SPONTANEOUS HEATING LIABILITY OF SOME WASHED COAL

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

BACHELOR OF TECHNOLOGY

IN

MINING ENGINEERING

BY

BHANJA KISHORE SA

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DEPARTMENT OF MINING ENGINEERING NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA – 769008

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Under the guidance of

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2012

National Institute of Technology, Rourkela

CERTIFICATE

This is to certify that the thesis entitled **"SPONTANEOUS HEATING LIABILITY OF SOME WASHED COAL"**submitted by **Sri Bhanja Kishore Sa** in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the 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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CONTENTS

ABSTRACT

65% of India"s energy requirement is met by coal. Out of the total resources of coal,85% is of the non-coking variety and is of inferior quality. The ash is delivered to major customers like power houses is averaging about 42%, since, 75% of the total coal produced in India is from opencast mines, and this also adds to the problem of inconsistency in the quality of coal.

Coal beneficiation or coal washing is a generic term which is used to designate the various operations on the ROM (Run of Mine) coal to prepare it for specific end uses without destroying the physical characteristics of coal.it has reached a stature of vital link between production and marketing of coal.

Coal preparation covers a vast range of coal processes from crushing the coal to elaborate gravity separation. Most of the processes impact the coal quality. Rotary breakers can remove out large rocks and debris from raw coal.

Different experiments were conducted to find the spontaneous heating susceptibility between the raw coal and washed coal. How a washed coal is different from the raw coal why it is used in the power generation sector, cement factory and sponge factory. The project deals with determination of spontaneous heating susceptibility of washed coal as well as raw samples by experimental techniques. The intrinsic properties and susceptibility indices of the coal samples were determined by following experimental techniques

Proximate analysis

Calorific value

Flammability temperature

Wet oxidation potential

Crossing point temperature

Washability Characteristic

Differential thermal analysis (DTA-TG)

(v)

LIST OF TABLES

LIST OF FIGURES

LIST OF PHOTOGRAPHS

Chapter-1 INTRODUCTION

1.1 BACKGROUND

India is the third largest coal producer in the world and represented about 9-10% of the total world coal reserves. Indian coals are generally contains higher amounts of integrated dirt and normally difficult to wash. Consequently controlled crushing of these coals became necessary for better liberation of dirt before the coals are upgraded by washing. The need to crush coal to smaller sizes for better liberation of dirt for its subsequent removal by washing, creates the problem of generation of more coal fines [18].Coal is the source of about 27% of the world"s primary energy consumption and it accounts for about 34% of electricity generated in the world, so much attention has been focused in recent years on coal as an alternative source of energy (Nimaje et al., 2010). Coal is the dominant energy source in India and meets 55% of country"s primary commercial energy supply. Mine fires in Indian coalfields is generally caused by spontaneous combustion of coal despite various preventive technologies being adopted. The spontaneous heating of coal varies over a wide range and it is important to assess their degree of proneness for taking preventive measures against the occurrence of fires to avoid loss of lives and property, sterilization of coal reserves and environmental pollution and raise concerns about safety and economic aspects of mining (Tripathy et al., 2001).

In order to find out the susceptibility of coal to spontaneous heating different methods have been adopted by various researchers of the world. A number of experiments have been done for assessing the spontaneous heating susceptibility of coal viz., Crossing point temperature method (Didari et al., 2000), Wet oxidation potential method (Tarafadar et al., 1989), Differential thermal analysis (Nimaje et al., 2010), Flammability temperature (Nimaje et al., 2010).

1.2 OBJECTIVE OF THE PROJECT

The objective of the project is to carry out comparison among all the coal samples of washed coal and non-washed coal, the parameters of coal in order to find out the properties that influence spontaneous heating propensity of coal The project was divided into the following categories.

Literature review- Collection of all the past works done by various researchers both national and international.

Sample collection and preparation – Four samples of washed coal were collected from MCL and BCCL and other four raw coal samples from respective MCL and BCCL and prepared to carryout different experiment as per the Indian Standards.

Experimentation – The experimentation are divided into two stages:

- Determination of intrinsic properties of coal proximate analysis, calorific value, washability characteristic
- Determination of susceptibility indices of coal wet oxidation potential, differential thermal analysis, flammability temperature, crossing point temperature

Analysis – compare the washed and non-washed coal samples to determine the susceptibility to spontaneous heating.

Chapter-2

LITERATURE REVIEW

2.1 WASHED COAL

A coal preparation plant (CPP) is a facility that washes [coal](http://en.wikipedia.org/wiki/Coal) of [soil](http://en.wikipedia.org/wiki/Soil) and [rock,](http://en.wikipedia.org/wiki/Rock_(geology)) preparing it for [transport](http://en.wikipedia.org/wiki/Transport) to market. A CPP may also be called a "coal handling and preparation plant".The coal delivered from the mine that reports to the coal preparation plant is called run-of-mine, or ROM coal. This is the raw material for the CPP, and consists of coal, rocks, middlings, minerals and contamination. Contamination is usually introduced by the mining process and may include machine parts, used consumables and parts of ground engaging tools. ROM coal can have a large variability of moisture and maximum particle size.

The washability characteristics of a coal reserve are provided by obtaining liberation data on the raw coal sample. Liberation refers to the amount of physical breakage required to separate material of different material densities. Low density material is clean coal whereas high density material is reject (rock). The intermediate density material is called middlings [19].

Washed Coal Characteristics (Hatt, 1995)

- Less Ash and High Moisture
- Smaller Sizing and More Consistent
- Less Abrasive and Lower Slagging Potential
- More Expensive in Cost per Calorific Value
- ❖ Improved Power Plant Operation

The demand for coal beneficiation would grow along with increases in production of coal for various reasons (Katzer,2008):

- \triangleleft Increase in coal based power generation
- \triangleleft Increase open pit mining and mechanization
- Depletion of good quality reserves
- High cost of transportation, which makes it uneconomical to transport inert material
- \triangle Environmental stipulation for minimizing pollution

The need of using washed coal in thermal power plants in India arises because high ash and inconsistency in quality lead to many problems that impact the performance of power station

Damage of crusher/conveyors leads to frequent break-down of plants[20]

- \triangleleft Reduced pulverizing capacity
- Reduce flame stability-leads to expensive oil support
- \bullet Slagging and fouling of water walls
- Faster erosion of coal burners
- \triangleleft Increased load on ash handling system
- Reduced PLF (Plant Load Factor) and station thermal efficiency
- \triangleleft Higher emission and environmental impacts.

