess the spontaneous heating susceptibility of coal.

In India, generally crossing point method is used for assessment of spontaneous heating susceptibility of coal. However, this method has certain draw backs. The results are dependent upon packing density, rate of heating and oxygen flow rate etc, and sometimes the results are not reproducible. Moreover it takes more than three hours to complete the experiment. Compared to CPT, the wet oxidation experiments only takes about 40 minutes for completion and the results are reproducible. From the correlation analysis, it was found that WOPD indicated a fair accuracy for the measure of spontaneous heating susceptibility as it showed high correlation with the intrinsic properties such as moisture and volatile matter. Thus, wet oxidation potential difference method may be a useful method for the assessment of liability of coal to spontaneous heating.

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CHAPTER 1

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INTRODUCTION

1.1 Background

The coal mining industry has to suffer losses due to coal fires which are caused mostly due to spontaneous heating. Thus, to prevent its occurrence there has been rigorous works and experiments carried out across the globe. Spontaneous heating occurs due to the rise in temperature of coal stack due to the exothermic internal reactions and finally, it reaches the ignition point where it leads to fire. At the point when coal is presented to air, some of its uncovered surface ingests free oxygen at a quicker rate than others and oxidation results in the emission of toxic gasses, for example, CO, CO_2, and so on. This happens at encompassing temperatures which prompts open flame. To adjust some preventive measures against these flames, numerous scientists have completed trials to comprehend the instrument of unconstrained heating of coal so as to have an uninterrupted production of coal without incurring huge losses. An appropriate method of different experiments of the spontaneous heating of coal is required, so that production of coal could be done within the incubation period. Different experimental procedures have been embraced taking into account the estimation of oxidation rate and ignition temperature, viz., Crossing Point Temperature, Differential Thermal Analysis, Differential Scanning Calorimetry, Russian U-index, Olpinskin Index etc. (Banerjee and Chakravarty, 1967; Gouws and Wade, 1989; Singh et al., 1985; Tarafdar and Guha, 1989; Panigrahi et al., 1996; Mahadevan and Ramlu, 1985, Sahu et al. 2005, Gouws and Wade, 1989b). It has also been observed by different researchers that some of these methods are time consuming, tedious and do not give reproducible results. Keeping this in view, the authors have carried out an extensive study for determining the spontaneous heating tendency of a large number of coal samples by using wet oxidation potential difference technique.

The spontaneous heating susceptibility of different coals varies over a wide range and it is important to assess their degree of proneness for taking preventive measures against the occurrence of fires. The susceptibility of spontaneous heating is used to get a better knowledge regarding the storage of coal and better methods of extraction so as to obtain maximum extraction within the safe limits. The correlation analysis provides a mathematical approach to the susceptibility of spontaneous heating and helps in identifying the different intrinsic properties on which spontaneous heating depends or the relation among the obtained results. The carried out experiments provided us with better information regarding the spontaneous heating of coal from different parts of India.

1.2 Objective

The current work was planned with the following objectives:

- Review of different experimental techniques for the assessment of spontaneous heating of coal.
- Determination of intrinsic properties of coal by proximate analysis and calorific value.
- Assessment of spontaneous heating of coal by wet oxidation potential difference method.
- Correlation study to find out the suitability of the method for assessment of spontaneous heating of coal

CHAPTER 2

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LITERATURE REVIEW

The workings of the different scientists and scholars on the spontaneous heating susceptibility of coal through different methods are mentioned as following:-

Mahadevan and Ramlu (1985) devised segmented approach to analyse crossing point temperature curve. They considered the temperature selection of FCC Index to be ad hoc and hence untenable. They identified three stages in crossing point temperature curve viz., Inflection point, Crossing point and Ignition point.

Tarafdar et al. (1989) carried out wet oxidation of coal using alkaline potassium permanganate ($KMnO_4$) solution and analysed the potential changes between a saturated calomel electrode & carbon electrode immersed in the coal oxidant mixture within a time period at a constant temperature.

Vancea et al. (1995) investigated the effect of moisture content of coal on the spontaneous ignition of oxygen. He observed that the heating rate was maximum at moisture content ranging at about 7 wt% for an initial inherent moisture content of the coal before drying (in dry nitrogen at 65°C) of 20 wt%.

Panigrahi et al. (1996) carried out work on wet oxidation & CPT with respect to intrinsic properties of coal sample.

Kaymakci and Didari (2002) carried out experiments to establish a relation between the spontaneous combustion parameters (experimental readings of the time dependent experiments) and the parameters obtained from the proximate, ultimate and petro graphic analyses. They established that ash (A), volatile matter (VM), carbon (C), hydrogen (H), exinite (E), inertinite (I) and mineral matter (MM) are the major factors affecting spontaneous combustion.

Panigrahi and Sahu (2004) carried out the application of adaptive resonance theory of artificial neural networks (ANN) on 31 samples for classification of coal seams with respect to their proneness to spontaneous heating. The intrinsic properties of the samples were determined by proximate, ultimate and petrographic analyses. The susceptibility indices of were studied by five different methods, viz. crossing point temperature, differential thermal analysis, critical air blast analysis, wet oxidation potential difference analysis and differential scanning calorimetric studies. Exhaustive correlation studies between susceptibility indices and the intrinsic properties was carried out for identifying the appropriate spontaneous heating susceptibility indices and intrinsic properties to be used for classification of coal seams. They applied the identified parameters as inputs and adaptive resonance theory of ANN was applied to classify the coal seams into four different categories.

Ray and Singh (2007) carried out fire suppression techniques like Infusion of inert gases or liquid nitrogen, Dynamic Balancing of pressure, Reversal of underground mine ventilation, Application of nitrogen foam, Inertisation of Goaf, Water mist etc. Their report included the successful application at different mines across the globe. Results of Science & Technology (S&T) project with regard to various fire suppression techniques like Infusion of liquid nitrogen, Injection of high pressure high stability nitrogen foam, and Water mist on open fire.

Beamish and Arisoy (2008) developed a large database of coal self-heating rates under adiabatic conditions at The University of Queensland. Coals from Australia (Queensland and New South Wales), New Zealand (North and South Island), Indonesia and the United States were tested. They found definitive relationships and trends for the effects of various intrinsic coal properties on self-heating rates and anomalous coals were also identified. A propensity rating scheme was also developed which was routinely used in Australia for assessing coals and identifying appropriate mining analogues for spontaneous combustion management planning.

Sahu et al. (2011) they used fuzzy expert system and the commonly used artificial neural networks (ANN) for forecasting the self heating of coals. They carried out proximate, ultimate and petrographic analyses on 30 samples of varying ranks from different coalfields of the country. Correlation studies between the intrinsic properties and CPT was carried out to identify the parameters for prediction purpose. Using moisture, volatile matter, and ash content as input parameters, CPT was predicted using fuzzy logic based on Takagi–Sugeno–Kang (TSK) model and ANN based on back propagation algorithm. Triangular fuzzy membership function was adopted for describing input variables.

Singh (2013) pointed out that the exact mechanism of the reaction of oxygen with coal is not completely understood as the chemical nature of coal is not yet fully established. But most of the workers agree that the reaction of oxygen with coal is a surface phenomenon and proceeds through a loosely bound coal-oxygen-water complex with subsequent steps being breakdown of the complex to simpler molecules such as CO, CO_2 and H_2O etc. Most popular hypothesis is that the overall reaction proceeds through a chain mechanism with moisture facilitating the formation of free radicals that act as chain carrier. Due to fire in coal mines, hues quantity of noxious gases liberated in the atmosphere which damage the ecological balance of nature. The main objective of his paper was to elaborate the causes, mechanism of spontaneous heating and technological advancement mainly development of chemical inhibitors for controlling and combating fire in coal mines.

