LEACHING CHARACTERISTICS OF COAL AND COAL ASH

A Dissertation submitted
in partial fulfilment of the requirements
for the award of degree of

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in

Thermal Engineering

by

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THAPAR UNIVERSITY, PATIALA

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CERTIFICATE

I hereby declare that the thesis entitled "**Leaching Characteristics of coal and coal ash**" is an authentic record of my work carried out as requirements for the award of the degree of Master of Engineering in Thermal Engineering at Thapar University, Patiala, Punjab under the supervision of **Dr. Satish Kumar**, Assistant Professor, Mechanical Department, Thapar University, Patiala during July, 2014 to July, 2016. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

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Date: 12/07/2016

It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

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Dedication

I dedicate this thesis to my beloved father S. Nanak Singh and my mother Rajinder Kaur, who are an ever supporting and encouraging with their great patience. I also dedicate this to my senior Mani Kanwar Singh, who is as an impression for me and to all my dearest friends.

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(JATINDER PAL SINGH)

Abstract

Coal is a major source of energy. Power generation in India is primarily coal based in the present scenario. About 70% electricity generation produced by combustion of pulverized coal in thermal power plants. The available Indian coal quality is very poor, generate the large quantities of ash produced as by-products of combustion. The objective of present study was to reduce the ash content and to produce ultra-clean coal. The coal was treated with dual chemical treatment of NaOH followed by HCl. The effect of particle size, temperature, shaking speed, reaction time and concentration on ash content were studied and found to be significant. During the experiments, concentration of NaOH was varied from 10 to 40% (by volume) with fixed concentration of HCl (10%). Effect of shaking speed and time was analysed at 0, 50, 100, 150 and 200 rpm and 1, 2, 3 and 4 hours respectively. After chemical leaching, the ash content was reduced from 35.33 to 0.98% in the ultra-clean coal. The concentration of alkali, shaking speed and time of duration was found as highly influencing parameter for reduction of ash content in the coal. Experimental influence parameters were optimized using Taguchi method. The result indicates that the temperature contribute the most dominants factor followed by acid concentration and particle size. According optimum condition was obtained as, particle size range 75-106µm, temperature 70˚C and concentration of NaOH 40 % respectively. After chemical leaching, the ash content was reduced from 35.33 to 0.65% in the ultra-clean coal. Moreover, the current study should result better option for removal of ash content from low rank Indian coals.

Key words: Coal, chemical treatment, ash content, ultra-clean coal, low grade coal

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Chapter 1

Introduction

1.1 Introduction

Coal is most extensively used fuel all over the world, around 860 billion tons of coal reserves are found all over the world. In India, coal reserves are around 286 billion tons, which includes 85% of non-coking coals, nearly 14% of coking coals are found in eastern areas of India. The coking coal is the necessity to run iron and steel industry, as it is used in a muffle furnace. Coal is also used in thermal power stations for the production of electricity. Coal is used as a source of energy in many processes like gasification, production of coal tar, coke etc. Coal reserves are found in almost every country. India, Russia, The United States and China have the largest coal reserves. According to the data provided by the world association of coal around 70% of the steel industry of the world is dependent on the coal, 40% of the electricity generated in the world takes place from coal.

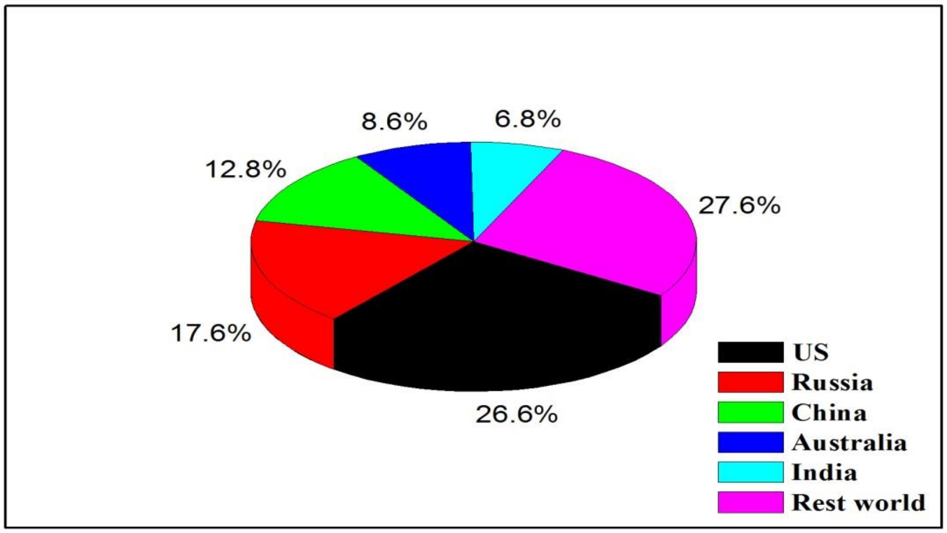

Figure 1.1: Global share of Coal reserves

Coal reserves are available around three times more than the oil and gas, so nuclear and coal are used as major source in the generation of power worldwide. From the report of world energy 2015, it has been seen that The United states of America have 26.6% of the total coal reserves share in the world, which turn out to be maximum. After US, Russia, China, Australia and India have 17.6%, 12.8%, 8.6% and 6.8% of global coal reserves respectively.

1.2 Indian Coal

Coals found in India are generally inferior quality. They carry large amounts of ash with them generally of 40 – 48 % in range. Thus the high amount of waste in the form of ash is generated after combustion of coal in thermal power stations, which create negative effect on water and air by polluting them. Presently, 170 million tons per of solid waste in the form of coal-ash is produced in India from thermal power plants. It is expected that during 12th and 13th Plans, more than 1, 00,000 MW power capacity is probable to be added which would result in an increase in ash production from power plants by twice by the year 2022. Coal is used as a major source of energy in India. According to the data received from Indian Energy Outlook, 2015. 60% of the total energy produced in India is generated with the help of coal. After coal the hydro energy is the major source of power generation in India. Oil, gas, nuclear, wind and solar has very low percentage in power generation.

Ash generated in the power plants is mixed with water and slurry is formed. This slurry is pimped to the ash ponds with the help of big pumps. Sometimes, ash ponds are overflowed and pollute nearby water bodies. The disposal of ash by using these methods not only pollute air and water but also requires a huge land area for proper disposal. However, after the restrictions applied by CREP in 2003, power plants are not able to dispose off the ash in a slurry pond after being overflown. The water from the ash pond have to be recycled and used in various purposes in power plant.

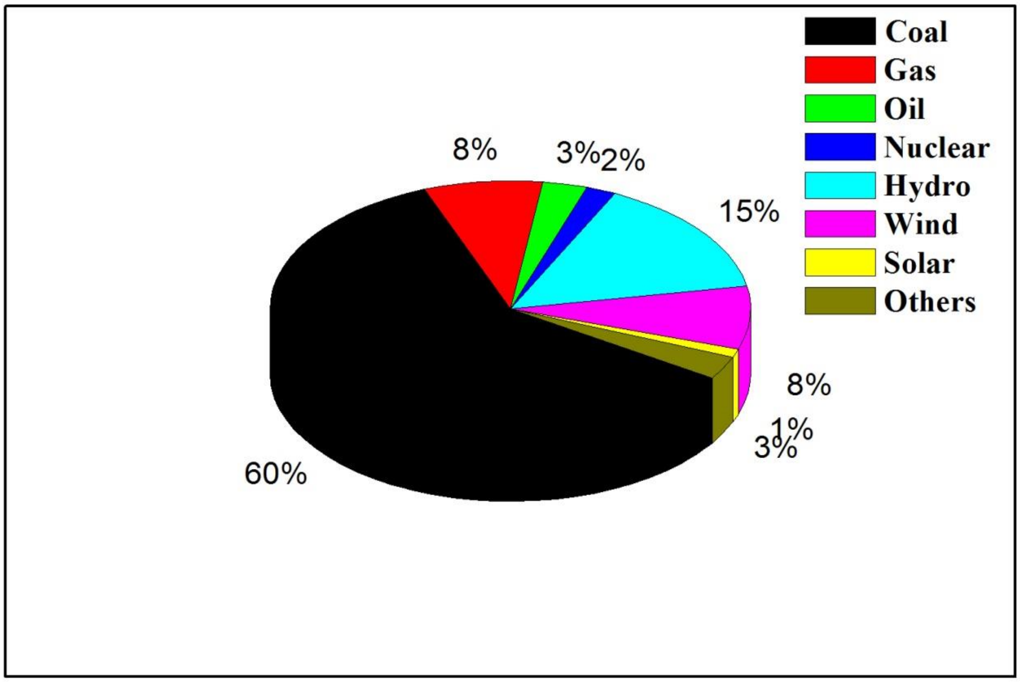

Figure 1.2: Fuel wise power generation in India

Indian coals are broadly classified into two categories on the basis of age of formation, namely Gondwana coal and tertiary coal. The Gondwana coal is the old coal and found in the catchment areas of Damodar, Wardha and Godavari rivers. This coal is very old and found in plenty. Around 90% of coal reserves found in India are of Gondwana coal. This coal is of superior quality, mainly bituminous type of coal is found in these reserves. Mainly lignite and subbituminous type of coal is found in the Tertiary coal reserves. This coal is not too much matured. These coals have high moisture content and low carbon in them.

Table 1.1: Coal reserves in India

Formation	**Proved**	**Indicated**	**Inferred**	**Total**
Gondwana Coals	125313	142405	32340	300372
Tertiary Coals	584	94	790	1430
Total	125897	142499	33130	301802

Table 1.2: State wise coal reserves in India

State	Proved	Indicated	Inferred	Total
West Bengal	13233	13103	4853	31189
Jharkhand	42577	32580	6549	80706
Bihar	0	0	150	150
Madhya Pardesh	10511	12182	2779	25472
Chhattisgarh	16352	33153	3128	52633
Uttar Pardesh	874	168	0	1042
Maharashtra	5467	3156	2140	10763
Odisha	27691	37673	9428	74792
Andhra Pradesh	9629	9570	3468	22667
Assam	445	45	3	493
Sikkim	0	56	44	100
Arunachal Pradesh	33	45	15	93
Meghalaya	85	15	461	561
Nagaland	8	0	317	325
Total	126905	141746	33335	301564

1.3 Classification of coal

1.3.1 Anthracite Coal

These coals are more superior and graded highest as compared to other types of coal all coals. Anthracite coal is very much matured and have a metallic type of luster on it. True anthracite was not found in India. Some coal samples found in

West Bengal and Jammu Kashmir have properties closer to anthracite. These coals have a high carbon content around 90% and low moisture content in them.