High ash coal needs cleaning to raise the efficiency of their utilization. Depending upon local conditions the upper limits of coal ash are fixed for acceptance by users in various industries. Indian coals are high in ash content. Therefore in India even metallurgical coke producers tolerate as much as 20% ash in coking coals, even though as upper limit of 10% ash in the norm for corresponding manufacturers abroad. Furthermore thermal power stations in India have to tolerate 30% to 35% ash in boiler coals. No doubt this tolerance is at the cost of efficiency. But there is no other alternative than to depend on indigenous fuel resources. Indian coals have many problems in washing. Washing is practiced only when it is essential [21]. A cost-effective and significant step toward improving power plant efficiency and reducing the GHG (Greenhouse gas) emissions from the coal-fired power plants in India would be to increase the availability of clean beneficiated coals using appropriate beneficiation technologies. Coal beneficiation (or cleaning) is widely viewed as the lowest-cost option for India to address these goals. According to IEA reports, increasing the quality of coal is an essential step toward the deployment of the state-of-the-art Clean Coal Technologies (CCTs) in India. Coal beneficiation is a low-cost solution [22] that can

- \bullet Produce higher quality coals that can be burned more cleanly and with greater efficiency,
- * Reduce the amounts of emitted fly ash and associated hazardous air pollutant precursors,
- Minimize capital, operating and maintenance costs associated with coal fired power generation,
- Lower costs and free up capacity on the overburdened saturated network of Indian railways;
- \triangleleft Reduce the need to import higher-quality coals;
- \triangle Improves health and safety and mitigates environmental degradation.

2.2 TYPES OF WASHERY

Depending on the medium used for cleaning, the various are grouped as (Mathur,1999)

1. Dry processes

2. Wet processes

Currently the washeries in India can be broadly divided into two groups.

1. Pit head washeries:- they treat coal from the same or two or more adjoining collieries.

2. Central washeries:- they recover their feed supplies from a large number of sources located in specified common areas.

Table 2.1 Classification of coal cleaning processes (Mathur,1999)

2.3 COAL WASHERIES IN INDIA

Table 2.2 Coal washeries in India (Sarkar,1996)

2.4 DEMAND OF COAL

Coal constitutes nearly half of commercial primary energy demand and one third of total energy requirements of India According to planning commission, the demand for coal is projected at 758 Million Tonnes (MT) in 2012.The demand supply gap is estimated at 51.10 Million Tonnes Per Annum (MTPA) for the year 2011-12 despite of the continual increment in production of coal with a CAGR(Compound Annual Growth Rate) of 7% On the other hand, the coal produced in India is of inferior quality with less calorific value and high ash content. In India, coking coal preparation has long been in operation but recently the trend has been shifted to beneficiation of non-coking coal due to huge demand from power sector for environmental and efficiency concerns Also, the long distance transportation of coal via land routes offers an ideal opportunity for coal washing in India. It not only helps preserve the environment but also offer substantial benefits to Indian economy. The quality of Run of Mine (ROM) coal from Indian mines is continuously decreasing due to the geographical pattern of coal seams in coal bed. The quality deteriorates as excavation process goes deep inside the mine. This very nature of coal quality from coal seams demand coal washing, providing bullish market opportunity for national and international players to enter the lucrative washery segment of Indian coal sector. CIL has been operating coking as well as non-coking coal washeries for a long period of time but due to man power constraints and operational cost, it has decided to outsource coal washery operation to private players. CIL has earmarked a whopping Rs 5000 crores for coal washery development in 4 years of time with a targeted capacity of 250 MTPA. Thus, it has planned for international competitive bidding to develop 22 number of coal washeries in different parts of India. 66 players have evinced their interest to develop coal washeries for the first phase of CIL"s bidding. This report canvases the prospects of coal washery in India and investment opportunities around the sector. It critically analyses existing and upcoming coal washeries in India, briefs about the existing players" profile. The report comprehensively covers the economic aspects of coal washeries, challenges and risks associated with it, financing of coal washeries and steps involved for setting up of a coal washery. It also focuses on existing as well as emerging technology in coal washing segment. The technology providers as well as the equipment manufacturers and associated industries will be getting a major boost due to this renewed interest in this segment of coal sector [4].

Chapter-3

EXPERIMENTAL TECHNIQUES

3.1 SAMPLE COLLECTION AND PREPARATION (IS 436 Part II– 1965)

Sampling is the process of collecting a small portion of a whole such that the substance of that constituent represents that of the whole It is the process by which physical and chemical features of a mineral or ore are determined with the desired accuracy. In the case for coal it covers the properties ascertained by proximate such as fixed carbon, volatile matter, ash and calorific value etc. The physical nature of the ore is sometimes requirement to be determined and the sampling process assumed should be able to give this information too. Samples are generally collected at regular interval. The interval of sampling point is governed by the regularity of the deposits as well as the accuracy for sampling projected. It should be coned and quartered on the sampling sheet, if the quantity is large before collecting it sampling bags. There is always change that missing of collected samples whereas the reduction in volume of samples has to be done individually. Different types of sampling are:

- a) Bulk sampling
- b) Chip sampling
- c) Drill hole sampling
- d) Grab sampling
- e) Channel sampling

Bulk sampling is the method of sampling and it is done where formal sampling methods do not give a instance scale, bulk sampling resorted to or large scale sampling. Bulk samples excrete the effect of irregular distribution of value.

Chip sampling can be taken in case of uniform ores and where the rock structures are independent of the values. It is done in hard ores where it is hard to cut the channels. It The sample is collected by breaking of small same sized chips from a face at points usually as spaced both horizontally and vertically.

Grab sampling is usually grab sampling of the ore broken in the stope is unreliable as accurate estimation of the volume of broken ore is unacceptable. In the stope or at the face which carried ore where the broken ore are applied.

For the project work, the coal mine samples were collected by Channel sampling method, which is the most common method followed and the washery coal samples were collected by grab sampling method.