Panigrahi and Ray (2014) carried out experiments on 78 coal samples collected from thirteen different mining companies spreading over most of the Indian and 936 experiments were carried out by varying different experimental conditions to standardize this method for wider application. For a particular sample 12 experiments of wet oxidation potential method were carried out. The results of wet oxidation potential (WOP) method was correlated with the intrinsic properties of coal by carrying out proximate, ultimate and petrographic analyses of the coal samples. Correlation studies was carried out with Design Expert 7.0.0 software. Further, artificial neural network (ANN) analysis was performed to ensure best combination of experimental conditions to be used for obtaining optimum results in this method. They determined the optimum conditions for carrying out experiment was 0.2 N $KMnO_4$ solution with 1 N KOH at 45°C to achieve optimum results for finding out the susceptibility of coal to spontaneous combustion. The results were validated with Crossing Point Temperature (CPT) data which is widely used in Indian mining scenario.

Ray et al. (2016) carried out 600 experiments with 50 coal samples collected from fiery and non-fiery seams covering different geographical locations in India. Physicochemical characteristics of coal like moisture, volatile matter, oxygen, and hydrogen contents were correlated with the results of wet oxidation potential method carried out at different experimental conditions. The optimum conditions were found to be 0.2N $KMnO_4$ solution in 1N KOH at 45°C. As for conclusion he found that the correlation analysis it was corroborating with field observations and a good correlation was obtained from the CPT carried out on the samples.

CHAPTER 3

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SPONTANEOUS HEATING AND ITS MECHANISM

The auto oxidation of the exposed coal surface leads to generation of heat through the exothermic reactions. Thus the process of spontaneous combustion of coal without the presence of any external source of fire is known as spontaneous heating. Though it is presumed that the main reason behind the spontaneous heating of coal is the auto oxidation process, there exist many theories given by different researchers across the globe which explains the spontaneous heating process through different mechanisms.

3.1 Mechanism

Coal on exposure to air oxidizes even at temperatures below ambient. The oxidation procedure of coal is exothermic in nature. The initial reactions of the spontaneous heating of coal are primarily physical reactions. The oxygen is adsorbed at the coal surface leading to emission of large amount of heat. Rate of heat released in oxidation of coal varies from 2.0 to 4.0 Cal per mole of oxygen adsorbed. The process takes place even at normal atmospheric temperature but it is slow and the heat evolved is not perceptible as it is carried away by the air unless the latter is stagnant. If, however, the rate of dissipation of heat is slow compared with the evolution of heat by oxidation, there is a gradual build-up of heat and slow rise in-the temperature of coal. At the raised temperature the process of oxidation is slightly accelerated and some other fractions of coal become susceptible to oxidation. A stage is reached when the build-up of heat and the rise of temperature reach the ignition point of coal which then catches fire. A good air current will effective1y prevent undue increase of temperature; absence of air will prevent oxidation; and somewhere between these two extremes conditions may permit marked heating to take place Once the coal reaches its ignition point (as distinct from slow oxidation), the air supply to it will only increase the combustion. The ignition temperature of bituminous coal is nearly 200°C and of anthracite coal, nearly 398°C. The coal may be smoldering in the beginning but it may soon break up into flames if sufficient oxygen or fresh air feeds the hot coal. This process of self-heating of coal resulting ultimately in its combustion is known as spontaneous combustion. There is a fall in the adsorption rate of oxygen in the exposed coal surface. The discharged heat generally gets disseminated into environment however at times it collects , leading to the rise in temperature which then leads to chemical reactions. The different stages in which this process continues is shown below:

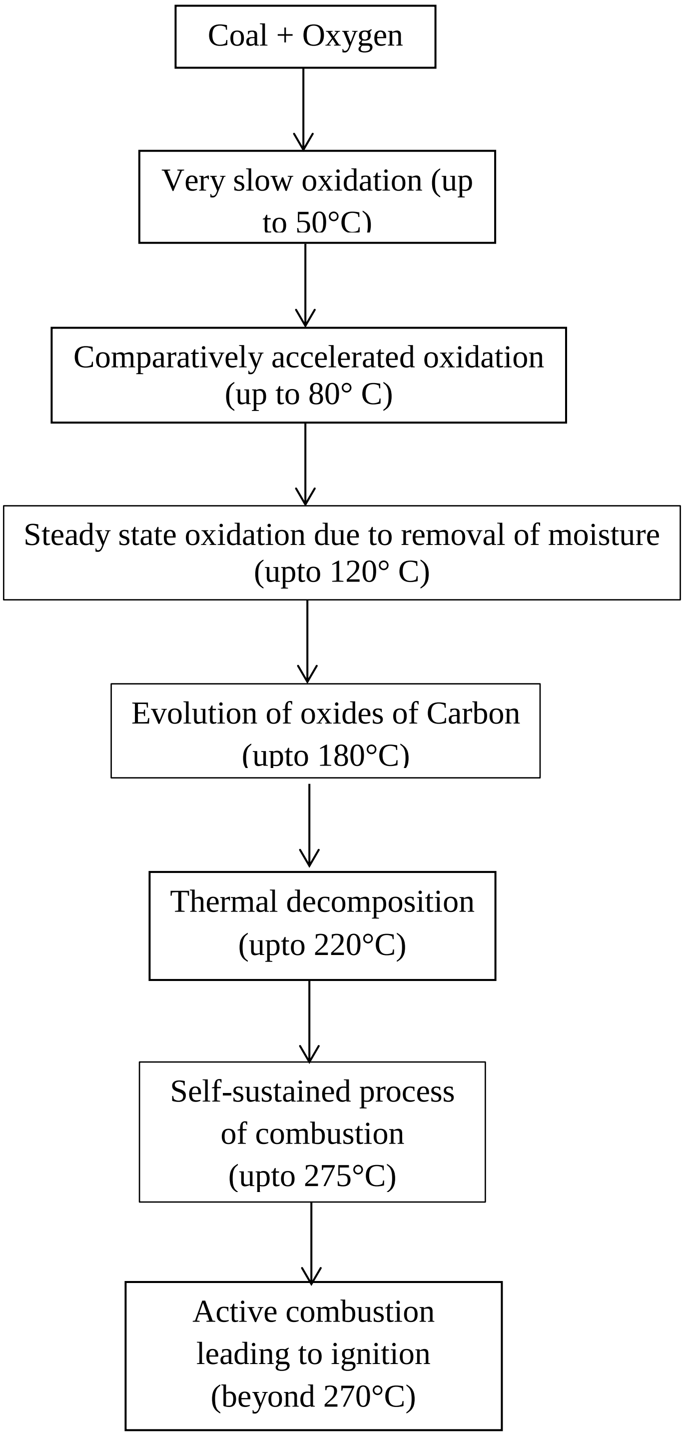

Figure 3.1: Stages in spontaneous heating of coal

The factors on which auto oxidation of coal depends are:-

- Temperature – the chemical reaction between coal and oxygen is directly proportional to the rise in temperature, i.e., increase in temperature assists in the chemical reaction and it is almost double for an increase of 10°C. Generally at room temperature chemisorption of oxygen occurs at the exposed or free surface of coal.
- Coal quality – oxidation mechanism is same for every type of coal but the rate at which spontaneous heating occurs depends on the rank of coal as well as its different intrinsic properties such as, moisture content, ash content and volatile matter content. High moisture content and low grade coals are more prone to auto oxidation because of ease of peroxy- complex formation.
- Time duration of oxidation – the rate of absorption of oxygen gradually decreases as time duration increases. At the starting more pores are available to the oxygen, hence rapid absorption but, at the later stage oxygen consumption becomes stagnant and reduces.
- Moisture availability– presence of moisture ceases the heat generation due to auto oxidation process but it helps in the reaction of formation of peroxy – complexes and thus it affects the rate of reaction. There is an increase in fresh spots for oxygen absorption due to release of moisture, thus increasing its proneness to spontaneous combustion.