1.3.2 Bituminous Coal

These types of coal are widely used and most commonly found all over the world. The bituminous coal is generally black in colour. These coals are hard and dense as compared to lignite. In India these coals are generally found in Rajmahal and Raniganj areas of West Bengal, Jharkhand, Orissa etc. around 80% of the carbon content is found in these type of coals.

1.3.3 Lignite Coal

These coals are formed in the second stage of coal formation process. Lignite coals are brown in colour, generally also called brown coal. Wax, residual mass and humic acid are the main constituents of Lignite. These coals have very low carbon content in then normally between 30-40%.

1.3.4 Peat

Peat is formed at the first stage during coal formation process. These coals are mainly consist of waxes, lignin, resins, pectin, humic acid etc. these are not suitable for production of energy at high scale because of having a very low carbon content in them.

1.4 Generation of ash in power plants from coal

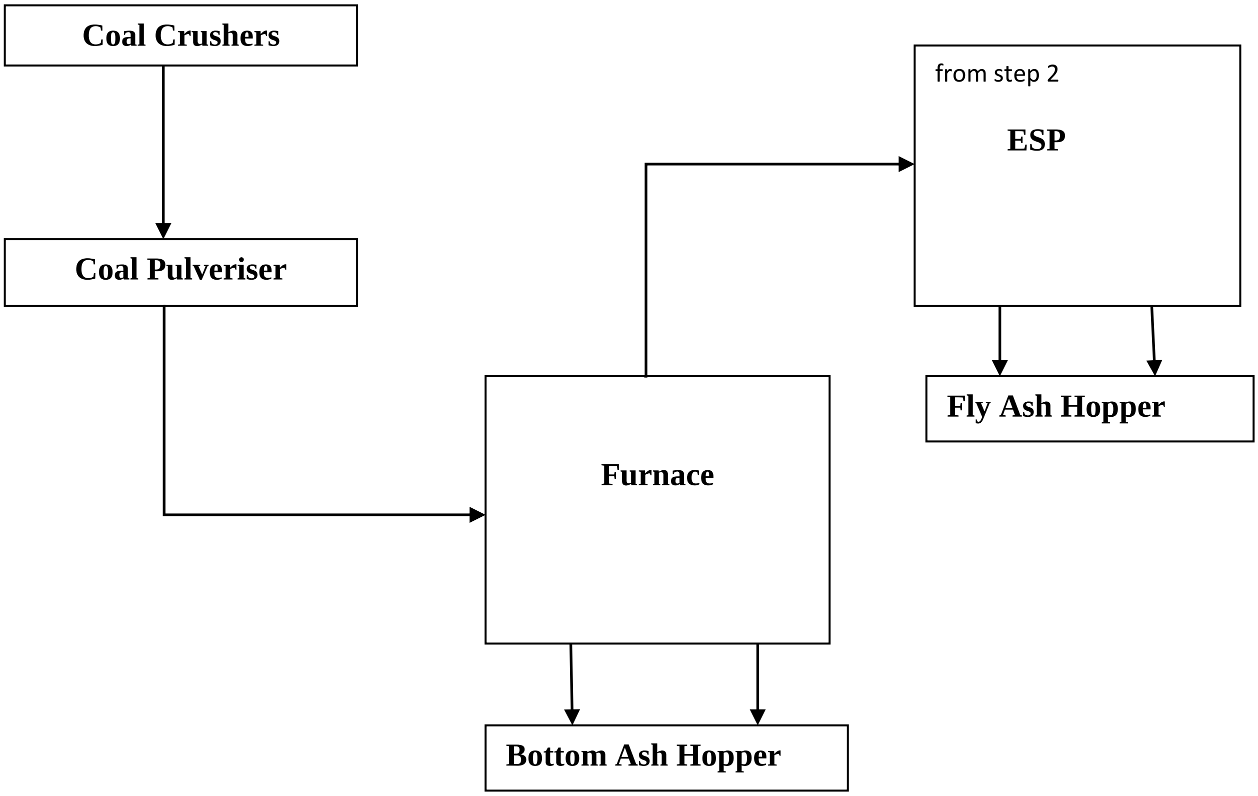

Figure 1.3: Fly ash generation in power plants

1.5 Types of coal ash

1.5.1 Fly Ash

Fly ash is the main solid waste left after combustion of coal in the thermal power stations. After the combustion of coal approximately 80% byproduct left is fly ash. The fly ash is a fine, light gray powder. It is collected from the ESP. It consists of oxides of aluminum, ferrous, Ca, Ti, Mg and many trace elements.

1.5.2 Bottom Ash

Coal when extract out from the coal mines may carry some non- combustible matter like stones with it. This incombustible matter is 10-15% of total solid waste generated in power station. The bottom ash is dark gray coarse sand. During coal combustion, traces of combustibles stick to walls of the furnace. These clinkers fall into the hopper fitted at the bottom of the furnace. This solid waste is known as bottom ash.

1.5.3 Pond Ash

The ash is collected from the ESP hopper and Bottom ash hopper. The slurry of both the ashes is made with water and pumped to ash pound. When ash pond was fully filled excess water is poured out to nearby water bodies and solid material which settle down is called pond ash.

1.6 Compostion of coal ash

Silica, Alumina and oxides of calcium, iron etc are generally found in ash but, silica and alumina are the major constituents. Ash includes all type of common elements in it as well as toxic also. The percentage of radioactive elements in ash is far higher than found naturally in any soil or rock. The carbon which is left unburnt gave ash black colour.

1.7 Utilization of fly ash

a. Used in cement industries
b. Provide strength to concrete
c. Used as a herbicide
d. Used in landfills

1.8 Utilization of bottom ash

a. Used in cement industry for clinker production.
b. Used in road construction and in cement kilns (clinker production).
c. In dry form mixed with concrete.
d. Used in landfills.

1.9 Health impact of coal ash

Ash is the solid waste in the form of power generated after the burning of coal in the electricity power generators. This powder form solid waste contains many harmful elements like Pb, Hg, Cr and Silica etc. These elements when come in the contact with water bodies and ground water ca left over after coal is burned to generate power, contains concentrated amounts of heavy cause serious effects on humans and animals.

Regardless of this hazard, Coal ash is mixed with water to form slurry and stored in pounds which are called “coal ash ponds” or “lagoons”. There is no provision of protective lining around the pound to prevent the seepage of heavy metals to the water bodies and ground water. These slurry ponds are generally located near the water bodies like rivers, lakes, ponds etc. because power plants need a large amount of water to run. The heavy metals from these ponds leached from ash and pollute the water bodies which we are used for drinking, bathing, washing and agriculture purpose. The harmful effects of the various heavy metals found in ash samples for human health are mentioned in the table 1.3. The permissible limits as per IS:10500(2009) and WHO limits for drinking water quality is listed in the Tables 1.4, 1.5,1.6. The general parameters related to the undesirable substances in the acceptable limit are mentioned in Table 1.4. Table 1.5 and 1.6 represent the parameters of toxic substances and radioactive substances of fly and bottom ash respectively.

Table 1.3: Harmful Effects of Heavy Metals on Human Health

Elements	**Known Risks**	**Organs affected**
Mercury	Mercury can reduce development in IQ of children. It can also cause serious effects on the nervous system.	Brain
Chromium	The consumption of Cr leads to stomach cancer, ulcers in intestines, anemia. Moreover, cancer in lungs and even cause asthma.	Lungs and Intestines.
Selenium	With the excessive intake of selenium failure of neurological system takes place. Sometime it can cause impaired vision and even death.	Spine and nervous

Lead	Ingestion of the leads to swelling in brain, failure of kidney, damage in nervous system. The lead also cause cancer in the intestines, its high concentration in water leads to death also.	Brain, Heart, Intestines and kidneys
Arsenic	Consumption of arsenic leads to damage of nervous system and cancer in the urinary tract. Inhale or absorption of Arsenic through skin leads to cancer in lungs and skin.	Lungs and brain
Boron	Injection of boron in excess amount leads to irritation in nose, eyes, throat etc. consumption in large amounts results in failure of brain, kidney, liver and even cause death.	Kidneys and liver

Table 1.4: Parameters Concerning Substances Undesirable in Excessive Amounts

S.no	Metals (mg/l)	Requirement(Acceptable limit)
1	Aluminum	0.03
2	Ammonia	0.5
3	Barium	0.7
4	Boron	0.5
5	Calcium	75
6	Chloride	250
7	Fluoride	1
8	Iron	0.3
9	Magnesium	30
10	Manganese	0.1
11	Selenium	0.01
12	Silver	0.1
13	Sulphate	200
14	Zinc	5

Table 1.5: Parameters Concerning Radioactive Substances

S.no	Characteristic(Bq/l)	Requirement(Acceptable limit)
1	Alpha emitters	0.1
2	Beta emitters	1.0

Table 1.6: Parameters Concerning Toxic Substances

S.no	Metals (mg/l)	Requirement(Acceptable limit)
1	Cadmium	0.003
2	Cyanide	0.05
3	Lead	0.01
4	Mercury	0.001
5	Molybdenum	0.07
6	Nickel	0.02
7	Arsenic	0.01
8	Chromium	0.05

1.10 Coal preparation and washing

Coal obtained from the mines was passed through series of test so that it can achieve desired standards. The impacts on the environment after and before burning were also investigated. Proximate and ultimate analysis of coal was done to check the ash content in the coal. Washing and other cleaning techniques are applied in the run of mine coal, which has a high ash content in it. The mineral matter in the coal is responsible for the amount of ash generation. This mineral matter is of two types organic and inorganic. The inorganic matter is removed by physical washing techniques, but organic matter was chemically bonded with the coal constituents, it is very difficult for this type of impurities from coal. If the coal is not cleaned before use it causes many impacts on environment, health and even failure of ash handling unit in thermal power plant. Coal cleaning before use very necessary in case of low rank coals which left a large amount of ash after burning. Coal cleaning reduces the amount of ash after burning which results in less solid waste, small ash handling units and leaching of heavy metals from ash ponds to nearby water bodies decreased. The calorific value of coal increased, the transportation cost is also decreased. Air pollution is reduced, increase in the efficiency of boilers.

1.11 Physical coal beneficiation

In physical cleaning techniques the coal is cleaned by different techniques like magnetic separation, oil agglomeration, froth flotation etc. the separation of impurities can take place due to different properties of coal like specific gravity, density etc. the coal beneficiation leads to decrease in ash, sulfur and many other inorganic matter which is mixed with coal on the time of mining like stones etc. some of the physical cleaning techniques are discussed below.