3.1.1 Channel sampling (IS 436 Part I/Section I - 1964)

In channel sampling the section of seam to be sampled shall be exhibited from the roof to the floor. The particular seam sample shall, be taken in a channel representing the total cross section of the seam having the dimensions of 30 x 10 cm, i.e. 30 cm in width and 10 cm in depth. For the channel sampling purpose there are two parallel lines, which are 30 cm obscure end at right angles to the bedding planes of the seam shall be labeled by a chalked string on the plane, freshly exposed surface of the seam. It is Obvious that, dirt bands exceeding 10 cm in thickness shall be omitted. The channel between the marked chalk lines in the seam shall be cut to a depth of 10 cm and the coal sample collected on a clean strong cloth or tarpaulin placed instantly at the bottom so that the chances of pieces flying off during excavation of coal are understated.

Fig. 3.1 Channel Sampling (Nanda, 2010)

3.1.2 Sample preparation (IS 436 Part 1/Section 1-1964 and IS 436 Part II-1965)

The samples received from the field and washery via channel and grab sampling methods are crushed in the laboratory as per the experimental requirements. The crushed sample is then sieved to required sizes and stored in air tight polythene packets. The packets are stored in air tight containers for further use in experimentation.

3.2 METHODS FOR DETERMINING INTRINSIC PROPORTIES OF COAL

3.2.1 PROXIMATE ANALYSIS (IS 1350 Part I -1984)

The objective of coal ultimate analysis is to determine the amount of fixed carbon (FC), volatile matters (VM), moisture, and ash within the coal sample. The variables are measured in weight percent (wt. %) and are calculated on different basis.

- \triangleleft Ar (ash-received) basis puts all variables into consideration and uses the total weight as the basis of measurement.
- \triangleleft Ad (air-dried) basis neglects the presence of moistures other than inherent moisture.
- \triangleleft db (dry-basis) basis leaves out all moistures, including surface moisture, inherent moisture, and other moistures.
- \triangleleft daf (dry, ash free) basis neglects all moisture and ash constituent in coal.
- \triangleleft dmmf (dry, mineral-matter-free) basis leaves out the presence of moisture and mineral matters in coal.

3.2.1.1 Moisture

Coal is always associated with some amount of moisture, which is both physically and chemically bound, due to its nature, origin and occurrence. It is customary to differentiate between extraneous and inherent moisture. When a wet coal is exhibited to atmosphere, the external moisture evaporates, but the obviously dry coal still contains some moisture, which can be removed only on heating above 100 0 C. External moisture is also called accidental or free moisture, whereas inherent moisture is named as equilibrium or air-dried or hygroscopic moisture. The quantity of external moisture counts mainly on the mode of occurrence and handling of coal, but the air-dried moisture is associated to the inherent hygroscopic nature of the coal.

Experimental Procedure:

- About 1g of finely pulverized -212 micron (-72 mesh BSS) air-dried coal sample is weighed in a silica crucible and then placed within an electric hot air oven. It is maintained at 110^0C .
- $\cdot \cdot$ The crucible with the coal sample is allowed to put in the oven for 1.5 hours and it is taken out with the help of tongues, and then cooled in a desiccator for about 15 minutes.
- \triangle Then weighed. The loss in weight is reported as moisture (on percentage basis).

The calculation is done as per the following.

% Moisture = $(X - Y)/X * 100$

Where,

 $X =$ Initial mass of the coal sample before heating (g)

 $Y =$ Final mass of coal sample after heating (g)

3.2.1.2 Volatile Matter

When coal is heated in defined equipment under appointed conditions, is concerned to as volatile matter, the loss of mass and corrected for moisture. The matter lost is composed of materials that form upon the thermal decomposition of the various constituents of coal. Some of the elements of coal volatile matter are hydrogen, carbon monoxide, methane and other hydrocarbons, tar vapours, ammonia, some organic sulphur and oxygen containing deepens and some incombustible gases, such as carbon dioxide and water vapour, all of which come from the decomposition of organic materials in coal. Inorganic materials in coal contribute the water of hydration of mineral matter, carbon dioxide from carbonates and hydrogen chloride from inorganic chlorides to the volatile matter.

Experimental Procedure:

For determining the volatile matter a special volatile matter silica crucible (38 mm height, 25 mm external diameter and 22 mm internal diameter) was used. First the empty silica crucible along with the lid uncovered was heated at 800 $\rm{^0C}$ for an hour in the muffle furnace and then cooled to room temperature. The empty volatile matter crucible was then weighed again.

Approximately 1g of coal sample was weighed in the volatile matter crucible and it was placed inside the muffle furnace maintained at 925 $\mathrm{^0C}$ with the lid covering the crucible. The heating was carried out exactly for 7 minutes, after which the crucible was removed, cooled in air and then in a desiccator and weighed again.

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

Where,

 $X =$ Mass of empty crucible and lid (g).

 $Y =$ Mass of crucible plus lid and sample before heating (g).

 $Z =$ Mass of crucible plus lid and sample after heating (g).

3.2.1.3 Ash

The coal ash is the residue left after the combustion of coal under defined conditions. It does not occur as such in the coal, but is formed as the result of chemical changes that take place in the mineral matter. Ash and mineral matter of coal are therefore not identical. The extraneous and inherent mineral matters are the two types of ash forming materials in coal. The extraneous mineral matter consists of materials like calcium, magnesium and ferrous carbonates, pyrite, marcasite, clays, shales, sand and gypsum. The extraneous mineral matter owes its origin to i) The substances which got linked with the decaying vegetable material during its transition to coal, which is difficult to remove by mechanical methods, and ii) Rocks and dirt getting mixed up during mining and handling of coal. The representation of inherent mineral matter the inorganic elements combined with organic components of coal. The origin of such materials is likely the plant materials from which the coal is formed. Ash from inherent mineral matter is unimportant as far as the total quantity of ash is pertained. But Indian coals suffer from the major disadvantage, that the mineral matter content is not only high, but of intimately associated type, due to its drift origin. The several changes that occur, such as loss of water from silicate minerals, loss of carbon dioxide from carbonate minerals, oxidation of iron pyrite to iron oxide, and fixation of oxides of sulphur by bases such as calcium and magnesium. Because ash is quantitatively and qualitatively different from the mineral matter originally present in coal. In fact, incineration conditions determine the extent to which the weight change takes place and it is essential that standardized operations should be closely followed to ensure reproducibility.