3.2 Theories

There are many theories regarding spontaneous heating of coal. Some of teh important theories have been presented here.

Pyrite theory: Presence of pyrites in coal has an adverse effect as it acts a source of heat generation since its oxidation leads to exothermic reaction. The oxidation reaction of pyrites is given as :

$$2\ FeS_2 + 7\ O_2 + 16\ H_2O \rightarrow 2\ H_2SO_4 + 2\ FeSO_4.7H_2O + 316\ kcal$$

The oxidation reaction is followed by emission of heat as it is an exothermic reaction. There is a break open of surface because of the by-products having large volume and can lead to spontaneous heating if present in considerable proportions. The presence of pyrites in a range of 5 – 10% has a significant affect but concentration less than 5% has negligible effect on spontaneous heating of coal.

Bacterium theory: It has been evidently found that bacteria can survive in the coal and its presence leads to a hike in temperature of coal surface which might trigger spontaneous heating under suitable conditions. Graham had observed that the rate of oxidation of sterilized coal and unsterilized coal (i.e., the coal with bacteria on it) was same without any significant change. However, Fuchs had a different observation regarding slight rise in temperature due to the presence of bacteria but, it did not had any significant effect on the spontaneous heating.

Phenol theory: It has been experimentally verified that phenolic hydroxyls and poly phenols oxidize at a very fast rate. This theory also helps us in determining liability of coal to spontaneous heating.

Electro chemical theory: The auto-oxidation of coal has been described as redox reaction processes taking place in micro galvanic cells made by coal components.

Humidity theory: The atmospheric oxidation of coal generates heat whose amount is lesser than the required heat energy in removal of moisture from coal. To cease the process of spontaneous heating, evaporation of water could be induced such that it uses the generated heat, thereby reducing the temperature of heating. This mechanism was proposed by Mukherjee and Lahiri (1957) as a mechanism of reaction between water and coal at 100°C. The following chemical process depicts the mechanism where the chemisorptions have been indicated in brackets:

$$H_2O \text{ - (H) (OH) - } (H_2) \text{ (0) -- } (H_2) + 0_2$$

$$C + 0 \text{ --- (CO) --- } CO$$

$$(CO) + (0) \text{ --- } (CO_2) \text{ --- } CO_2$$

Water is a by-product of the oxidation reaction at low temperature oxidation of coal and thus the mechanism provides us knowledge regarding the sources for CO and CO_2 at low temperature oxidation reaction of coal.

3.3 Factors Affecting Spontaneous Heating of Coal

It is very important to know the contributing factors to the spontaneous combustion of coal. Over a period of time, many accidents and mishaps have led to the understanding of the key factors. Spontaneous combustion makes the working environment risky and hazardous, thus to prevent huge losses to the mankind as well as environment, the following factors have been studied.

Intrinsic factors: These factors are related to the nature of coal, i.e., physically and chemically :

- The composition of coal – the higher percentage of ash leads to significant decrease in susceptibility of spontaneous heating of coal but few other components such as lime, soda and iron components leads to increased spontaneous combustion while inert materials such as alumina and silica has adverse effect on spontaneous combustion
- Rank and petrographic constituents – low rank coals are more vulnerable to spontaneous combustion in comparison to medium and higher rank coals
- The size of particles, surface area and coal friability have a crucial role - the particle size has an inverse relation to the exposed free surface, i.e., the smaller the particle size, more surface area would be available for oxidation, thus enhancing the spontaneous combustion
- Presence of moisture – it may have a ceasing effect or sometimes it also might help in the spontaneous combustion
- The presence of pyrites – higher content of pyrites increases the proneness of coal to spontaneous combustion

Extrinsic factors: these factors depends on the geological, mining and atmospheric conditions :

- Temperature – it affects the rate of reaction directly. Increase in temperature leads to increased rate of oxidation which further leads to spontaneous heating of coal.
- Presence of moisture – it has an inhibiting effect on spontaneous heating but evaporation of moisture from coal surface leads to release of heat of wetting thereby increasing the temperature and also proneness to spontaneous combustion. The presence of atmospheric moisture assists in spontaneous combustion of coal.
- Oxygen concentration – the presence of oxygen enhances the rate of oxidation and increases the susceptibility of spontaneous combustion of coal.

- Timber as support systems – it contributes to the increased susceptibility of spontaneous combustion because the bacterial decomposition of timber leads to emission of heat to the atmosphere.
- The working methods, ventilation and air flow rate – different working methods have different level of proneness to spontaneous combustion. The conventional bord & pillar method has a high risk of spontaneous combustion than longwall mining method since the pillars left as support are prone to oxidation. The extent of extraction also plays a vital role as the amount of coal extracted should be processed within the stipulated incubation period or else it might lead to some hazardous accidents. Sufficient air flow is required so that it does not lead to accumulation of toxic gases and provide safe and clean environment for the workers but higher air flow rate increases the spontaneous heating of coal.
- Presence of faults in coal seams and surrounding environment increases the chance of air leakage thus, increasing the rate of oxidation

CHAPTER 4

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EXPERIMENTAL INVESTIGATIONS

In order to assess the spontaneous heating susceptibility of coal, 20 coal samples were collected from different Indian coal fields. The Intrinsic properties of these samples were determined by carrying out proximate analysis and calorific value. The wet oxidation potential difference experiment was conducted to assess the spontaneous heating susceptibility of coals. The details of the experimentation has been presented here.

4.1 Sample collection and preparation

Sample collection

Sampling is done to take a smaller representative of the large ore body or in other words the best represented ore body sample is used for the experiments. The different parameters such as moisture content, volatile matter content, ash content, and fixed carbon were determined for the coal samples. It is assumed that the sample taken will represent the coal seam appropriately and provide us with the proper results. To ensure that the samples will give correct readings, samples were often collected at regular intervals. There are different methods for sample collection so that the consistency of the sample represents that of the whole ore body or seam. Different types of sampling methods are discussed below:

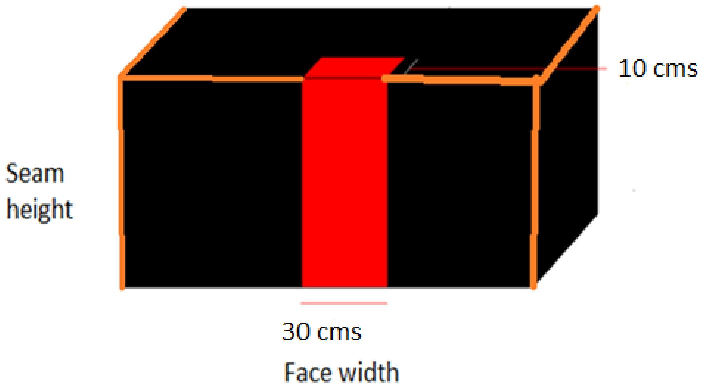
- Channel sampling
- Chip sampling
- Grab sampling
- Bulk sampling

Chip Sampling – It is usually applied for hard ore bodies where channel sampling is not easy. Generally the sample is taken in the form of uniform chips collected from the centre part of the ore or rock which is equally spaced both vertically and horizontally.

Grab Sampling – It is a method of collecting sample from broken ore in the slope or at the face, transported ores. The accuracy of grab sampling might be questionable but the sampling is effective when it is collected from tubs and ships since the samples are collected from the regular consignment of materials.

Bulk Sampling – It is done where conventional sampling methods are not effective. Bulk sampling eliminates the effect of minor distribution.