1.11.1 Types of Physical coal beneficiation methods

a. Pneumatic table

Coal is fed on the perforated deck inclined transversely and reciprocating motion was given to it. Coal in the form of small stream fed from the top of the deck. Coal gets spread on the deck and clean coal is collected from the bottom side of the deck under the effect of reciprocating motion and air flow. The impurities are generally of heavy weight. They struck in the riffles and collected at the end of the deck.

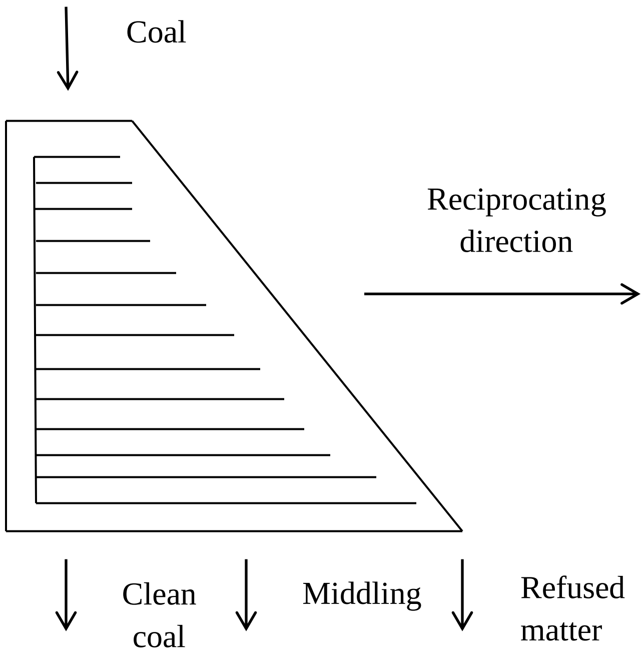

Figure 1.4: Pneumatic coal cleaning

b. Gravity separation

In this method the mineral matter is separated from coal by the means of specific gravity. This method is widely used in coal preparation. This method is used for cleaning the coal which was coarser. Jig washing, centrifuge cleaning techniques are working on this principle.

c. Froth flotation

In this process the impurities are removed by the difference in surface properties of coal. The coal is mixed with water as we know coal is hydrophobic in nature it does not dissolve in water. The impurities in the coal are settled down and get separated. The equipment requires less space and low capital cost. The high yield was obtained, but this process leads to use high amount of water.

d. Oil agglomeration

In this method separation of inorganic and organic matter takes place due to differences in the surface properties. In this method very fine coal particle is used. Coal particles are hydrophobic in nature, they get agglomerate in the oil, but mineral particles were remain unaffected and are separated from coal.

e. Magnetic separation

In this method the separation of ash producing mineral matter is removed due to differences in the magnetic properties of coal and impurities associated with it. The magnetic separation can done by both ways dry and wet. The Strong magnetic field should be needed to apply. Coal is not sensitive to magnetic field, so this method is useful for coal cleaning.

1.12 Bio-processing

This is the latest technology for the cleaning of coal. The main purpose of this method of cleaning is to remove trace elements from coal and reduce sulfur from it. This method usually requires low capital as well as operating cost. The coal is cleaned by microbial treatment at very small scale and also be commercialized. This method insures a high degree of desulfurization and removal of pyrite from coal by lowering down the wastage.

1.13 Chemical coal beneficiation

In chemical coal, beneficiation technique coal samples are treated with chemicals so as to remove the organic matter from the coal, which is bounded chemically. The mineral matter bounded chemically is difficult to remove from coal by using physical coal beneficiation techniques. Low degree of demineralization is obtained by using physical washing methods. Physical beneficiation technique is suitable to remove pyritic sulfur associated with coal. There are three types of chemical leaching techniques adopted by many researchers in their study. Acid cleaning, alkali cleaning and acid followed by alkali cleaning.

1.13.1 Types of chemical coal beneficiation methods

a. Acid Cleaning

The use of acid directly in the treatment of coal is a powerful technique to remove mineral matter from coal. The leaching behavior of coal under the action of acid is noticed by many researchers. Commonly used acids are HF, HCl, H_2SO_4, HNO_3, Fe_2 (NO) $_3$ etc. HF and HNO_3 both are also used in many research papers for the production of high rank coal. A Combination of many other acids used by many researchers gave positive results in the removal of ash, sulfur and other heavy metals from the low rank coal.

b. Alkali cleaning

The effect of alkali treatment on the leaching behavior of coal is investigated by many researcher. By treating the low rank coal with alkaline chemicals such as NaOH, $Ca(OH)_2$ etc. NaOH is chosen by many researchers in their study, decrease in the ash content was noticed in all studies. Na_2CO_3 is also used now a day on the place of NaOH, Na_2CO_3 is cheaper and gave good response on the amount of ash and sulphur removal from coal.

c. Acid and Alkali cleaning of coal

Two stage cleaning of the coal is very effective for the removal of mineral matter from the coal. Alkali leaching agents like NaOH and KOH are used. These convert the alumina and silica type ash constituents to alumina silicate. NaOH followed by HCl leaching is widely used technique for effective removal of ash, pyritic sulfur and organic sulfur by using this combination no effect on calorific value of the fuel is noticed in any research.

Chapter 2

Literature Review

Various studies on the leaching behavior of coal, heavy metals from bottom ash and fly ash were carried out by many researchers in past. Chapter reviews the previous published literatures, which lays the foundation and basics for further work in this report

- **Sharma et al. (1991)** studied the effect of alkali and acid on leaching characteristics of coal at atmospheric pressure. They collected coal samples from Indraprastha and National Thermal power plant of Delhi. 5gram of the sample was mixed with 100ml aqueous solution of NaOH and mechanically stirred for 1.5 hour. The coal samples were treated with 5%-40% concentrated aqueous NaOH solution. The NaOH treated coal was filtered with filter paper and washed again with 10% H_2SO_4. They observed 75% decrease in ash content after the treatment.

- **Bolt et al. (1998)** studied the effect of leaching behaviour on low rank bituminous Turkey coal. 5 grams of coal sample was mixed in 80ml aqueous solution of different chemicals HCl, HF, H_2SO_4, NaOH and HNO_3 and shake for 20 minutes. The coal samples were than filtered and washed with distilled water. The coal sample which was treated with NaOH was washed with aqueous solution of HCl, HNO_3 and H_2SO_4. They observed that the sample which was treated with HF shows 87.53% of reduction in mineral content, which is highest in all the samples. Also coal sample treated with alkali and washed 10%, 20% and 30% of HCl, HNO_3 and H_2SO_4, shows maximum degree of demineralization in the case of 30% HCl. They concluded that by using 10% HCl with NaOH gives maximum amount if ash reduction content from coal, use of HCl alone in coal cleaning process may give good results.

- **Querol et al. (2000)** investigated the mobility of water soluble elements on Spanish ash samples at room temp called open leaching and at 90^0C called closed leaching. Open leaching was done by column leaching technique and for closed leaching distilled water at 90^0C is mixed with ash samples and mixture was stirred for 24 hours in a reactor. They observed that movement of heavy metals is decreased by inducing lime. Major and trace elements are determined by plasma mass spectrometry. They found that pH and thermal conductivity of mixtures first increase and then decrease after reaching a break point. They also reported that the mobility of Al is 10 times higher in open system as compared to closed system. The concentration of silicon and vanadium in leaching system is doubled in open system as compared to closed.

- **Mukherjee et al. (2001)** studied the effect on demineralization of high sulphur coal by chemical cleaning method. They collected coal samples from Makum coal fields, Assam they mixed 212µm coal with different concentrations of sodium hydroxide with coal to solution ratio of 1:5 (g/ml). Coal samples were stirred with stirrer having 90-95˚C temperature for 8 hours. The alkali leached samples were filtered and washed with distilled water, later on treated with 10% HCl. The observed decrease in ash content in coal samples whether they were treated with alkali or alkali followed by acid. Also the rate of decrease in ash content was increased with the increase of alkali concentration but this decrease was less as compared to the same alkali sample which was leached with acid also. Two stage alkali followed by acid leaching technique was effective technique for ash as well as sulphur removal. 43-50% of ash, complete deduction of inorganic and 10% of organic sulphur was detected by them.

- **Balaz et al. (2001)** investigated the effect of alkali on leaching behaviour of coal by GACL technique. They grounded coal to 500µm and mixed with 5% aqueous NaOH solution with solid to liquid ratio of 1:10 and stirred with help of stirrer at 90˚C temperature for 30-120 minutes. NaOH treated sample was filtered and later on washed with 100ml solution having 0.1M HCl concentration for 6 hours. The acid treated samples were filtered in the vacuum for 6 hours at 105˚C temperature. They concluded that use of GACL technique was effective in coal cleaning process. They observed decrease in the sulphur content from 3% to 1.5%. Nearly 96% of decrease in arsenic was noticed by using above technique.

- **Mukherjee et al. (2003)** studied the effect alkali and acid on leaching behavior of coal. They took two samples from Boragolai and Makum coal field of Assam. They treated both samples with KOH at different concentrations of 2%-16%. KOH samples were again stirred with 10% HCl solution for 8 hours at 95ºC and 150ºC. The gradual decrease in ash and sulfur was observed by them in both samples. The decrease of 19% and 45% in ash content was noticed in Boragalai and Makum coal sample respectively. Also 35% decrease in sulfur was observed in both coal samples. They concluded that with an increase in temperature and concentration rate of demineralization and desulphurization was increased. They reported 100% reduction of inorganic and decrease in organic sulfur by cleaning with KOH and HCl.

- **Batra et al. (2006)** investigated the leaching characteristics of ash collected from different power stations of India. They used “Flame Atomic Absorption Spectrometry”. They analysed the presence of Cromium, lead, Zinc, copper and cobalt. They found that the concentration of heavy metals is higher in fly ash than that of bottom. Cromium and Zinc is found more in flyn ash and concentration of manganese is higher in bottom ash. This is due to the fact that elements with lesser mass are carried away with fly ash and higher mass elements can settle down quickly after the combustion. Wet disposal technique using ash pond without lining make more mobility of heavy metals to mix in water bodies. The storage of ash in dry form as compared to wet is a good technique.. The main disadvantage of this method is high cost of transportation but it results in decrease in effect on environment.

- **Steel et al. (2007)** investigated demineralization of bituminous coal sample collected from UK coal mine using two stage chemical leaching technique. 30 grams of Coal sample was mixed in 3.51M HF solution in a beaker and stirred on a hot plate magnetic stirrer at 65˚C temperature for 4 hours. Coal sample was filtered using polypropylene funnel and dried. 10 grams of HF treated coal sample was mixed with 100ml aqueous solution of $Fe(NO_3)_3$ and put on magnetic stirrer at 100˚C for 6 hours in second stage of leaching. They observed less than 0.1% of ash content was left in the coal. Decrease trend was found in almost all metals such as Alumina, silica, calcium and manganese.