Experimental Procedure:

Weight of the empty crucible is taken. 1g of desired coal sample is weighed in the crucible and is taken in a muffle furnace at 450° C for 30 minutes and the temperature of the furnace is raised to 850° C for 60 minutes. After that time interval, the crucible is taken out and placed in a desiccator and weighed.

% Ash = $100 * (Z - X)$ / (Y – X)

Where,

 $X =$ Mass of crucible (g). $Y =$ Mass of crucible and sample (g). $Z =$ Mass of crucible and ash (g).

3.2.1.4 Fixed Carbon

Fixed carbon of coal is calculated using the following formula:

 $FC = 100 - (M + V + A)$

Where,

 $M = M$ oisture content (%) $V =$ Volatile matter content $(\%)$ $A = Ash content (%)$

3.2.3 CALORIFIC VALUE (IS 1350-1959)

The calorific value of coal is the amount of potential energy in coal that can be changed into actual heating ability. The value can be estimated and compared with different grades of coal or even other materials.

Materials of different grades will produce differing quantities of heat for a given mass. The calorific value of coal is commonly determined by the bomb calorimeter method. This apparatus consists of a cylindrical chamber known as bomb and it is made up of stainless steel. This chamber is equipped with an air tight cover which can be screwed on the chamber. There are three terminals; two for sparking and one for the entry of oxygen. After forcing the oxygen into the chamber the enactment can be blocked by screwing in the third terminal.

On the other side of the cover, there are two bent rods connected to two ends. The bent rods have small holes through which two fuse wires are connected. There is the provision for putting the crucible containing the pellet tied to the fuse wire by means of a cotton thread. This whole set-up is placed in a bigger vessel holding a quantity of water in it. A stirrer is used for stirring the water in the bigger vessel.

Fig. 3.2 Bomb Calorimeter [23]

Experimental Procedure:

1g of air dried coal sample is taken by weighing in a balance of - 212 micron (-72 mesh BSS). A pellet is made with the coal and weighed. The calorimeter cover is taken and about 10 ml/min of distilled water is poured into it. The pellet in the crucible is brought in contact with the fuse wire by means of a thread. The cover is then tightened. Oxygen is then admitted into the calorimeter at a pressure of about 300 - 400 psi atmospheres. Then 2L of water is put into the bigger vessel. Necessary electrical connections are made and stirrer is adjusted in the adjusted position. The

stirring is done softly for 5 minutes. The initial temperature reading is then taken. A sparking and combustion of coal has taken place in the calorimeter after the fire of bomb. The maximum reached temperature is then noticed. The bomb is removed and the pressure exhausted. The bomb internal is examined for unburnt or sooty deposits. If such material is found, then the test is discarded.

The calorific value of coal is calculated by:

Calorific value = $(T_2 - T_1)$ * Water equivalent / Weight of the pellet

Where,

 T_1 – Initial temperature

 T_2 – Final temperature

The following formula designed by CFRI (Central Fuel Research Institute):

If $M < 2\%$ then Useful heat value (UHV) = 91.7F + 75.6 (V-0.1A) - 60M

If $M > 2\%$ then Useful heat value (UHV) = 85.6[100-(1.1A+M)-60M]

Where,

F=Fixed Carbon V=Volatile Matter A=Ash

M=Moisture

Grade	Useful Heat Value (UHV)	Ash% + Moisture % $(60\% \text{ RH} \& 40^0 \text{ C})$	Gross Calorific Value (GCV) (at 5% moisture level)
A	Exceeding 6200	Not exceeding 19.5	Exceeding 6454
B	Exceeding 5600 but		Exceeding 6049 but not
	not exceeding 6200	19.6 to 23.8	exceeding 6454
C	Exceeding 4940 but		Exceeding 5597 but not
	not exceeding 5600	23.9 to 28.6	exceeding. 6049
D	Exceeding 4200 but		Exceeding 5089 but not
	not exceeding 4940	28.7 to 34.0	Exceeding 5597
E	Exceeding 3360 but		Exceeding 4324 but not
	not exceeding 4200	34.1 to 40.0	exceeding 5089
$\mathbf F$	Exceeding 2400 but		Exceeding 3865 but not
	not exceeding 3360	40.1 to 47.0	exceeding. 4324
G	Exceeding 1300 but		Exceeding 3113 but not
	not exceeding 2400	47.1 to 55.0	exceeding 3865

Table 3.1 Grading of non-coking coal (IS 1350 - 1959)

Table 3.2 Grading of Coking Coal (IS 1350 - 1959)

Plate 3.1 Bomb Calorimeter

3.2.3 WASHABILITY CHARACTERISTIC (IS-436-Part l/Set 1-1964)

The raw coal contains impurities after its primary sizing operations. It contains the minerals matter with which it was associated underground and some other materials getting mined up during handling. But these should not be operation by which coal is cleaned is known as coal cleaning. The properties which are used in coal cleaning are specific gravity, shape and size of the particles, friction, resilience, surface tension etc. Cleaning process generally depends upon differences in density between clean coal and its impurities. They suitably remove the free dirt but not the inherent dirt. The extent of removal of free dirt on the amenability of a coal to improvement in quality is more commonly known as the "washability" of coal and is more commonly indicated by the "float and sink" analysis of coal. These washability investigations are conducted before average proposal for installation of a coal washery is considered.

Experimental Procedure:

A coal sample of $(-2+1)$ mm size is taken and of which 100 g is weighed. Liquids of different specific gravity varying from 1.3 to 1.8 are prepared using $CCI₄$, benzene and water in different concentrations. The liquids are taken in fuel jars and arranged in the order of increasing specific gravities (1.3, 1.4 … and so on). The sample is first placed in the lowest specific gravity liquid. The fraction higher than the liquid floats and heavier ore sinks. The portion which floats on a particular specific gravity and the portion which sinks is known as sink fraction. Then the sink is placed in next higher specific gravity and the float and sinks fractions separated. In this way, the float and sink fractions of different specific gravities are collected and weighed, taking care that no coal particles are lost. Determination of the ash content of coal the float and sink fractions are carried out and the results are tabulated. The washability curves are plotted taking total floats vs. ash, total sinks vs. ash and the washability characteristic curves on instantaneous ash curve. Three curves are drawn. These are

- Total floats Ash curve,
- Total Sinks Ash curve
- Washability Characteristic curve or Instantaneous Ash curve.