In the present work, channel sampling procedure (IS 436 Part I/Section I - 1964) was followed. The sampling was done in open and exposed place from the roof to the floor. The sample was taken in the form of a channel having dimensions of 30 x 10 cm, i.e., 30 cm in width and 10 cm in depth. The procedure for cutting out the sample was initiated by first, marking two parallel lines 30 cm apart almost perpendicular to the bedding planes of the seam by a chalk. The dirt bands exceeding 10 cm was excluded. The marked sample was then cut to a depth of 10 cm and the coal sample was collected on clean cloth or tarpaulin placed at the bottom so as to prevent flying of broken pieces during the cutting of sample.



Channel Sampling

4.2 Determination of intrinsic properties of coal through Proximate Analysis

Proximate Analysis (IS 1350 Part I -1984)

The proximate analysis provides the moisture content, ash content, volatile matter and fixed carbon present in the coal sample through the experiments in which generally, the coal sample is subjected to heat at different conditions according to the requirement. The method for conducting the proximate analysis for different parameters has been specified in the IS (Indian Standard) 1350 (Part- I)-1984 and is followed accordingly.

Determination of Moisture Content (M)

Moisture is associated with the coal since almost every coal mined has some moisture over its surface. The presence of moisture is mainly physical or chemical depending on the nature of coal and its origin and also the method of extraction. Since all the process of coal extraction requires water to suppress coal dust generation thus, all the coals have some moisture bounded to them. The moisture present can be distinguished as extraneous and inherent moisture, where, extraneous moisture is physically bounded to coal and can be removed from the coal sample by simply placing the sample in the sunlight, whereas, inherent moisture is chemically bounded to coal and should be remove from it by placing the sample at furnace for 2 hours at about 35-40°C. The inherent moisture can be removed only by heating the coal sample above 100°C. The extraneous moisture associated with the coal is mainly due to the method of extraction and transportation but the inherent moisture is due to the inherent hygroscopic nature of coal towards moisture.

Procedure

- The air dried coal sample of -212µ size is weighed in a silica crucible, about 1gm of coal sample is taken.
- A pre heated electric hot air oven maintained at 108°C is used for the experiment where the coal sample is kept for a stipulated time of 1.5 hours.
- After the duration of 1.5 hours, the coal sample in the silica crucible is taken out of the oven wearing safety gloves and tong and then it is allowed to cool in a desiccator for 15 minutes before weighing it.
- The weight loss is the moisture which is expressed in percentage.

The formula for the determination of moisture is given as:-

$$\text{Moisture \%} = (Y-Z/Y-X)*100$$

Where,

X = weight of the empty silica crucible (gm)

Y = weight of the silica crucible along with the coal sample taken in it (gm)

Z = weight of the silica crucible and coal sample after heating (gm)

Plate 4.1 Electric hot air oven

Determination of Volatile Matter (VM)

The chemical reaction of the organic matter in the coal leads to the formation of some volatile matter such as hydrogen, carbon monoxide, methane and few other hydrocarbons , ammonia and few sulphur compounds and its oxides as well as formation of incombustible gases such as carbon dioxide and water vapour. The water of hydration of mineral matter, carbon oxides from the carbonates and hydrogen chloride from inorganic chlorides are closely associated to the inorganic materials present in the coal.

Procedure

The volatile matter test is carried out in a special silica crucible with the given dimensions (38 mm height, 25 mm external diameter and 22 mm internal diameter). First, the empty silica crucible is weighed and then about 1 g of coal sample is taken in the crucible and weighed. The silica crucible along with the coal sample in it is placed in the muffled furnace which is maintained at 925°C with the crucible being covered by a lid. The coal sample is heated in the furnace for 7 minutes after which it is safely taken out using tongs and then placed in the desiccator to cool down and later, when it cools down, the crucible is again weighed without the lid.

The calculation for the determination of volatile matter is give as:

Volatile Matter % = (Y-Z/Y-X)*100

Where,

X = weight of empty crucible, g

Y = weight of crucible and coal sample before heating, g

Z = weight of crucible and coal sample after heating, g

Determination of Ash Content (A)

The residual material left after the combustion of coal under certain conditions is known as coal ash. It is a by-product of the chemical reaction of the mineral matter but is not the same in coal. Thus there is a difference between coal ash and mineral matter content. There are two types of mineral matter present, viz., extraneous and inherent mineral matters.

The extraneous mineral matter consists of elements like calcium, magnesium, pyrite, ferrous carbonates, shales, sand and gypsum. The different types of extraneous mineral matter based on the coal formation are:-

- During the formation of coal, the rotten green vegetation might have mixed with coal lumps and it is hard to remove by mechanical methods.
- The mining extraction and transportation leads to the mixing of dirt materials

The inorganic elements associated with the organic components of coal is known to comprise the intrinsic mineral matter which mostly has the origination from the vegetation or plants from which the coal formation is associated with. The mineral matter present in the coal is different from the ash in both quantitative and qualitative ways because of all the alterations that takes place during the formation of coal such as loss of water from silicate minerals, loss of carbon dioxide from carbonate minerals, formation of ferrous oxides due to the oxidation of pyrites.

Procedure

The silica crucible is pre heated at 800°C for 1 hour to ensure that it is free from any other mineral matter other than the coal. After heating, it is allowed to cool at the room temperature and weighed. About 1 gm of the prepared coal sample of -212µ size is taken in the cooled crucible and again it is weighed and then it is placed in the muffle furnace which is preheated at 450°C for 30 minutes and then the furnace is set raise the temperature to 850°C for 1 hour. After 1 hour, the hot crucible is removed from the furnace wearing gloves and using tongs to hold the crucible and then it is placed in the desiccator for 15 minutes to cool down and then it is weighed.

The calculation for ash content is given as:

Ash % = (Z-X/Y-X)*100

Where,

X = weight of empty crucible (gm)

Y = weight of (coal sample + crucible) in grams (Before heating)

Z = weight of (coal sample + crucible) in grams (After heating)

Plate 4.2 Muffle Furnace for determination of Volatile Matter and Ash Content

Determination of Fixed Carbon (FC)

The portion excluding the moisture, volatile matter and ash is known to be the fixed carbon as per definition. The approximated yield of coke from coal is mainly comprised by the fixed carbon and ash content of the coal. Thus, the fixed carbon could be easily determined by the method of subtracting summation of the moisture content, volatile matter and ash content together from 100%.

FC = 100 - (M+VM+A)

The results of proximate analysis for all the coal samples have been presented in table 4.1

Table 4.1 Results of Proximate Analysis

Sl. No.	Sample	M (%)	VM (%)	A (%)	FC (%)
1.	MCL 1	4.261	30.92	36.71	28.109
2.	MCL 2	4.48	30.897	30.58	34.043
3.	MCL 3	6.31	28.41	23.62	41.66
4.	SECL 1	6.46	28.52	20.13	44.89
5.	ECL 1	4.64	28.59	22.18	44.59
6.	SECL 2	2.22	31.75	36.79	29.24
7.	BCCL 1	0.93	21.5	23.92	53.65
8.	CCL 1	0.86	26.2	20.09	52.85
9.	BCCL 2	0.93	20.68	27.45	50.94
10.	ECL 2	0.9	25.09	21.05	52.96
11.	MCL 4	6.74	26.25	15.56	51.45
12.	ECL 3	0.71	22.84	15.54	60.91
13.	MCL 5	11.53	33.52	28.23	26.72
14.	CCL 2	5.68	28.78	21.53	44.01
15.	CCL 3	6.48	32.12	16.51	44.89
16.	SCCL 1	3.57	34.99	6.19	55.25
17.	SCCL 2	3.06	28.49	25.26	43.19
18.	NCL 1	6.15	36.15	7.99	49.71
19.	NECL 1	1.57	41.08	5.88	51.47
20.	MCL 6	5.82	24.85	27.31	42.02

4.3 Determination of calorific value

The bomb calorimeter Parr 6100 (Plate 4.3) was used to determine the calorific value of the coal samples. The bomb calorimeter consists of a strong stainless steel vessel, called bomb, capable of withstanding high pressures. It is provided with a lid which can be screwed firmly on the bomb. The lid in turn is provided with two electrodes and an oxygen inlet valve. One of the electrodes is provided with a ring to accommodate the silica crucible. The bomb is placed in a copper calorimeter having a known weight of water. The copper calorimeter, in turn, is surrounded by an air jacket and a water jacket to prevent loss of heat due to radiation. There is an electrical stirrer for stirring water. The Parr 6100 is a modern instrument which can calculate the calorific automatically and it needs to be fed the required data.