- **Lin et al. (2007)** studied the adsorption of coal bottom ash for removal of Cu from the waste water. They adopted the batch extraction technique by varying the different parameters like temperature, pH, contact time and concentration. They reported that bottom ash can remove Cu, Fe, Mn and Zn from waste water. They found adsorption of Cu increased with increase in contact time and by increasing the pH value. There was a decrease in removal efficiency of Cu was noticed by increasing the dose of bottom ash or concentration. They concluded that bottom ash has a higher capacity to adsorb Cu as compared to activated carbon.

- **Liu et al. (2008)** investigated the effect of NaOH on desulphurization of coal at atmospheric conditions. They used flask with three necks and put 0.25N NaOH solution and coal in it. The temperature was controlled by the heater, thermometer was installed on one neck. While air supplied with the help of a pump at 0.136 m^3/h flow rate, this was controlled by the flow meter. They observed that there was decrease in organic sulfur, sulfide sulfur and pyrite sulfur by 66%, 44% and 15% respectively, when coal was treated at 90˚C. NaOH treated coal was further shaken for 1 hour with HCL. This led to further decrease in organic, sulfide and pyrite sulfur by 73%, 83% and 84% respectively. They do X-ray photoelectron spectroscopy and found that carbon, sulfur bond was broken with the help of oxygen present in atmosphere and this leads to the decreased inorganic sulfur of coal.

- **Nabeel et al. (2009)** experimentally studied the effect of alkali accompanied by acid on leaching characteristics of coal. They used NaOH and H_2SO_4 as leaching agents for chemical cleaning of coal. Coal samples were treated at room temperature with 20%, 5% and 1% concentrated aqueous NaOH solution for 2 hours. The NaOH treated coal was further leached with 10% H_2SO_4. In order to achieve a high degree of demineralization at low concentration of NaOH, they treated same coal sample three times under the same conditions. They observed decrease of 75-80% in mineral matter. They concluded that it was possible to remove the mineral matter from the coal at lower NaOH concentrations NaOH, but the number of steps should be increased.

- **Alam et al. (2009)** investigated the parametric effect on the desulfurization of coal after treating with HNO_3 and HCl using taguchi technique. Coal desulfurization was performed in two steps froth flotation and leaching at various parameters. They observed that 35.7% of ash and 36.9% of sulfur was removed when the coal sample was washed by froth flotation process. Coal samples were leached with nitric acid and HCl separately. They detected that HNO_3 was found more effective than HCl. HNO_3 was selected by them in further study to see the effect of stirring speed, time, temperature and concentration on desulfurization of coal. They apply L9 taguchi technique with temperature 30˚C, 60˚C, 90˚C, time intervals 30, 60, 90 minutes, concentrations 10%, 20% and 30% at stirring speeds 0, 500 and 1000rpm. After applying design of experiment nine different test runs were obtained. Experiments were performed on obtained test runs. They concluded 30% concentration, 1000rpm, 90min and 90˚C gave the best results when HNO_3 and HF are used as lechants.

- **Manoj et al. (2009)** investigated the effect of chemical leaching characteristics of low rank coal. They also perform characterization using different techniques such as SEM and FTIR. Coal samples were treated separately with HF and EDTA. Coal samples were treated with 0.1N EDTA for 24, 48, 72 and 96 hours after this sample were filtered, dried and used for further investigations. Same coal samples were treated with Hydrofluoric acid at concentration 10%-50% for 24 hours. They concluded that coal samples which were treated with EDTA removes little amount of sulphur content, whereas HF removes almost all the sulphur present in the coal and also removes major ash constituents such as alumina, silica and calcites. They observed increase in porosity of coal from the picture obtained from SEM which was the indication of removal of inorganic matter from the coal. After comparing the results of FTIR it was noticed that EDTA removes large minerals from the coal sample which was treated for long time and HF was considered as a better lechant than EDTA.

- **Zahir et al. (2009)** studied the effect of caustic on the leaching properties of coal. Thay collected coal samples from Hazro Coal field, Turkey. They treated coal samples with molten NaOH followed by acid demineralization was also done. Coal samples were mixed with sodium hydroxide pellets in ratio 1:1, 1:2 and 1:5 and put in muffle furnace for 30-90 minutes at 200-400˚C temperature. After leaching process was over the coal sample was washed with 1M HCl solution. Acid washed sample was filtered, dried and used in further experimentation work. They reported that it was effective to remove the ash, organic as well as pyritic sulphur from coal using molten caustic followed by acid leaching technique. Also rate of ash reduction have a positive effect of time and temperature. They detected 55% of organic sulphur, 100% reduction of pyritic sulphur and 63% of ash removal from the treated coal.

- **Dutta et al. (2009)** investigated leaching behavior of fly ash collected from different power stations of West Bengal. Their main purpose is to use the coal ash in the mines from which the coal was mined. The ash which is at the surface makes contach with liquids of different pH value for lengthier time intervals. By keeping this in mind they perform leaching by two different methods sequential extraction and long period leacing. They observed that the percentage of iron and manganese is less when the medium of leachate is alkaline in nature. However the percentage concentration of toxic elements is found to be more than detected. In long term leaching percentage concentration of iron, Mangenese, Calcim, sodium, potassium, Copper, Cromiun and Arsenic increases with reaction time. Whereas concentration of Pb and Ca decreases under the same experiment. So they conclude that releasing of heavy metals from coal fly ash is maximum when the medium is acidic so the fly ash is properly conditioned with the lime for the refilling of coal mines and prevent that area for acid drainage.

- **Vaccaro (2010)** investigated the effect of alkali and acid leaching characteristics of coal. Four different coal samples were taken having ash content of 10.7%, 15.4%, 31.7% and 37.7%. They mixed 38µm coal samples with HF at 80˚C temperature for 5 hours. The coal cake was dried out from the slurry and washed with distilled water, this washing continues till the pH value of the washed solution becomes closer to 7. They observed that with the increase in the concentration of HF the amount of ash content in coal decreased. In first coal sample ash reduced to 0.7% from 10.7% when treated with 50% HF concentrated solution, gradual decrease in the trend was noticed in all the samples. Coal samples were treated with HF and H_2O_2 to see the effect of desulfurization on coal. He concluded that HF was the effective solvent for coal demineralization and use of HF and H_2O_2 before treatment of coal with alkali seems to be best for desulfurization.

- **Jorjani et al. (2011)** studied the effect of HF and HNO3 on the chemical leaching characteristics of physically washed coal. Two coal samples with initial ash content of 8.3% and 10.3% were selected for the analysis. The batch reactor technique was used in performing the research. The coal was stirred at 0.5, 2, 3.5 and 5N aqueous HF solution. They observed that there was decrease in the ash content with the increase in the concentration of HF. Also the rate in ash reduction increases with the increase in temperature, time and particle size. They concluded that after 3.5M concentration the rate of decrease in the ash was less, so at 3.5M maximum decrease in ash was obtained. Ash content in the coal samples were reduced to 0.69%, 0.39% from 8.31% and 10.36% respectively.

- **Pandit et al. (2011)** have investigated the concentration of radio active metals in ash. The samples of fly as well as bottom ash was collected from defferent thermal power stations of India. They did gamma analysis on all the collected samples. They observed that fly and bottom ash have four times more concentration of radio active elements in it as compared to the coal sample which was feed in the furnance.

- **Manoj et al. (2012)** investigated the effect of chemical leaching behaviour on bituminous Indian coal and its characterization after cleaning. Coal samples were treated with aqueous HF solution having concentration range between 10%-30% at 80˚C temperature for 24 hour. SEM-EDS testing of the treated coal sample was done, results shows that particles like bassanite, kaolinite was removed completely and surface brightness was decreased. They observed morphological changes in the coal structure takes place which shows changes in the mineral matter of coal. Ash content in the coal was decreased from 8.2% to 1.27%, also increase in the carbon content was noticed with decrease in the sulphur.

- **Singh et al. (2012)** investigated the leaching characteristics coal fly ash collected from thermal plant in NTPC Dadri, Delhi. They have studied the leaching characteristics of metal elements with shake extraction of solid waste water at different time intervals and pH. They reported the behavior of trace elements from ash is affected by time of contact and pH value. The concentration of all the six elements Fe, Cr, Cu, Pb, Cd and Ni increased in the leachate solution and all the six elements showed their presence in the ground water sample nearby area of power plant. Out of six elements Cr, Cd, Ni and lead has crossed the prescribed standard limit of drinking water in the ground water samples. The elements in drinking water may cause lung tumors, damage of nervous systems, blood disorders, hypertension, and may also affect the kidneys and liver.

- **Lokeshappa et al. (2012)** studied the leaching properties of fly ash ash in open and closed system. They investigated the leaching behavior of trace elements from ash to nearby water bodies and ground water. They made a synthetic pound by fabricating the sheets of size 30×30×31cm. Ash was mixed in distilled water in 1:1 ratio and pond was filled up to 20cm with free water column of 10cm above fly ash for 11months. Water sample was taken once every month and analyzed for pH and concentration of elements. After 11months they found that pH of almost all pond increases from alkaline to acidic. Ar, Cr, Zn, Pb and Br were the main toxic metals detectable. Concentration of Ar and Cr increases with time in silica rich ash where as decrease was recorded in calcium rich ash. Zn, Pb, and Br concentration were seen to be decrease.

- **Dash et al. (2014)** investigated the effect of alkali and acid on the leaching behavior of coal. They collected five different samples from Indian coal mines. Coal samples were mixed with aqueous NaOH solution of concentration 10-40% with solid to liquid ratio of 1:10 (gm/ml). All samples were treated at temperature of 85˚C for 2.5 hours. NaOH treated samples were washed with water and later on by 10% HCl. They have observed that ash contents decreases in all samples with increase in NaOH concentration. The decrease in ash content also increased with the increase in temperature, time and stirring speed while decrease in size of coal particles. The proportion of silica, alumina and phosphorus was also decreased in ash of chemically treated coal. They revealed that it is possible to remove more than 50% of ash content from physically cleaned coal by using the chemical leaching of coal.

- **Saikia et al. (2014)** investigated ultrasonic cleaning of coal by using H_2O_2 as a leaching agent. They studied physical and chemical properties of treated and untreated coal by XRD, FT-IR, SEM and TG-DTG. They detected decrease of 31% in sulphur and 32% in ash after cleaning of coal. The decrease in the presence of illite, albite, pyrite, hematite was noticed with improvement in the gross calorific value of coal.