Fig. 3.3 Washability Curve (Mishra,2009)

The representation of the above said curves are as follows :

Curve 1 - Total floats – Ash curve

Curve 2 - Total Sinks – Ash curve

Curve 3 - Instantaneous Ash curve

The advantage of drawing all the curves on a common diagram are that all the essential information required for studying the cleaning possibilities of a coal can be readily obtained by cross projections. For example, if one is interested to recover 15% ash clean coal, he has to read first from the total floats curve the percent yield of cleans corresponding to 15% ash. Then from this yield point, a horizontal line is drawn to cut the total sinks-ash curve, the ash content of the sinks is read from the ash-axis below and at the cut point of the yield- gravity cut, the required density of separation is read from the gravity axis above.

Interpretations from Graphs

- From curves 1 & 2 we can directly find out the yield and ash of the clean product & the heavy waste at a certain specific gravity of washing.
- $\cdot \cdot$ If we want to know the specific gravity at which cleaning should be done to have maximum yield of clean coal within a certain upper limit of ash value, then Curve -1 is consulted.
- Curve 3 shows how far it is possible to separate the dirt's from the clean coal by mechanical methods.
- For easily washable coal Curve 3 should have a sharp bend.

In a very difficult coal the above is a straight line. The specific gravity at which a coal is to be cleaned is determined from the washability data and economic considerations. The ease of washing at this specific gravity may be judged from the amount of near gravity material (ngm) present in the coal. The amount of this material is defined as the percentage of the coal that will float in a range within plus minus 0.10 specific gravity of the separation value. The presence of ngm causes misplacements of sinks in floats and floats in sinks. The larger the amount of ngm, the more difficult the cleaning operation, and vice versa. The following table shows the estimate of coal washing problem from the amount of near-gravity material.

Table 3.3 Estimation of coal washing problem from the amount of near-gravity material (ngm) (Mishra, 2009)

The following formulae were used for calculation of the yield of total sinks, ash of total sinks and cumulative yield up to the middle of fraction (CMF) for all the samples:

Yield of total sinks $= 100 -$ yield of total floats

Ash of total sinks $= {100[*] coal ash - total floats [*] ash of total floats } / Total sinks$

CMF percent of fraction = Total floats up to fraction $(F - 1) + \frac{1}{2}$ (Yield of fraction, F)

3.3 METHODS FOR DETERMINING SPONTANEOUS HEATING SUSCPETIBILITY OF COAL

3.3.1 FLAMABILITY TEMPERATURE (Nimaje et al., 2010)

Flammability of explosiveness of the coal dust is defined as its ability. To determine the efficiency of coal dusting, it is essential to carry out the flammability test of coal dust with the help of flammability apparatus. For the finding of the flammability temperature of coal consists of vertical tubular furnace of internal diameter 50 mm, length 300 mm, open at both ends, a dust dispersing unit, a solenoid valve a reservoir for air, a mercury manometer, a drying tower and an aspirator bulb. Coal dust sample is kept in the helical dust disperser. Air from the reservoir is made to pass through the disperser and on emergency from the divergent mount, forms a uniform dust-air mixture inside the furnace. The lowest temperature at which this mixture catches fire, which is indicated by the appearance of flame coming out of the bottom of the tubular furnace is the flammability temperature of the coal dust.

Experimental Procedure:

- 200 mg sample of coal having mesh size -72 micron (-200 mesh BSS) placed in a helical tube.
- By aspirator bulb and turning off the tap the mercury column difference is maintained at of 8 cm.
- After switch on the solenoid valve, at desired temperature of furnace, which allows the air to pass through it very fast and find out the status of coal sample (spark, smoke or flame).
- \cdot Incase flame appears then find out the exact temperature in lower temperature range by trial and error method, if it is not appears then go for higher temperature range.

Fig. 3.4 Schematic diagram of flammability temperature (Ramlu, 2007)

3.3.2 WET OXIDATION POTENTIAL (Tarafdar et.al., 1989)

The coal molecule may be considered as consisting of two parts such as one is condensed aromatic structure, which are resistant to oxidation and other one is the aliphatic or hydro aromatic structure that are more prone to oxidation and Presence of hydroxyl group in the aromatic structure part gives a very high degree of responsiveness to coal structure and they get oxidized faster. This is the cause for low rank coals are rather easily oxidized due to the above and also due to smaller degree of contraction of aromatic structures in them. Because low rank coals carry more branch aliphatic hydro-carbons. Since the high rank coals have structure close to that of graphite, it is less liable to oxidation and the products contain more aromatics than aliphatic. Lower rank coals on oxidation method large amounts of aliphatic acids compared to higher rank coals. When coal is contributed to alkaline permanganate, oxidation takes place and the concentration of manganite ion in solution increases relative to permanganate and there will be outcome change in the potential till all the oxidation possible in coal molecule is finish.

Therefore, addition of coal to alkaline permanganate solution results in a change of potential of carbon electrode sank in the solution.

Experimental Procedure:

- The electrodes are placed in the beaker along with a magnetic stirrer such that a homogeneous mixture of coal and alkali solution is maintained.
- \div The Teflon coated fish of the magnetic stirrer is placed inside the beaker. 0.5 g of coal sample of -212 micron(-72 mesh BSS) size was mixed with 100 ml of decinormal solution of Potassium permanganate $(KMnO₄)$ in 1N potassium hydroxide (KOH) solution in a beaker and the coal sample was subjected to wet oxidation process.
- $\hat{\mathbf{v}}$ The suspension of coal-oxidant was continuously stirred by using the magnetic stirrer.

- The potential difference (EMF) was recorded between the calomel and carbon electrodes over a period of time by using a milivoltmeter (mV) till the potential difference attained a nearly constant value.
- The EMF readings are taken at 1 minute time separation up to 30 minutes or till a constant value of EMF is attained.
- The graphs among Time vs. EMF (millivolt) for all the samples are plotted

3.3.3 CROSSING POINT TEMPERATURE (Ramlu, 2007**)**

This is one of the oldest approaches for determining susceptibility towards spontaneous heating of coal. It is the temperature at which the coal temperature coincides with that of the furnace temperature or bath temperature in ${}^{0}C$. In this method, the coal sample is heated in a furnace within a reaction tube at constant rising temperature with oxygen passing through it at a predetermined rate till the coal temperature crosses the furnace temperature.