Procedure

A weighed amount of coal sample between 0.5g to 1g is placed in the silica crucible. The crucible is supported over the ring. A fine magnesium wire touching the coal sample is stretched across the electrodes. Oxygen supply is forced into the bomb till a pressure of 25-30 atm is reached. The water jacket is filled with 2ltrs of water and then the bomb is placed inside it and then the weight of sample is entered manually and then the process is started. The current is switched on the fuel in the crucible burns with the evolution of heat. The heat produced by the burning of fuel is transferred to water which is stirred throughout the experiment by the electric stirrer. Once the bomb fires it gives a high pitch sound and then after the coal sample is completely burned it automatically gives the calorific value.

Plate 4.3 Parr 6100 Calorimeter (Bomb Calorimeter)

Table 4.2 Calorific Values of coal samples

Sample	Calorific Value (Kcal/kg)
MCL 1	6335.58
MCL 2	4737.61
MCL 3	5114.38
SECL 1	6080.33
ECL 1	6641.64
SECL 2	4932.65
BCCL 1	6352.23
CCL 1	6634.47

BCCL 2	5963.30
ECL 2	6528.48
MCL 4	6312.08
ECL 3	5370.17
MCL 5	5554.18
CCL 2	5029.71
CCL 3	5760.03
SCCL 1	6810.03
SCCL 2	5262.16
NCL 1	6137.47
NECL 1	7861.22
MCL 6	5104.93

4.4 Wet oxidation potential difference method

The two primary constituents of a coal molecule are:

1. The condensed aromatic structure which are resilient towards oxidation
2. The aliphatic or the hydro aromatic structure which are easily oxidised.

The presence of hydroxyl group in the aromatic structure increases the sensitivity of coal molecule which plays a crucial role in the spontaneous combustion of low grade coal because of presence of hydroxyl group and they comprise more branches of aliphatic hydrocarbons. The high rank coals have graphite like structure, thus they are resistant to oxidation. The oxidation of coals leads to the formation of aliphatic acids which is high in the case of oxidation of low rank coals compared to the high rank coals. In the alkaline permanganate solution, coal oxidation occurs and the concentration of magnetite ion increases compared to the permanganate ion and thus it leads to the potential difference. The potential difference change is measured by the carbon electrode sank in the alkaline permanganate solution. The change in concentration occurs due to the chemical reaction of coal with the KOH and $KMnO_4$ solution.

The $KMnO_4$ and KOH solution with the coal sample forms an electrochemical cell which is stirred by a magnetic stirrer to generate EMF against a standard potential of 0.56 V. A graph is plotted between EMF and time which gives an idea about the spontaneous combustion of coal.

Plate 4.4 Wet Oxidation Potential Difference Apparatus

Principle of Wet oxidation

An alkaline potassium permanganate ($KMnO_4$) solution is prepared and used for the wet oxidation potential experiment. The reduction of permanganate ion to magnate ion is represented as follows:

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

The standard electrode potential (E^0) for the redox reaction of the permanganate ion is 0.56V. The electrode potential can be calculated by the following equation:

$$E = E^0 - (RT/F) \ln ([MnO_4^{2-}] / [MnO_4^-])$$

Where,

R = Universal gas constant

T = Temperature

F = Faraday’s constant

The addition of coal leads to oxidation of coal sample while the permanganate ion is reduced to magnate ion which results in the change in EMF and the change in potential occurs till the whole oxidation is completely over. The change in potential of the carbon electrode is measured for taking the results. The electrode is represented as carbon/ MnO_2^-.

Procedure

At first, 100ml of deci-normal solution of potassium permanganate ($KMnO_4$) in 1N potassium hydroxide (KOH) solution is prepared in a glass beaker, and then it is place on the magnetic stirrer machine along with the Teflon coated fish of the magnetic stirrer. After that the carbon electrode is fixed as the cathode and the calomel as anode. The magnetic stirrer and the wet oxidation apparatus (Plate 4.4) is switched on. Then about 0.5 gm of coal sample of (-212µ) size is weighed and mixed into the alkaline solution. The magnetic stirrer ensures homogeneity in the mixture because of its rotation which could be controlled accordingly. The readings are noted down from a volt meter at an interval of 1 minute till the potential difference tends to become constant.

The graphs are plotted between Time and Potential difference obtained for all the coal samples and have been presented in Figures 4.1 to 4.4. It could be seen from the graphs that the potential difference becomes constant for all the coal samples after 30 minutes. Thus, 30 minutes was selected as the time interval for comparison of the potential difference values. The results of potential difference values after 30 minutes for all the coal samples have been presented in Table 4.3.

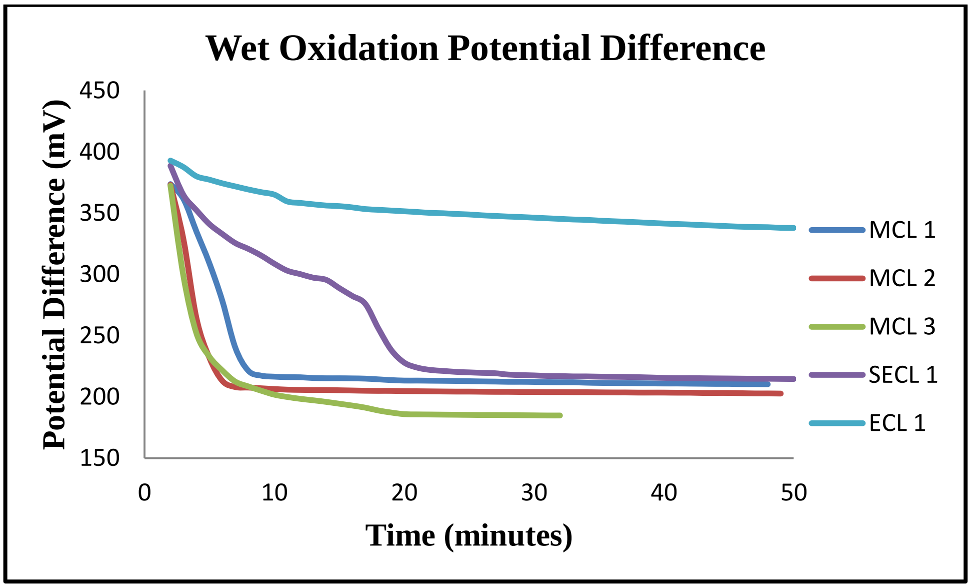


Fig. 4.1 Wet Oxidation Potential curve (Sample 1 – 5)