- **Singh et al. (2014)** investigated the harmful impact of ash disposal system on the ground water and nearby water bodies. They collected fly ash sample from Rajghat power plant,Delhi situated near the bank of Yamuna River. Leaching ability of some toxic elements was examined at different pH levels. The technique of leaching used was batch extraction leaching. The shake test was performed at 100rpm with 20:1 solid liquid ratio over different intervals of time. They reported that the leaching is depend on time and pH values of the lechants. The leaching ability of Cu, Cr, and Ni show the trend $L_{ACIDIC}>L_{ALKALINE}>L_{NEUTRAL}$ and leaching of Pb and Cd fluctuates over time and Fe shows the trend $L_{ALKALINE}>L_{ACIDIC}>L_{NEUTRAL}$. Pb and Cr concentration in the leachant is obtained under acidic conditions. They conclude that to minimize the leaching the medium should be alkaline.

- **Meshram (2015)** comprehensive study on demineralization of high ash coal. They discussed the various methods for the cleaning of the coal like physical methods, bio-processing and chemical leaching. They conclude that physical method is not suitable for cleaning high and medium ash coal. Bio-processing technique takes a long time due to this reason this process is very slow, so this method is not feasible. In chemical washing method expensive chemicals are used to clean the coal, removal of fine coal from the slurry of coal and aqueous mixture is also a difficult task. They conclude that combined use of chemical and physical techniques will be the best option for the desulphurization of coal and this leads to low water consumption and also cost beneficial.

- **Wahab et al. (2015)** studied the effect of caustic molten technique on leaching properties of coal. They studied the effect of alkali cleaning on ash, sulphur and calorific value. They mixed coal with NaOH beads in 1:1 ratio and put them in a sealed reaction vessel. Nitrogen gas was purged in the vessel which was maintained at 250ºC and reaction continued for 1 hour. The vessel was cooled below 50ºC and coal was extracted from the slurry. Coal sample washed with boiling water and 10% HCl solution. They studied the effect of particle size and the coal caustic ratio. The observed 80% decrease in ash content also calorific value of coal was increased.

- **Dash et al. (2015)** investigated the effect of aqueous alkali and acid on leaching behaviour of coal. They collected coal samples from the Tata steel plant. Coal samples were initially treated with 20% and 40% aqueous NaOH solution and then washed with 10% HCl. Experiments was done at 5bar pressure and within the temperature range of

85ºC-140ºC. They observed gradual decrease in the ash content with the increase in concentration of NaOH and pressure. The improvement in the crucible index number was noticed with an increase in the temperature and concentration of the NaOH. They noticed that the rate of decrease in ash content was even more when NaOH treated sample was washed with 10% HCl. They concluded that up to 70% of ash content were removed with the removal of Silica and alumina up to 51.3% and 58.8% respectively.

- **Dash et al. (2015)** studied the characterization of Indian coals which were chemically cleaned. They used x-ray diffraction, Fourier transform infrared spectroscope (FTIR), optical microscope and scanning electron microscope (SEM) techniques to find out physical and chemical characteristics of coal. They mixed 300 mesh size coal samples with 10%-50% concentrated aqueous NaOH solution. The coal chemical slurry was treated in the Batch reactor having a stirrer fitted in it runs at 600rpm to insure that coal was not settled down. They observed that ash was decreased with increase in the NaOH concentration and reaction time. From the results obtained from all characterization techniques they concluded that a cross linked structure of hydroxide compounds was formed partial dissolution of mineral matter at higher NaOH concentrations. Acid washing of coals helps in removal of hydrates. No change in organic bonding was noticed in alkali followed by acid treated coal.

- **Lingam et al. (2015)** investigated the effect of caustic leaching followed by acid washing on the physically beneficed coal. They collected coal samples from west bokaro mine. Ash content was found to be 59% and having 80% of silica and alumina content in it. They mixed coal with caustic solution in ratio of 1:5 to 1:10 and treated the slurry for at 160˚C for 1hour. Coal samples were filtered with the help of filter and separation of coal cake and alkali solution was taken place. Coal cake obtained after filtration was washed with water till its pH value becomes seven later on washed with acid solution for 30 min. They observed that decrease of 25.8% in ash was achieved by treating the coal only with alkali. Also at 160˚C temperature, 20% alkali concentration and 60 minutes of reaction time, maximum decrease in ash content with 62.6% of yield was achieved.

- **Balakrishnan et al. (2015)** studied the effect of ultrasonic and alkali coal washing on removal of alkali elements such as Na and K from the coal. They carried out four different tests to see the effect of the removal of alkali content from the coal. Coal samples were agitated with water, ammonium acetate at 1500rpm, ultrasonically with water and ammonium acetate. They mixed 210µm of coal with distilled water and stirred at the speed of 1500rpm. They observed 30% and 25% decrease in sodium in coal samples cleaned with sonication and stirring respectively. 5% of decrease in potassium content was noticed in coal cleaned by both the ways, so ultrasonic washing removes more alkali content from coal as compared to samples cleaned by agitation. They concluded that samples which were washed with water only shows same percentage of alkali content removal with both the methods, but the samples in which ammonium acetate was used as leachate shows more amount of alkali content removal in case of ultrasonic washing, so ultrasonic washing was more effective than the washing done by mechanical stirrer.

Chapter 3

Methodology and Experimentation

3.1 Introduction

The coal available in India has high ash content, which is not at all desirable because it leads toward increase in solid waste after combustion. Due to the availability of low grade coal large amount of coal is imported from foreign countries. Thermal power plants running on low grade coals are suffering through major problems of ash handling and disposal system. Coal containing high ash content is not suitable for use in combustion, liquefaction and gasification process. Coals are heterogeneous compounds made up of inorganic and organic components. The inorganic part generally consists of mineral matter which converts into ash after combustion and causes many hazardous effects like leaching of heavy metals into ground and nearby water bodies during the ash disposal process. Therefore the cleaning of high ash coal is necessary before use.

Coals found in India are mainly bituminous and sub-bituminous types which have ash content between ranging between 30 to 50%. Coal mines of superior coal are depleting at very fast rate, so there is a need to convert the low grade coals to high grade coal. In present situation, coal cleaning was done by physical methods like gravity separation, froth flotation, magnetic separation etc. these methods are cost effective, but unable to decrease the ash which is intermixed in the coal structure. Chemical cleaning is the technique by which high degree of dematerialized coal is obtained. Three types of chemical cleaning techniques are generally adopted by different researchers in their study that are acid leaching, alkali leaching and alkali followed by acid leaching. Chemical cleaning either alone or after physical cleaning has been used to convert low grade coals to high grade coals. The effect of ash removal by chemical leaching techniques has been investigated by many investigators in previous years. More than 75wt% of decrease in mineral matter was observed by them after treating the coal with different chemicals.

3.2 Equipment details

Mechanical sieve Shaker was used to study the physical properties of coal. The sieve shaker was according to British Standards 410 (BS 410) manufactured by a Mody testing instruments corporation, Vadodara. Sieves were arranged in the shaker from 2mm to 53µm sieve size. The sieve shaker is shown in Fig. 3.1.

Figure 3.1: Mechanical Sieve Shaker, Weighing Balance, Muffle Furnace

High precision Weighing balance machine manufactured by Adair Dutt and Co. Private Limited, Calcutta was used to weigh the coal samples. Weighing balance was also used to weigh the coal samples during proximate analysis of coal shown in Fig. 3.1.

Magnetic stirrer manufactured by IKA was used for the proper mixing of coal in the aqueous solution before putting the samples in shaker. The Orbital type magnetic shaker was used to shake the samples at desired temperature, time and RPM. The shaker was manufactured by

Remi Elektrotechnik Ltd., Vasai. It has a temperature limit between 0˚C to 100˚C. R-22 refrigerant was used in the shaker to control the temperature. Whatman Filter papers of 30µm pore size were used to filter the coal samples from coal water slurry.

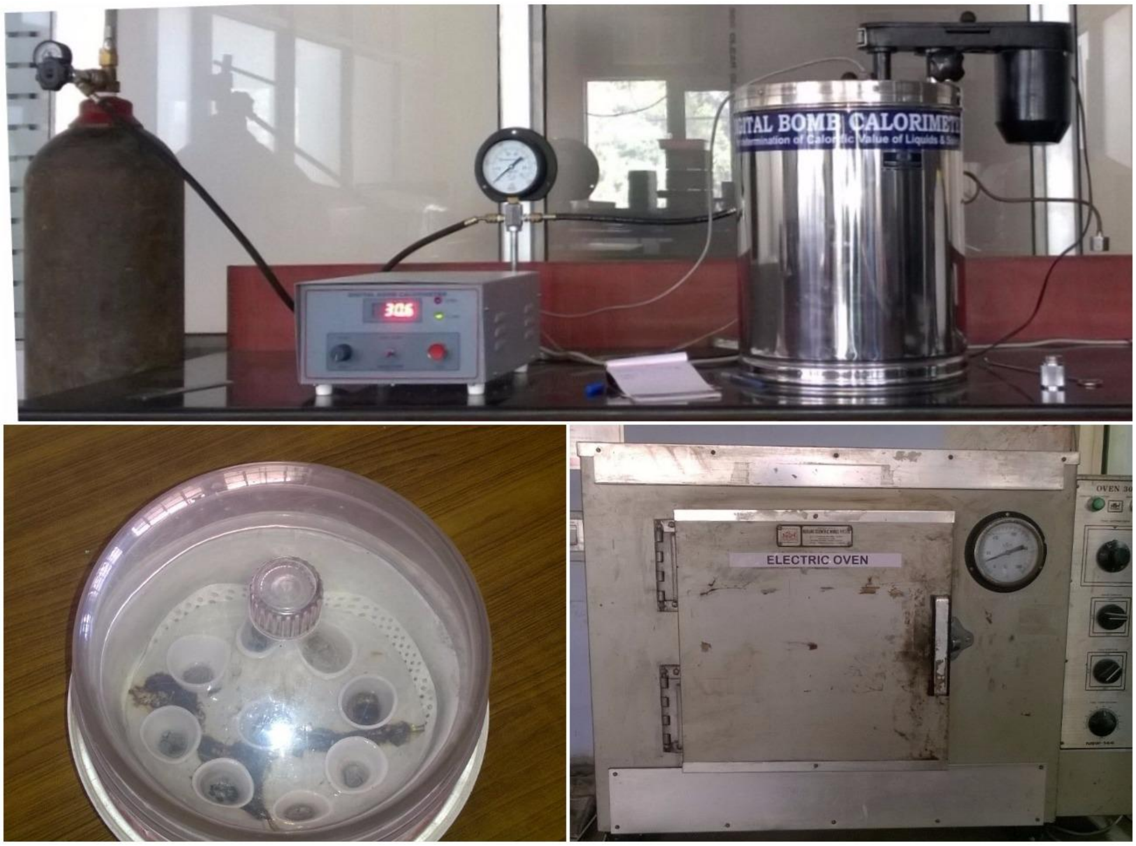

Figure 3.2: Bomb calorimeter, Desiccator, Electric oven

Hot air oven manufactured by Narang Scientific work Pvt. Ltd., having temperature range between 0-300°C was used for dry the coal samples after the treatment with chemicals. The oven was also used to calculate the moisture content of coal during proximate analysis shown in Fig. 3.2. Muffle Furnace manufactured by Macro Scientific works Pvt. Ltd. Delhi, have a temperature range of 0-1200°C was used to perform proximate analysis of coal shown in Fig. 3.1. Desiccator was used to cool down the samples before weighing so that the samples did not absorb moisture from the surroundings shown in Fig. 3.2.