Experimental Procedure:

The setup for the determination of crossing point temperature (CPT) of coal consists of following: Vertical tubular furnace which has an internal diameter of 50 mm and a heating capacity of 3kw. The furnace is provided with a temperature controller and a printer. Glass reaction tube is of 26 mm internal diameter and 150 mm in length. The reaction tube has spiraling glass tube of 6 mm internal diameter around it which is connected to the bottom (inside) of the reaction tube for air inlet and a small out-let tube at the top acts as air/gas outlet. Flow meter and pressure flow control valves. Purifying and dehumidifying trains for air or nitrogen. A potassium hydroxide bubbler is used to remove carbon dioxide in the incoming air.

Fig. 3.6 Time vs Temperature curve for CPT (Didari et.al. 2000)

A sulphuric acid bubbler is used to remove moisture in air. A drying tower containing granular calcium chlorides is used to remove moisture from air. 4gm sample of size $-100+200$ mesh (Dp = 112 micron) was placed in the reaction tube followed by glass wool at the bottom most position and a small sieve of 200 mesh ($Dp = 72$ micron) on that. The tube is then lightly tapped a fixed number of times to achieve uniform packing density of the samples. The reaction tube is then placed in the tubular furnace and a chromel-alumel thermocouple is inserted at the center of the sample. The entrapped air and occulted gases are removed from the coal samples by passing a mild current of nitrogen through the sample for three minutes, without disturbing the packing. The furnace is switched on and simultaneously oxygen is allowed to pass through the sample, with an average rate heating of $1^{0}C$ per minute and at 80 ml/ min. the temperature of the furnace (bath) and the coal sample are recorded at every five minute interval till the temperature of coal crossed over and gone beyond the furnace temperature.

3.3.4 DIFFERENTIAL THERMAL ANALYSIS (Nimaje et al., 2010)

The rate rise of heat evolution of coal during aerial oxidation may be compared using DTA technique. DTA is a good tool to measure qualitative and quantitative heat changes of any physico-chemical transitions and can be used for comparing the spontaneous heating susceptibility of coals. DTA is thermo analytic technique, in DTA, the material under study and inert temperature difference between sample and reference. This differential temperature is

plotted against time, or against temperature (DTA curve or thermogram). In differential thermal analysis, the difference in temperature between a substance and a thermally inert reference material against temperature is recorded as the two specimens are subjected to identical temperature exchanges in a block which is heated at a linear heating rate. The record is the differential thermal or DTA curve; the temperature difference should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right. Changes in the sample can be observed relative to the inert reference by either exothermic or endothermic reaction. Thus DTA curve furnishes data on the transformations that have took place. The area under a DTA peak is enthalpy change is not involved by heart capacity of the sample. The DTA apparatus consists of a sample and reference holder, a furnace, a temperature programmer to maintain constant temperature rate and an output to monitor the test. The sample holder has two thermocouples one for coal sample and another for reference material. The sample is contained in a small crucible By the temperature programmer the temperature is made to rise at a constant rate and the temperature difference of the sample and reference is plotted against time. The plot consists of three parts – stage-I, II, III. The temperature falls down due to release of moisture during stage-I because mostly endothermic reactions take place. Stage II consists of two parts such as stage-II A and stage-II B. At the starting of stage-II A the heating tendency starts accompanied by a small amount of endothermic reactions. The point where stage-II A begins is called as the inflexion point as the thermo gram suddenly rises. In stage-II B exothermic reactions start to prevail. The beginning of stage-III is called as Transition temperature. This temperature is very significant as it is directly related to spontaneous heating tendency of coal. The lower the transition temperature the higher is the susceptibility of coal and vice versa. From stage-III onwards complete exothermic reactions placed and the temperature preserves to rise steeply.

Experimental Procedure:

- \div The furnace is lifted by controlling the switch and the crucible for sample and reference were put in position on the post so that thermocouple tips of both the sample holders were just below them
- About 10 mg of -212 micron (-72 mesh BSS) coal sample is taken in the crucible provided with the apparatus.

Plate 3.2 Experimental Set up of Differential Thermal Analysis Apparatus

- Oxidizing atmosphere was preserved by keeping the coal sample exhibited to air.
- $\hat{\cdot}$ The reference material taken is alpha alumina (Al₂O₃) and atmospheric air is taken as medium.
- $\cdot \cdot$ The DTA machine is switched on and the software is set according to required conditions viz., heating rate is maintained at 5° C/minute and the final temperature is taken as 450[°]C.
- After the heating programme was terminated, thermo gram is obtained for coal sample.
- The plots found are then analyzed for the slopes of various stages and transition temperature.

Chapter-4 RESULTS

RESULTS

4.1 ABSTRACT FOR EXPERIMENTALTECHNIQUES

4.1.1 Proximate analysis (IS 1350 part-1, 1984)

A. Determination of moisture:

- \triangleleft Amount of coal : 1 g coal
- Size of coal : -212 micron (-72 mesh BSS)
- \div Heating time : 1.5 hours at 110⁰ C

B. Determination of volatile matter:

- \triangleleft Amount of coal : 1 g of coal
- Size of coal : -212 micron (-72 mesh BSS)
- \div Heating time : 7 minutes at 925⁰ C

C. Determination of ash:

- \triangleleft Amount of coal : 1 g of coal sample
- Size of coal : 212 micron (-72 mesh BSS)
- \div Heating time : 30 minutes at 450⁰ C and 60 minutes at 850⁰ C

4.1.2 Wet Oxidation Potential Study (Tarafdar et al., 1989)

- \triangleleft Amount of coal : 0.5 g of coal sample
- Size of coal : -212 micron(-72 mesh BSS)
- System : Coal + (1 N KMnO₄ + 0.1 N KOH)= 100 ml

4.1.3 Flammability Temperature (Nimaje et al. 2010)

- Amount of coal : 200 mg of coal sample
- Size of coal : 72 micron (-200 mesh BSS)
- \triangleleft System : Coal + Air
- \triangleleft Pressure of air : 8 cm of Hg

4.1.4 DTA (Nimaje et al. 2010)

- \triangle Amount of coal : 10 mg of coal sample
- \div Size of coal : 212 micron (-72 mesh BSS)
- \triangleleft Heating rate : 5⁰ C/min
- \div Hold time: 450⁰ C
- \bullet System : coal + air

4.1.5 Calorific Value (IS 1350-Part II - 1970)

- \triangleleft Amount of coal : 1 g of coal sample
- \div Size of coal : 212 micron (-72 mesh BSS)
- pressure :- 300 400 PSI

4.1.6 Crosssing Point Temperature (Ramlu, 2007**)**

- \triangleleft Amount of coal : 4 g of coal sample
- \div Size of coal: 112 micron(-100+200 mesh BSS)
- Heating rate: 1˚C/min
- Oxygen flow rate: 80 ml/min.