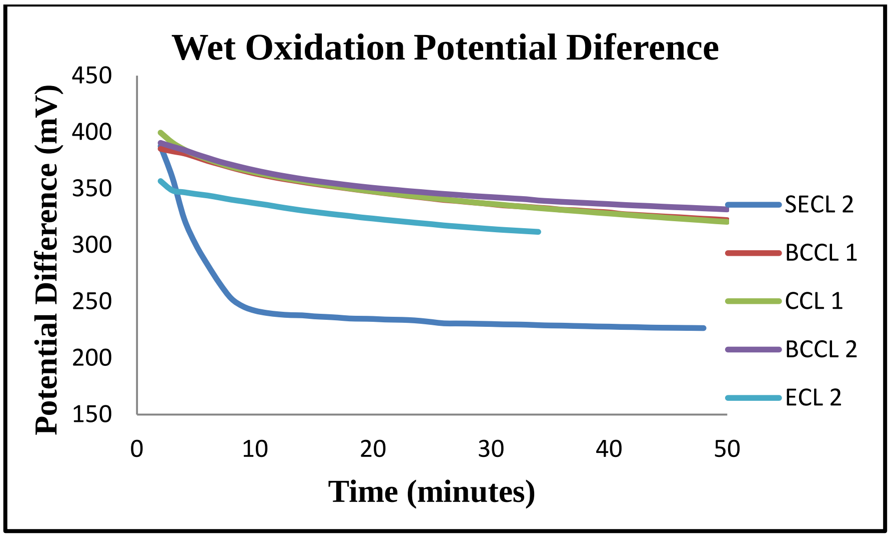


Fig. 4.2 Wet Oxidation Potential curve (Sample 6 – 10)

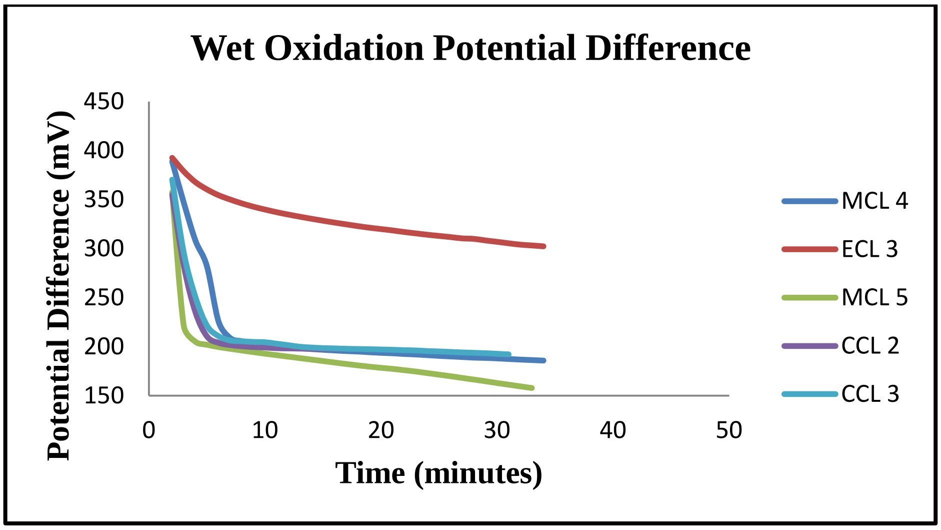


Fig. 4.3 Wet Oxidation Potential curve (Sample 11 – 15)

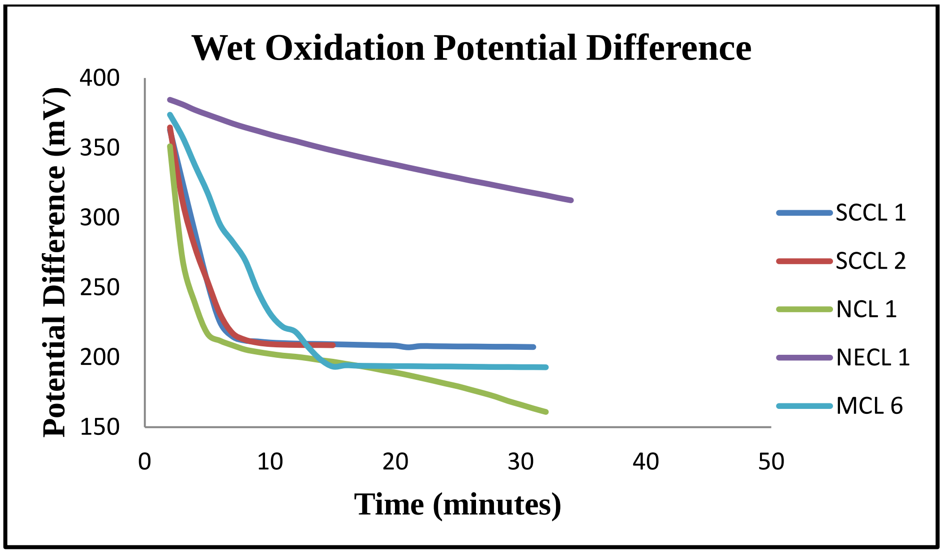


Fig. 4.4 Wet Oxidation Potential curve (Sample 16 – 20)

Table 4.3 Results of the wet oxidation potential difference

Sample	WOPD after 30 minutes
MCL 1	161.8
MCL 2	169.3
MCL 3	187.6
SECL 1	171.7
ECL 1	47.6
SECL 2	157.9
BCCL 1	50.7
CCL 1	65
BCCL 2	49.3
ECL 2	43.8
MCL 4	202
ECL 3	88.5
MCL 5	198
CCL 2	157.1
CCL 3	178.2
SCCL 1	155.5
SCCL 2	156
NCL 1	190.3
NECL 1	68.4
MCL 6	180.9

CHAPTER 5

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DISCUSSION AND CONCLUSION

5.1 Discussion

The evaluation of 20 samples for the intrinsic properties as well as their wet oxidation potential difference is carried out. For the experiments to be carried out, 20 samples were collected in which 6 samples were from MCL, 2 samples from SECL, 3 samples from ECL, 2 samples from BCCL, 3 samples from CCL, 2 samples from SCCL and 1 sample each from NCL and NECL. The sample collection was done following the Indian Standards. The determination of intrinsic parameters were done conducting Proximate Analysis whereas the spontaneous heating susceptibility was measured by the Wet Oxidation Potential Difference. The Gross Calorific Value was also determined by the Bomb Calorimeter.

The moisture content of the coal samples varied from 0.71% (ECL 3) to 11.53% (MCL 5). It was observed that the coal samples from MCL had higher moisture content than others followed by coal samples from SCCL and SECL. It was observed that the samples of higher moisture content were more susceptible to spontaneous heating.

The volatile matter of the coal samples varied from 20.68% (BCCL 2) to 41.08% (NECL 1). It was observed that coal samples from BCCL had lower volatile matter than others. The SECL and SCCL coal samples had notably high volatile matter content than MCL and CCL coal samples.

The ash content of the coal samples varied between 5.88% (NECL 1) to 36.79% (SECL 2). The MCL coal samples showed a higher average ash content. The fixed carbon content varied between 26.72% (MCL 5) to 60.91% (ECL 3).

The gross calorific values varied between 4737.615 Kcal/kg (MCL 2) to 7861.22 Kcal/kg (NECL 1). The CCL coal samples showed notably high calorific values.

In order to establish the effects of intrinsic properties on the spontaneous combustion susceptibility of coal samples, correlation studies were carried out. The correlation coefficients between the intrinsic properties and susceptibility indices were found out by taking the parameters determined by proximate analysis viz. moisture, volatile matter, ash; and gross calorific value as independent variables and the susceptibility indices determined by wet oxidation potential analyses as dependent variable. Empirical relations were also established between them and curves were plotted taking independent variables in horizontal axis and dependent variables on vertical axis. The correlation plots have been presented in Figure 5.1, 5.2, 5.3, 5.4, 5.5. and the empirical relationship and correlation coefficient between wet oxidation potential difference value and the intrinsic properties are presented in table 5.1.