Bomb calorimeter was used to calculate the Calorific value of the coal samples. Bomb calorimeter used in research work was manufactured by Widsons Scientific Works, Delhi shown in Fig. 3.2.

3.3 Materials

Coal samples of different piles were collected from the coal yard of Guru Gobind Singh Super Thermal power plant, Ropar. The collected coal samples were in the form of big lumps. These lumps were crushed to small size with hammer type coal crusher and then pulverized with rotary ball mill. The powdered coal was dried in the oven at 120°C and used in further investigation.

3.4 Experimental procedure

The Coal sample obtained after milling was in pulverized form. In order to study the physical properties of coal particle size distribution of coal sample was done. The coal sample of known weight was taken and passed through a series of sieves in a mechanical sieve shaker. The sieve shaker was left in running condition for 30 minutes. The coal particles are sieved from 2mm mesh size sieve to 53µm mesh size. Sieve shaker is switched off and coal samples from the respective sieves were collected and put in sealed bags.

The leaching experiments were conducted with changing the NaOH concentration from 10 to 40% (by volume) further treated with 10% HCl. The particle of the coal sample was taken in the range of 75–106 µm. The coal was mixed with aqueous solution in ratio of 1:10 (g/ml). As the coal is hydrophobic in nature so to insure the proper mixing, the slurry was stirred with the help of magnetic stirrer (manufactured by IKA, Bangalore, India) for 10 minutes. The detailed procedure of the investigation is represented in Fig. 3.5. After mixing, shaking operation was performed using orbital shaker (manufactured by Remi Elektrotechnik Ltd., Vasai, India) at 150 rpm, 50°C for 2 hours. Coal sample was filtered with 11µm Whatman disc filter paper and dried in oven at 120°C to scrub out coal from filter paper as shown in Fig. 3.3. The treated coal samples were repeatedly washed with distilled warm water until natural pH value didn't achieved. The demineralized coal was again treated with 10% HCl (Hydrochloric acid) for 1 hour duration. After filtration of treated coal, percentage of ash in the coal sample was determined using muffle furnace (manufactured by Macro Scientific works Pvt. Ltd. Delhi, India). In second stage, first stage processed coal sample was again treated with respective concentrations of NaOH and 10% HCl for duration of 2 and 1 hour respectively, again suspension was filtered at room temperature and percentage of ash content analysed.

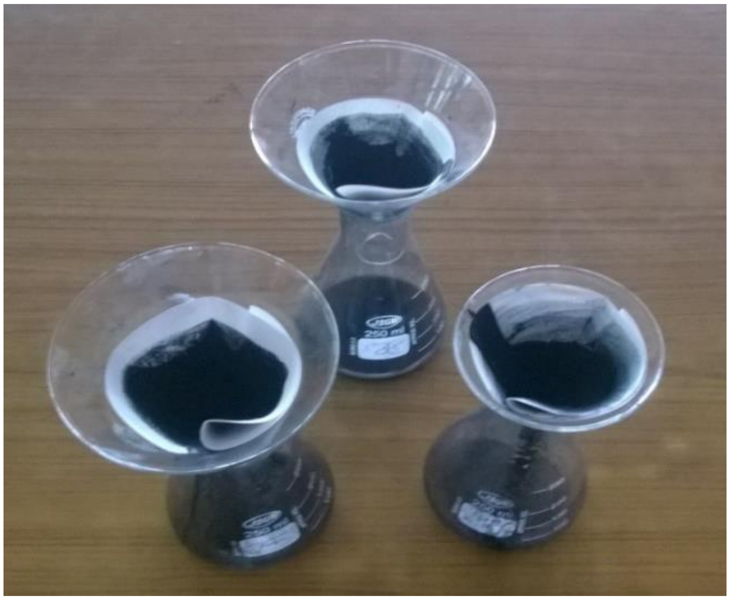

Figure 3.3: filtration of coal after chemical treatment

Same procedure was followed in the third stage chemical leaching. Second stage processed coal sample further treated with NaOH and HCl. Final coal suspension was filtered, dried and preceded for ash content analysis. To analyse the effect of shaking speed, temperarure and particle size the leaching experiments were performed at 0, 50, 100, 150, 200 rpm, 25, 40, 55, 70˚C and 53-75, 75-106, 106-150 and 150-250μm respectively for 2 hours. Further analysis was carried out to test the effect of reaction time at constant speed of 150 rpm with temperature 50ºC for 1, 2, 3 and 4 hours.

3.5 Proximate analysis of coal

The proximate analysis of coal includes the calculation of moisture, volatile matter, ash and fixed carbon content in it.

3.5.1 Calculation of Inherit moisture

1 gram of coal sample was taken in the silica crucible. The weight of empty silica crucible and the weight of crucible with 1 gram coal was noted down. The sample was put in the oven at a temperature of 120˚C. Sample was taken out after fixed time intervals from the oven and cooled in the desiccator up to room temperature. The samples were weighed till the change in weight was negligible. Moisture content in coal was calculated by formula given in Eq. (3.1).

$$\text{Moisture content (\%)} = \frac{B-C}{B-A} \times 100 \qquad (3.1)$$

Where as

A= weight of empty crucible in grams

B= weight of coal sample and crucible in grams

C= weight of coal sample and crucible after oven drying in grams

3.5.2 Calculation of volatile matter

The coal sample obtained after determination of moisture content was used further for calculation of volatile matter. The sample with the crucible put in the muffle furnace maintained at the temperature of 950˚C. After approximately 7 minutes the samples were taken out from the furnace and cool down with the help of cold plate. The samples were further cool down by placing them in the desiccator and the weight of the sample was noted down. The volatile matter was calculated by the under given formula.

Volatile matter (%) = $\left(\frac{\mathrm{B-C}}{\mathrm{B-A}} \times 100\right) - \text{moisture content}(\%)$ (3.2)

Where as

A= weight of empty crucible in grams
B= weight of coal sample and crucible after oven drying in grams
C= weight of coal sample and crucible after heating in a furnace

3.5.3 Calculation of Ash content

The solid waste left after combustion of coal is known as ash. Ash is generated due to burning of mineral matter in the coal. The sample obtained after determination of volatile matter was put in the muffle furnace maintained at 950˚C temperature for 30 minutes. The sample was taken out of the furnace, to insure the complete combustion the colour of ash left was investigated. If the colour of ash is black then it indicates incomplete combustion, but if it is white or pale brown in colour complete combustion is insured. The ash in coal was calculated by under given formula.

Ash content (%) = $\left(\frac{D-A}{C-A} \times 100\right)$ (3.3)

Where as

A= weight of empty crucible in grams
C= weight of coal sample and crucible after oven drying in grams
D= weight of the sample and crucible left after combustion in grams

3.5.4 Calculation of Fixed Carbon

The fixed carbon content in the coal was calculated by subtracting the volatile matter, ash content and moisture content from 100.

$$\text{Fixed carbon} = 100 - (\text{moisture } (\%) + \text{volatile matter } (\%) + \text{ash content } (\%)) \tag{3.4}$$

Figure 3.4: Various process of proximate analysis

3.5.5 Calorific value

The calorific value of the fuel was calculated on the bomb calorimeter. The tablets of the coal samples were prepared, so that when the burning of coal takes place inside the bomb uniform rise in the temperature of water takes place. The calorific value was obtained in kcal/gm by using the formula.

$$\text{Calorific value} = \left[\frac{(2334.3 \times \Delta T) - A - B}{X}\right] \tag{3.5}$$

Where as

ΔT = temperature change

X= weight of coal sample

A= weight of nicron wire

B= weight of cotton thread

The effect of concentration, particle size, shaking speed, temperature, reaction time and calorific value is investigated in the present study. The schematic representation of procedure adopted in this study is represented in Fig. 3.5.