4.1.7 Washability Characteristic (IS 436-Part l/Set 1– 1964)

- \triangleleft Amount of coal : 100 g of coal sample
- \div Size of coal : 2+1 mm

Sl. No.	Sample Code	Name of the Organization		
1	$MCL-1-W$			
$\overline{2}$	MCL-1-NW	Mahanadi Coalfield Limited, Odisha		
3	$MCL-2-W$			
4	MCL-2-NW			
5	BCCL-1-W			
6	BCCL-1-NW	Bharat Coking Coal Limited,		
7	BCCL-2-W	Jharkhand		
8	BCCL-2-NW			

Table 4.1 List of coal samples

Table 4.2 Results of proximate analysis parameters

Sl. No.	Coal samples	Basis	$M(\%)$	A(%)	VM $($ %)	FC(%)
$\mathbf{1}$	$MCL-1-W$	air dried	3.75	26.5	31.5	38.25
		dry		27.53	32.72	39.74
		daf	---		45.16	54.86
		dmmf			43.00	57.00
$\overline{2}$	MCL-1-NW	air dried	3.2	32.5	35.55	28.75
		dry		33.57	36.72	29.70
		daf			55.28	44.72
		dmmf	---	---	52.91	47.09
3	$MCL-2-W$	air dried	3.95	31.0	30.65	34.4
		dry		32.27	31.91	35.81
		daf			47.12	52.88
		dmmf			44.47	55.53

Calculation on different basis:

Dry Basis

$$
Ash = \frac{\%ash on air dried basis}{100 - %moisture} x 100
$$

$$
VM = \frac{\% \text{ volatile matter on air dried basis}}{100 - \% \text{moisture}} \times 100
$$

 $FC = 100 - (Ash + VM on % dry basis)$

Dry Ash Free Basis

 $VM = \frac{\% \text{ volatile matter on air dried basis}}{100 \times 100 \times 1000 \times 100$ $100 - (moisture + ash)$

 $FC = 100 - VM$ (on % daf basis)

Dry Mineral Matter Free Basis

 $VM = \frac{\% \text{ volatile matter on air dried basis - 0.1 ash on air dried basis}}{80 \times 100 \times 1000 \times$ $100 - (moisture + 1.1ash)$ on % air dried basis

 $FC = 100 - VM$ (on % dmmf basis)

Flammability Temperature

Table 4.3 Results of Crossing Point Temperature, Wet Oxidation Potential and

Table 4.4 Results of DTA – TG

Sample	Stage II A	Stage II B	Stage II	Transition temperature (T_c^oC)
$MCL-1-W$	0.075	0.151	0.0978	207.82
MCL-1-NW	0.123	0.206	0.135	193.78

$MCL-2-W$	0.096	0.231	0.136	176.06
MCL-2-NW	0.101	0.173	0.118	161.75
BCCL-1-W	0.053	0.078	0.057	219.90
BCCL-1-NW	0.061	0.140	0.084	206.68
BCCL-2-W	0.027	0.012	0.056	234.93
BCCL-2-NW	0.033	0.078	0.013	216.62

Table 4.5 Results of Float and Sink

Table 4.6 Results of Calorific Value

Chapter-5

DISCUSSION AND CONCLUSIONS

5.1 DISCUSSION

The susceptibility of coal to spontaneous combustion depends on its intrinsic properties. Therefore, the comparison have been carried out between the different susceptibility indices such as wet oxidation potential, differential thermal analysis and flammability temperature, The susceptibility indices are taken as dependent variables and each constituent obtained from the proximate and ultimate analyses as an independent variable. In general following things are to be noted from the results of all experiments:

- \div The highest moisture content was found to be in MCL-2-W which is 3.95% as the seam is watery in nature.
- \div The ash percentage of MCL-2 –NW is highest and has low FC content; hence these are high susceptibility to spontaneous heating.
- \div MCL-1-W with highest VM content which shows the highly susceptible to spontaneous heating
- \div BCCL-1-NW has the highest EMF values with 171 mV which shows that it is highly susceptible to spontaneous heating.
- \div BCCL-2-W has the lowest EMF values with 101 mV which shows that it is poorly susceptible to spontaneous heating.
- * The lowest transition temperature was found to be for MCL-2-NW showing it has highly liable to spontaneous heating.
- BCCL-2-W has highest transition temperature; hence it is less liable to spontaneous heating.
- DTA results show that MCL-2-NW is the moderately susceptible sample but the transition temperature is also high.
- BCCL-2-W is the poorly susceptible with a reasonably high transition temperature.
- The slope for Stage II A was found to be maximum for MCL-1-NW and lowest for BCCL-2-W.
- The slope for Stage II B was found to be maximum for MCL-2-W and lowest for BCCL-2-W
- MCL-1-NW has lower flammability temperature; hence it is highly susceptible to spontaneous heating.
- BCCL-2-W has high flammability temperature which shows poorly susceptible towards spontaneous heating.
- BCCL-1-NW has maximum crossing point temperature, so it is poorly susceptible to spontaneous heating.
- BCCL-2-W has minimum crossing point temperature, so it is highly susceptible to spontaneous heating
- BCCL-2-W has highest calorific value which shows less liable to spontaneous heating and BCCL-2-NW has lowest calorific value which shows highly susceptible to spontaneous heating.
- $\hat{\mathbf{v}}$ From the washability characteristics curve, we can see there is an uncertain bend in the instantaneous curve of washed coal. This shows that the coal sample is not easy-to-wash coal.