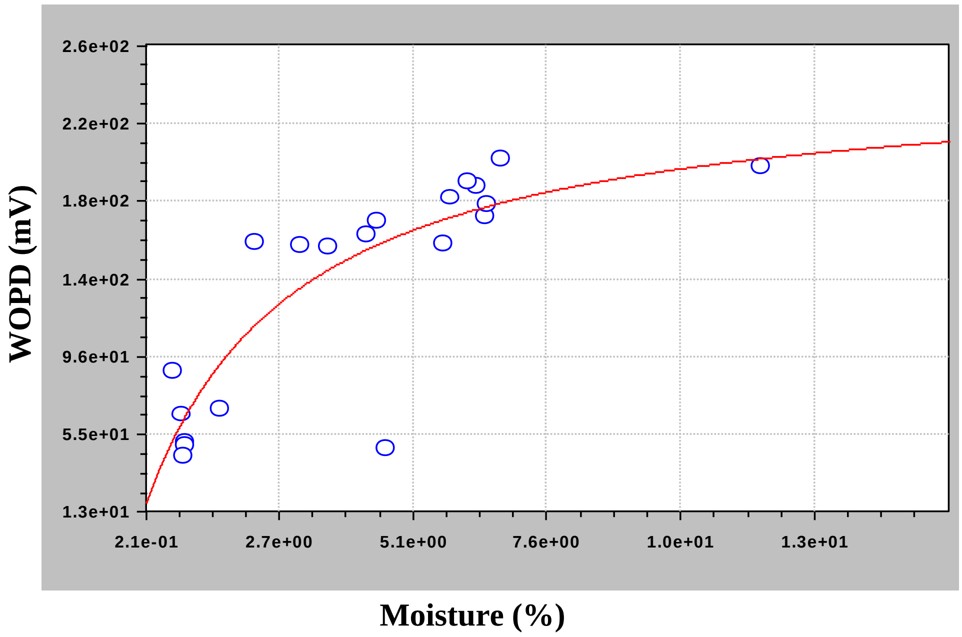

Figure 5.1: Correlation plot between WOPD and Moisture content

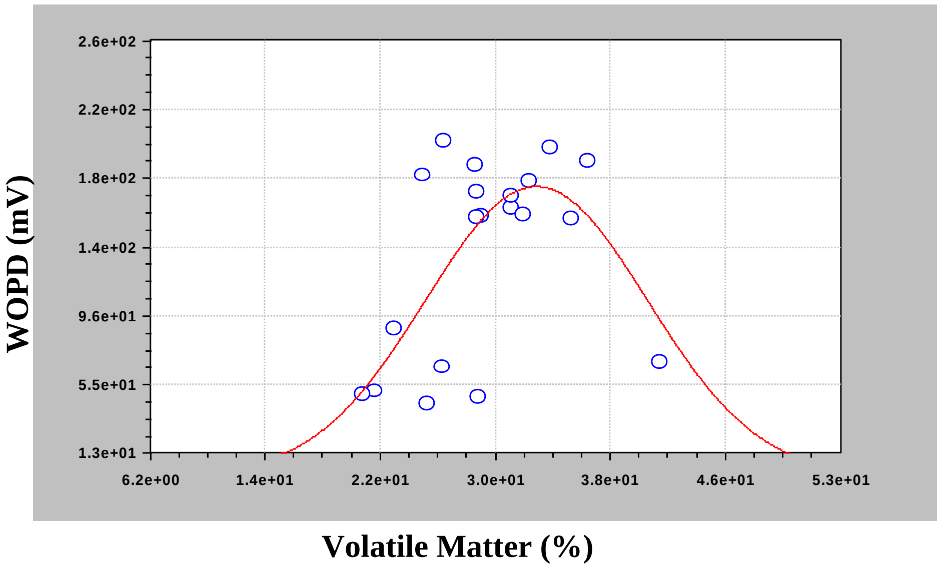

Figure 5.2: Correlation plot between WOPD and volatile matter

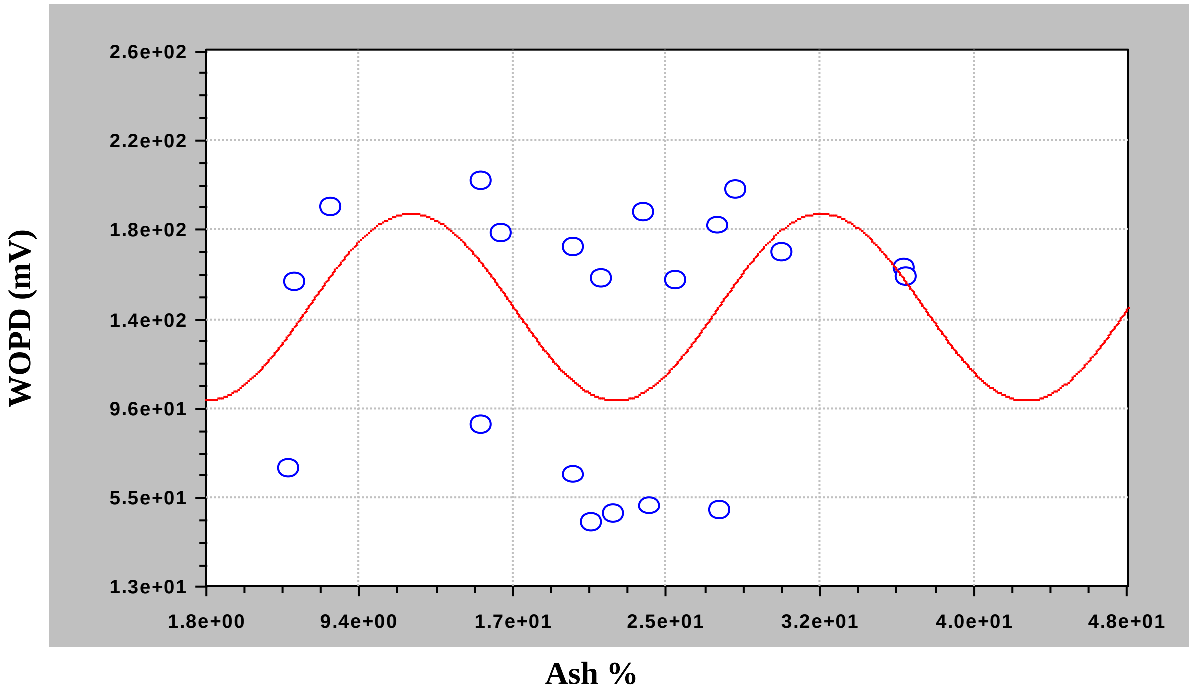

Figure 5.3: Correlation plot between WOPD and Ash content

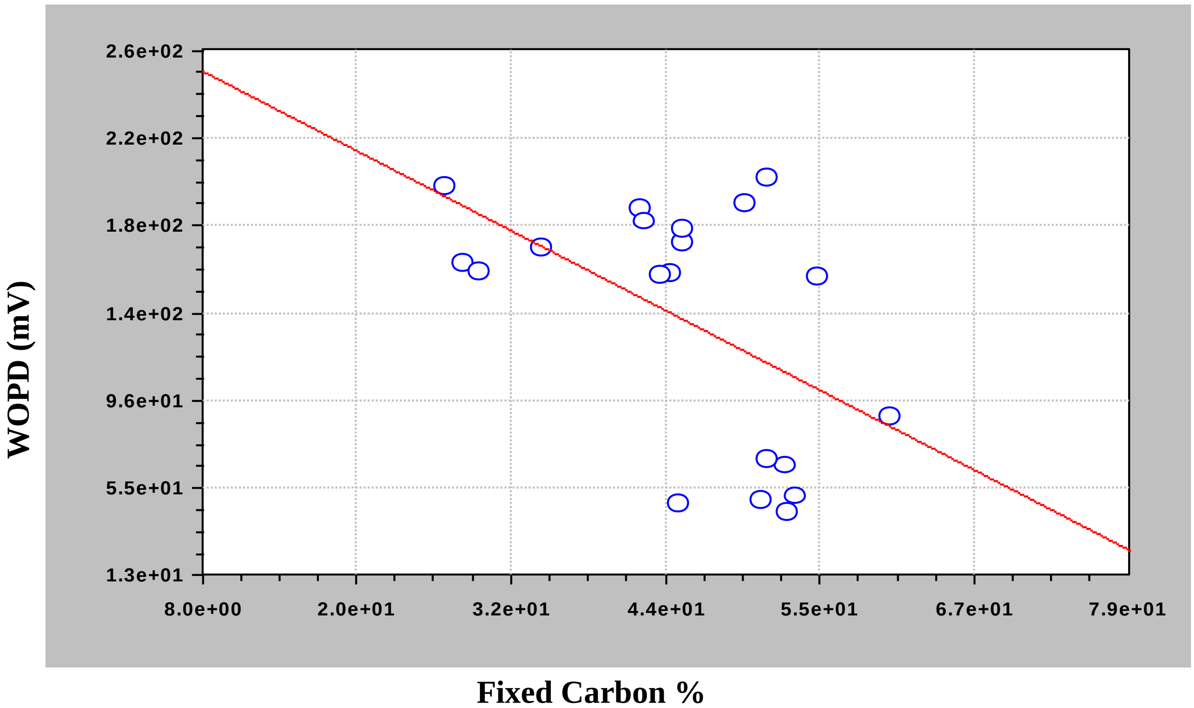

Figure 5.4: Correlation plot between WOPD and Fixed Carbon content

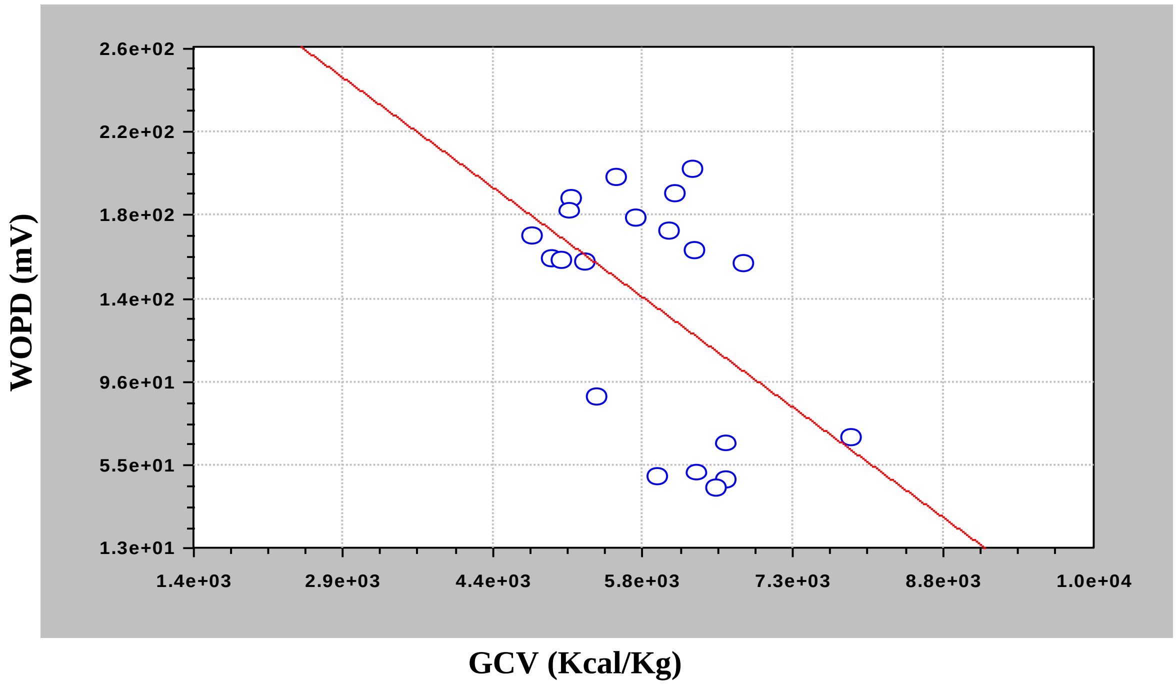

Figure 5.5: Correlation plot between WOPD and Gross Calorific Value

Table 5.1 Correlation between Wet Oxidation Potential Difference (WOPD) and Intrinsic Properties

Sl. No.	Independent variable	Empirical relation	Correlation Coefficient
1	M	$\mathrm{WOPD} = \frac{248.168}{2.634 + \mathrm{M}}$	0.84
2	VM	$\mathrm{WOPD} = 174.45e^{\frac{-(VM-32.55)^2}{2(7.58)^2}}$	0.67
3	A	$\mathrm{WOPD} = 143.337 + 43.501Cos(0.306A + 2.613)$	0.44
4	FC	WOPD =278.132-3.194FC	0.52
5	GCV	WOPD = 355.243-3.194FC	0.50

It may be seen that Moisture and Volatile Matter values showed a good correlation but other intrinsic properties showed low values. Thus, they are not reliable for the assessment of susceptibility of spontaneous heating of coal.

The wet oxidation potential differences show correlation values around 0.5 with fixed carbon and gross calorific value. It is clear from the correlation plots that the wet oxidation potential difference after 30 minutes is lower for coals having high fixed carbon and high calorific value, which means they are of higher rank. This corroborates the findings of earlier research (Tarfadar, Ray et al), this method may not be an optimum measure of spontaneous heating susceptibility. Thus this method could be accepted as an alternative method for teh assessment of spontaneous heating of coal.

The wet oxidation potential values varied between 43.8 mV (ECL 2) to 202 mV (MCL 4). The coal samples having WOPD values less than 100 mV were ECL 1, BCCL 1, CCL 1, BCCL 2, ECL 2 & NECL 1 indicating that they are poorly susceptible to spontaneous heating. The coal samples MCL 1, MCL 2, MCL 3, SECL 1, SECL 2, MCL 4, MCL 5, CCL 2, CCL 3, SCCL 1, SCCL 2, NCL 1 & MCL 6 were highly susceptible as they had WOPD values greater than 120 mV.