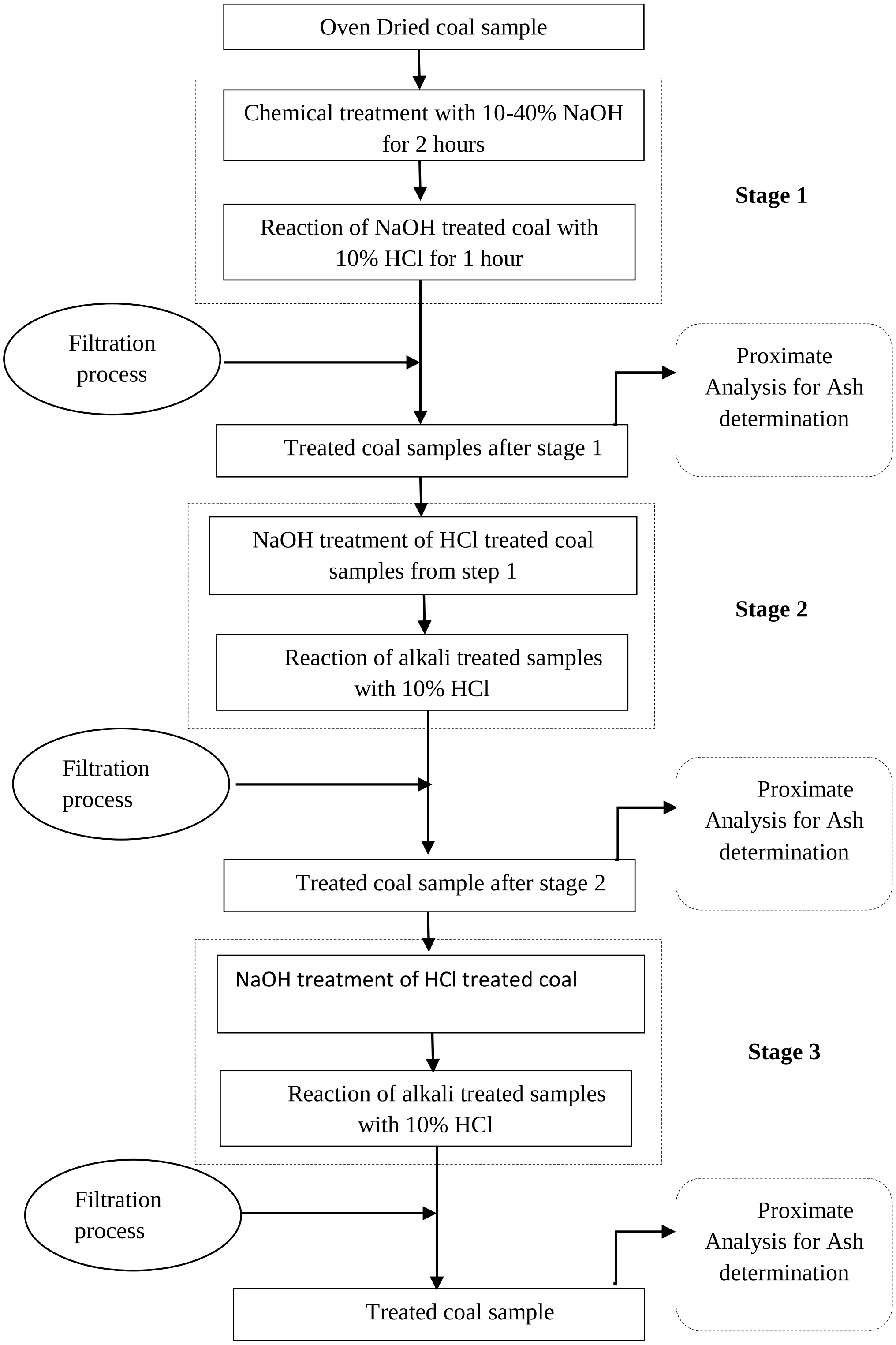

Figure 3.5: Schematic representation of process flow

Chapter 4

Results and Discussions

4.1 Particle size distribution

In order to study the physical properties of coal the particle distribution was done on the mechanical sieve shaker (BS 410). A known amount of coal sample was passed over series sieves. The amount of sample retained on each sieve was measured and percentage is calculated. Fig. 4.1 show that 94.43% particles are finer than 250µm, 86.09% particles are finer than 150µm and 10.8% particles are finer than 75µm.

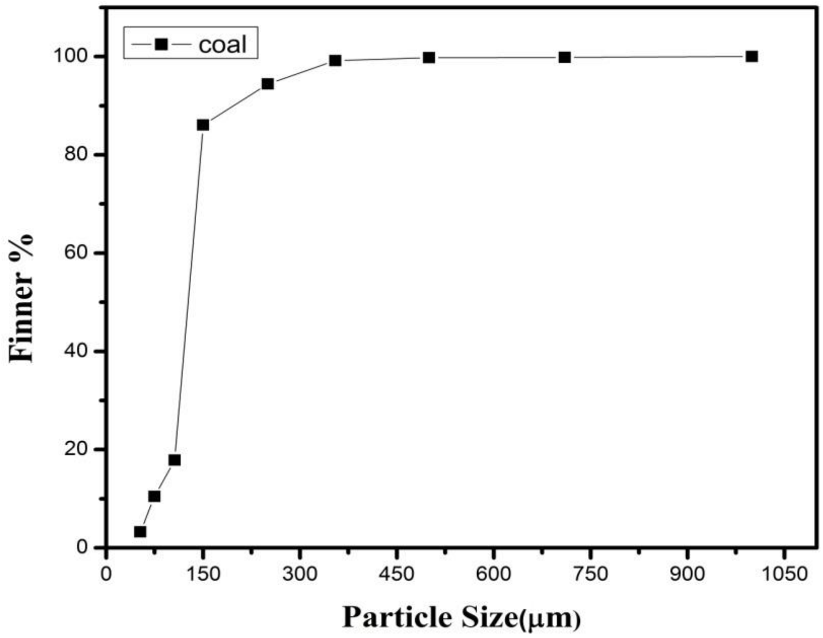

Figure 4.1: Particle size distribution of coal

4.2 Effect of NaOH concentration on ash content

Three stage chemical treatment of coal has been carried out to investigate the effect of alkali NaOH concentration on ash content in coal sample, which is shown in Fig. 4.2. During the experiments, concentration of NaOH was varied from 10 to 40% (by volume) with fixed concentration of HCl (10%) at 150 rpm shaking speed for duration of 2 hours. The ash content was determined by proximate analysis with the help of muffle furnace (IS-1350). The percentage decrease in ash content was calculated by using Eq. (4.1).

$$\text{Percentage decrease in ash content} = \frac{a-b}{a} \times 100 \tag{4.1}$$

Where 'a' represents ash content in parent coal sample and 'b' is reduced ash content percentage in chemically treated coal. From Fig. 4.2, it is observed that ash content present in the coal sample decreases with increase in NaOH concentration. In the coal sample, initially ash content was found 35.33% (by weight). After first stage of the experimentation, ash content in the coal sample was reduced to 24.71, 24.02, 21.28 and 17.665% (by volume) with 10, 20, 30 and 40% NaOH concentration respectively. First stage processed samples were not sufficient to produce ultra-clean coal (having ash content less than 1%) so, further experiments were carried out. While the value of ash content was reduced to 10.59, 9.54, 7.71 and 5.29 % after second stage. After third stage ash content reduced to 7.06, 5.36, 3.29 and 0.98%. Results shows that ultra-clean coal was produced with 40% NaOH and 10% HCl solution after third stage of chemical leaching process. Alumina and silica present in coal reacts with NaOH and to forms soluble compounds such as silicates and aluminates as represented by the following reactions.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{4.2}$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \tag{4.3}$$

As the NaOH concentration increases, the concentration of silicate and aluminate ions also gradually increases in the solution until alumina silicate did not start accumulating. The mineral matter present in the form of alumina and silica in coal was dissolving out from coal.

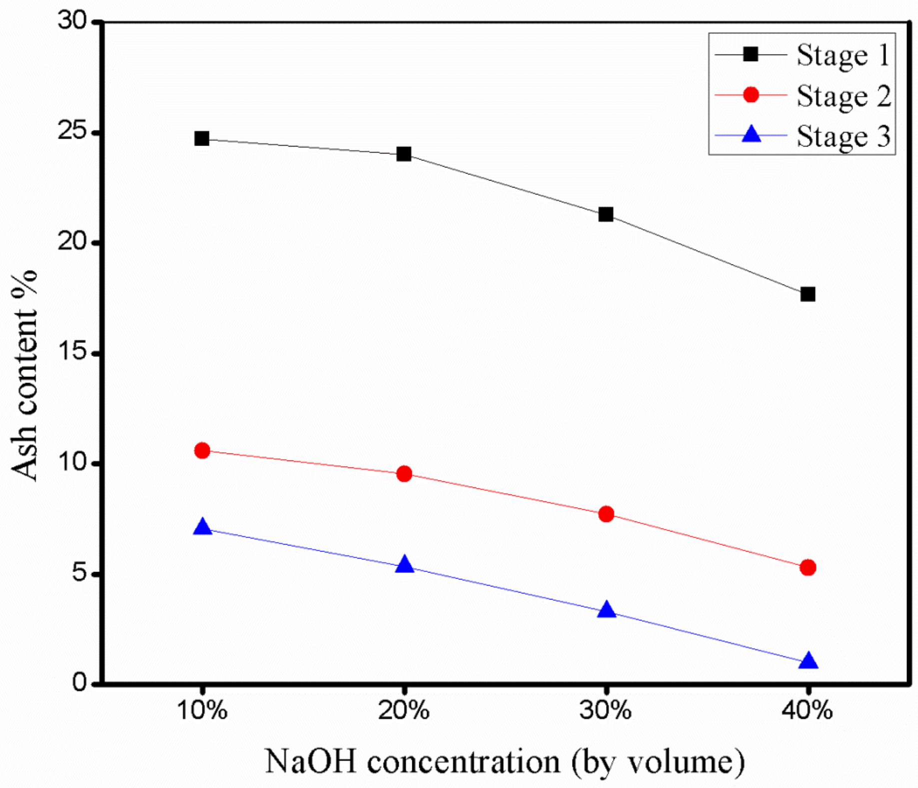

Figure 4.2: Effect of NaOH concentration on ash removal

4.3 Effect of shaking speed on ash content

The chemical leaching experimentation was also performed to investigate the effect of shaking speed on ash content in the coal sample. Experiments were performed at different shaking speed 0, 50, 100, 150 and 200 rpm with 40% NaOH and 10% HCl (by volume) solution. Samples were shaked in orbital shaker for duration of 2 hours at 50ºC temperature. Variation of ash reduction with shaking speed is shown in Fig. 4.3. The decrease in the ash content was observed with increase in shaking speed. In the initial stage ash content in coal was reduced to 30.23, 25.67, 21.59, 17.66 and 15.852% (by weight) with shaking speed of 0, 50, 100, 150 and 200 rpm respectively. Similarly ash content was reduced to 20.43, 15.54, 10.32, 5.29 and 3.72% after the second stage. However the values of ash content were reduced to 16.45, 11.32, 6.65, 0.98 and 0.62% after third stage. Result data shows that ultra-clean coal was produced with 40% concentrated NaOH solution at shaking speed of 150 and 200 rpm. The gradual decrease in ash content at higher rpm was due to increase in mass transfer rate between coal and leaching agents.