5.2 CONCLUSIONS

- Wet oxidation potential difference method is good for predicting the spontaneous heating susceptibility of low and high moisture coal.
- * The washed coal having lower ash content, low volatile matter, high moisture content as compared to the non-washed coal.
- Calorific value of washed coal is more as compared to the non-washed coal.
- Flammability temperature of washed coal is low as compared to the non-washed coal.
- \div Crossing point temperature of washed cola is less as compared to non-washed coal.
- Wet oxidation potential difference is less in washed coal..
- $\hat{\mathbf{v}}$ From the washability curve, it can be inferred that the coal sample is not easy to wash.
- \triangleleft Based on the corrected coal samples
	- 1. BCCL-2-W is highly susceptible to spontaneous heating.
	- 2. MCL-1-W, MCL-2-W and BCCL-1-W are moderately liable to spontaneous heating
	- 3. BCCL-1-NW, MCL-1-NW, BCCL-2-NW and MCL-2-NW are less liable to spontaneous heating

REFERENCES

REFERENCES

- 1. Didari, V. and Kaymakci, E., Relations between coal properties and spontaneous combustion parameters, Turkish Journal of Engineering & Environmental Sciences, vol.26, 2002; pp. 59-64.
- 2. Hatt, R., Correlating the slagging of a utility boiler with coal characteristics, Engineering Foundation Conference, Waterville Valley, New Hampshire, USA, Jul, 1995, pp.16-22.
- 3. I.S. (Indian Standard): 13810, 1993, Code of Practice for Float and Sink analysis of Coal, Bureau of Indian Standards; New Delhi, pp.3-21.
- 4. I.S. (Indian Standard): 436 (Part II) 1965, Method of sampling of coal and coke: sampling of coal, bureau of Indian Standards, New Delhi; pp. 3-12.
- 5. I.S. (Indian Standard): 1350 (Part-I) 1984, Methods of Test for Coal and Coke: Proximate Analysis, Bureau of Indian Standards, New Delhi; pp. 3-28.
- 6. I.S. (Indian Standard): 1350 (Part II) 2000, Methods of Test for Coal and Coke: Determination of Calorific Value, Bureau of Indian Standards, New Delhi, pp. 3-24.
- 7. Katzer, J., The future of coal-based power generation, Chemical Engineering Progress, 2008; pp. 83-86.
- 8. Mahadevan, V. and Ramlu, M. A., Fire risk rating of coal mines due to spontaneous heating, Journal of Mines, Metals and Fuels, Aug, 1985; pp. 357-362.
- 9. Mathur, S.P., Coal mining in India, 1st edition, M.S. publication, 1999; pp. 399-414.
- 10. Mishra A, Assessment of coal quality of some Indian coals, B.Tech. thesis, 2009; pp. 21- 23.
- 11. Nanda A, Correlation analysis of spontaneous heating of some SECL coals, B.Tech. thesis, 2010; pp. 20-23.
- 12. Nimaje, D.S. and Tripathy, D.P., Thermal studies on spontaneous heating of coal, The Indian Mining & Engineering Journal, 2010 ; pp. $10 - 21$.
- 13. Ramlu, M.A., Mine Disasters and Mine Rescue, Oxford & IBH Publishing Co. Pvt. Ltd., second edition, 2007; pp. 1-19.
- 14. Sarkar, S., Fuels and Combustion, second edition, Orient Longman Publication, 1996; pp.105-121.
- 15. Tarafdar, M.N. and Guha, D., Application of wet oxidation processes for the assessment of the spontaneous heating of coal, Fuel, Vol. 68, Mar, 1989; pp. 315-317.
- 16. Tripathy, D.P. and Pal, B.K., Spontaneous Heating susceptibility of coals evaluations based on experimental techniques, Journal of Mines, Metals and Fuels, Vol. 49, 1996; pp. 236-243.
- 17. http://www.scribd.com/doc/74694249/Coal-Benefia-Cation
- 18. http://en.wikipedia.org/wiki/Coal_preparation_plant
- 19. http://coal4india.com/Coal4India/(S(ciyyxscp53aq0dd40r3wramy))/CoalWashing.aspx
- 20. http://www.bharatbook.com/market-research-reports/infrastructure-market-researchreport/coal-washeries-in-india-a-5-billion-opportunity.html
- 21. Improving Efficiencies of Coal Fired Plants in Developing Countries, Annual Report 2002 –2003, © Copyright IEA Coal Research 2003, ISBN 92-9029-378-0, Gemini House 10-18, Putney Hill, London SW15 6AA
- 22. http://wiki.chemeddl.org/mediawiki/images/c/ce/Chapter_15_page_10.jpg

APPENDIX-1: WET OXIDATION CURVES APPENDIX-2: CROSSING POINT TEMPERATURE CURVES APPENDIX-3: DTA-TG CURVES APPENDIX-4: WASHABILITY CHARACTERISTIC CURVES

Fig: A-1 Wet oxidation curve of washery and non-washery coal samples

Fig: A-2 CPT Curve of MCL-1-W

Fig: A-3 CPT Curve of MCL-1-NW

Fig: A-4 CPT Curve of MCL-2-W

Fig: A-5 CPT Curve of MCL-2-NW

Fig: A-6 CPT Curve of BCCL-1-W

Fig: A-7 CPT Curve of BCCL-1-NW

Fig: A-8 CPT Curve of BCCL-2-W

Fig: A-9 CPT Curve of BCCL-2-NW

Fig: A-11 DTA – TG curve of MCL-1-NW

Fig: A-13 DTA – TG curve of MCL-2-NW

Fig: A-15 DTA – TG curve of BCCL-1-NW

Fig: A-17 DTA – TG curve of BCCL-2-NW

Fig: A-18 Washability curve of MCL-1-W

Fig: A-19 Washability curve of MCL-1-NW

Fig: A-20 Washability curve of MCL-2-W

Fig: A-21 Washability curve of MCL-2-NW

Fig: A-22 Washability curve of BCCL-1-W

Fig: A-23 Washability curve of BCCL-1-NW

Fig: A-24 Washability curve of BCCL-2-W

Fig: A-25 Washability curve of BCCL-2-NW