5.2 Conclusion

In India, generally crossing point method is used for assessment of spontaneous heating susceptibility of coal. However, this method has certain draw backs. The results are dependent upon packing density, rate of heating and oxygen flow rate etc, and sometimes the results are not reproducible. Moreover it takes more than three hours to complete the experiment. In the present study, wet oxidation potential difference method was attempted for the evaluation of spontaneous heating of coal. Compared to crossing point temperature, the wet oxidation experiments only takes about 40 minutes for completion. The wet oxidation potential difference method gives excellent repeatability of the experimental results for the same sample, but in case of crossing point temperature; the repeatibility of the experimental results is not as good as wet oxidation method. The correlation analysis between potential difference and intrinsic properties was found to be fairly accurate, which indicates that this method may be adopted as a measure of spontaneous heating susceptibility. Moreover, the wet oxidation method is very handy and easy to perform compared to CPT. Thus, wet oxidation potential difference method may be a useful method for the assessment of liability of coal to spontaneous heating.

From the above discussion, it may be concluded that the coal samples from MCL, SCCL and SECL had extreme values in the WOPD experiments which indicates that it is highly susceptible to spontaneous heating. Among other samples, CCL 2, CCL 3 and NCL 1 are also highly susceptible to spontaneous heating.

5.3 Scope for further study

The wet oxidation potential difference experiment was conducted at room temperature, but for a better analysis, the experiment may be attempted at different temperatures and the results may be compared with other experimental techniques such as CPT, DTA and DSC. The experiment could be performed on more samples for a better correlation, thus increasing the reliability of wet oxidation potential difference technique for assessment of spontaneous heating susceptibility of coal.

CHAPTER 6

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