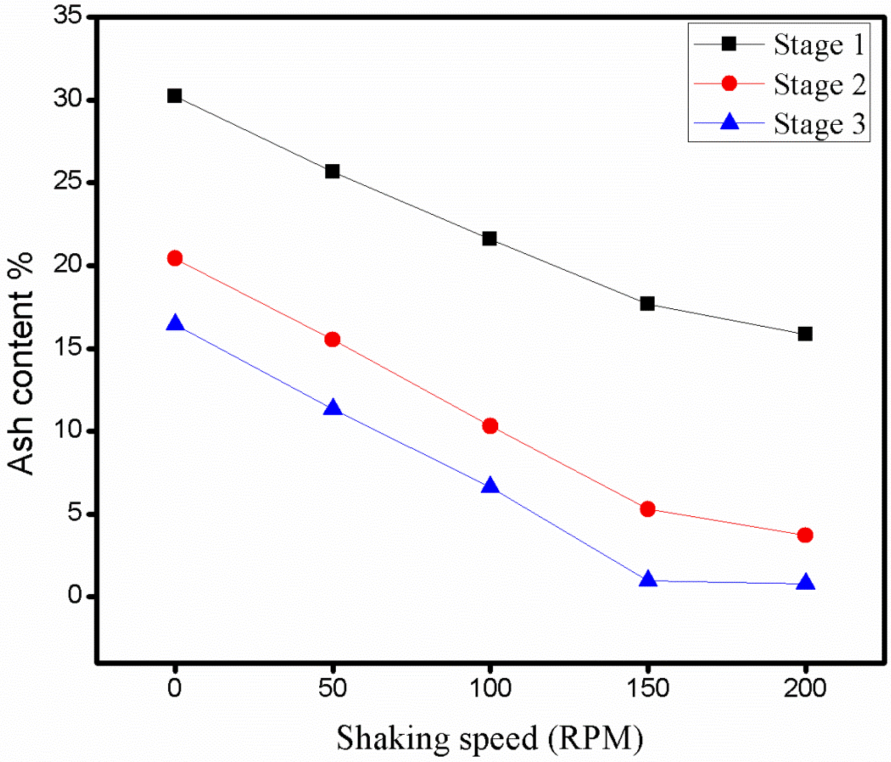

Figure 4.3: Effect of shaking speed on ash reduction

4.4 Effect of reaction time on ash content

The effect of time duration on chemical washing of coal is investigated in this section. Coal particles of size 75–106 µm were treated with 40% NaOH and 10% HCl (by volume) for duration of 1, 2, 3 and 4 hours. Details of reduction of ash content with variation of time are represented in Fig. 4.4. The decrease in the ash content was noticed with increase in reaction time. The ash content from the parent coal was reduced to 19.96, 17.66, 15.84 and 13.32%

after first stage with reaction time period of 1, 2, 3 and 4 hours respectively. Similarly the weight percentage of ash content was reduced to 8.32, 5.29, 4.53 and 3.52% after the second stage of chemical leaching. Subsequently ash content was reduced to 5.64, 0.98, 0.45 and 0.3% after final stage. The ultra-clean coal was produced with 40% NaOH and 10% HCl solution while treating in the duration of time such as 2, 3 and 4 hours.

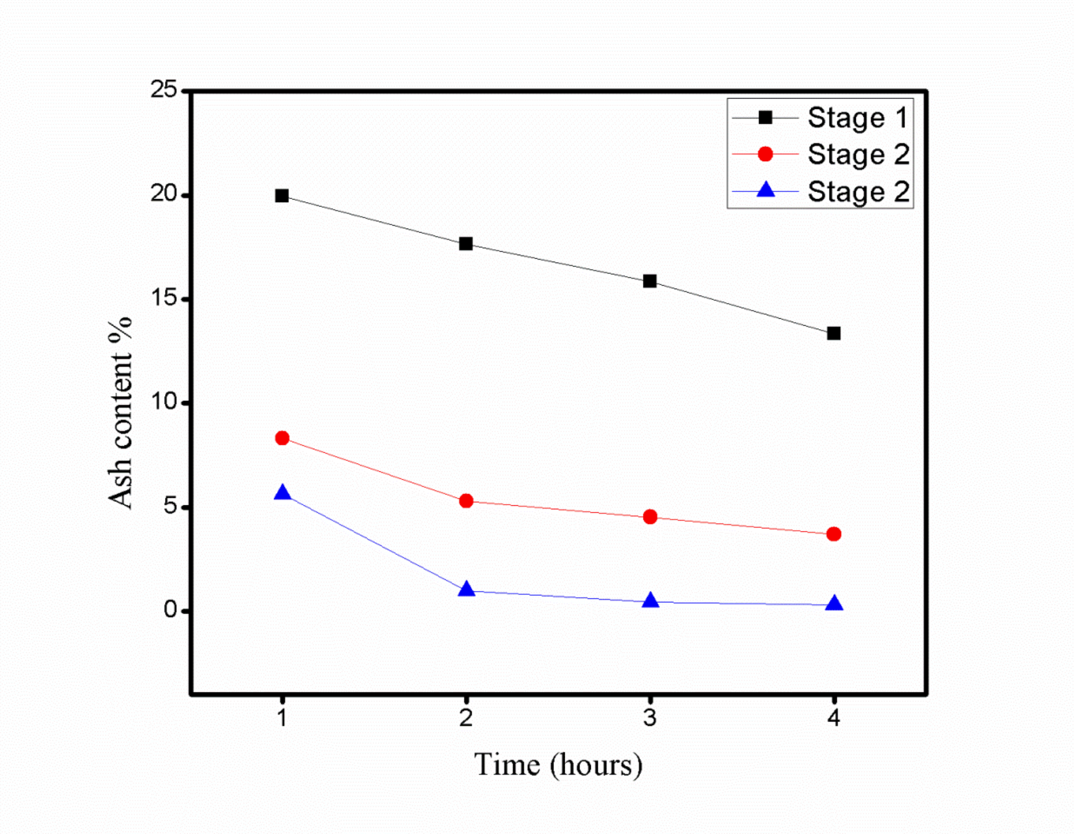

Figure 4.4: Effect of reaction time on ash removal

4.5 Effect of Temperature on Ash Content

The experimentation was performed to investigate the effect of temperature on ash content in coal sample. Experiments were carried out at different temperature condition 25, 40, 55 and 70˚C. Coal samples of particle size 53-75 µm was treated with 40% NaOH and 10% HCl (by volume) solution. Samples were shaked in orbital shaker at 150 rpm for duration of 2 hours at 40ºC temperature. The decrease in ash content was noticed with increase in temperature as shown in Fig 4.5. In first stage ash content from coal was reduced to 20.98, 17.66, 14.69 and 12.48% with temperature 25, 40, 55 and 70˚C respectively. While ash content in coal was reduced to 7.54, 5.29, 3.38 and 2.12% respectively after the second stage. However the values of ash content were reduced to 4.54, 0.98, 0.73 and 0.65% after the final stage. Decrease in ash content was observed at higher temperatures due to increase in reaction kinetics with temperature .

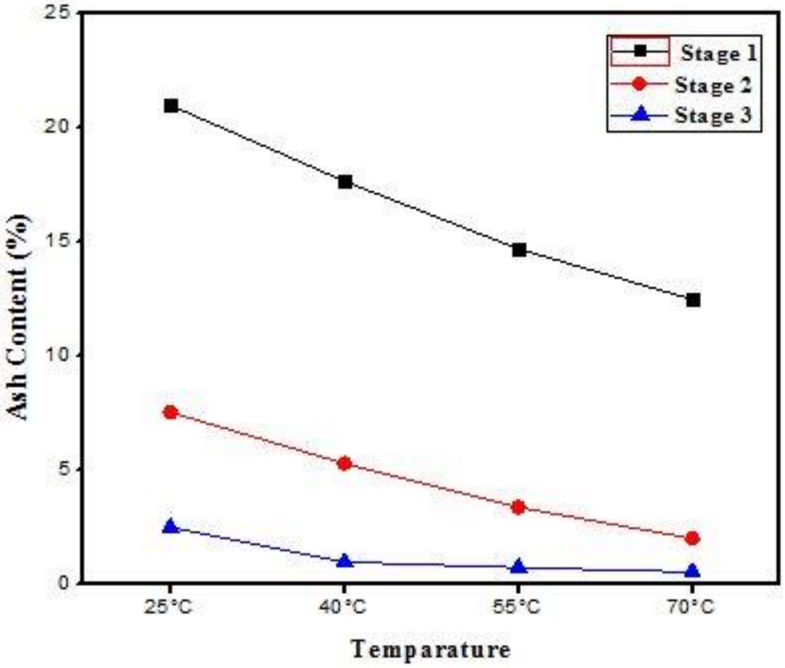

Figure 4.5: Effect of temperature on ash reduction

4.6 Effect of Particle Size on Ash Content

The effect of particle size on chemical leaching of coal was also investigated. During the experimentation coal sample was taken in the particle size range of 53-75, 75-106, 106-150, 150-250 µm. The coal samples were treated with 40% NaOH and 10% HCl (by volume) for duration of 2 hours. The variation of ash content of coal with the different particle size rage is represented in the Fig. 4.6 From the result data, it is observed that the ash content in the coal sample decreases with decrease in particle size range. Lowest ash content is observed with the finer particles of coal sample in the particle size range of 53-75 µm whereas highest ash content observed with the coarser particles of coal sample in the range of 150-250 µm. The ash content in the coal sample after first stage was reduced to 25.43, 21.32, 17.66 and 14.32% from the particle size of coal in the range of 150-250, 106-150, 75-106 and 53-75 µm respectively. In the second stage the ash content was reduced to 16.65, 10.56, 6.29 and 2.43%. Similarly ash content was reduced to 6.34, 3.54, 0.98 and 0.35% after the third stage. The ultra-clean coal was produced from coal sample in the particle size range of 53-75 and 75-106 µm after third stage.

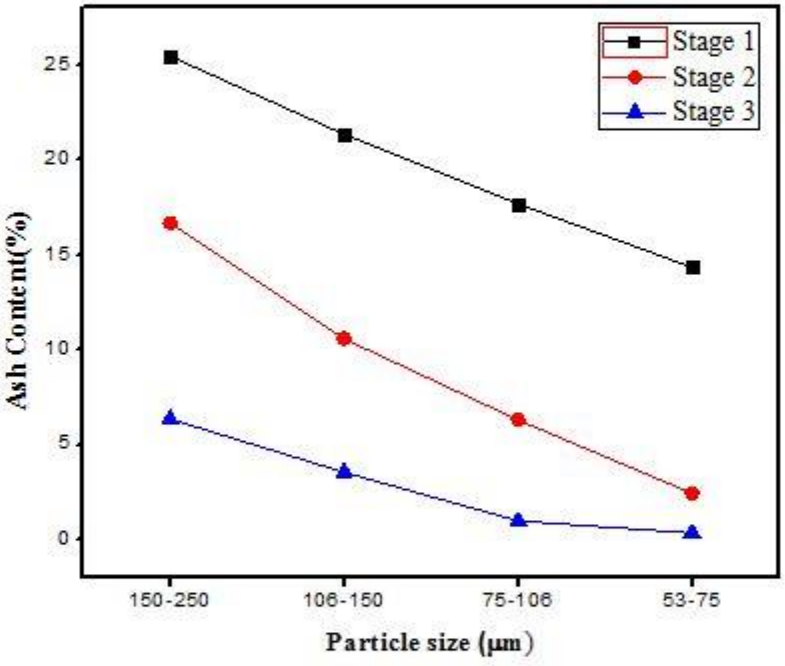

Figure 4.6: Effect of particle size on ash removal

4.7 Effect of chemical leaching on Calorific Value and ash constituents of coal sample

Chemical characterization of parent coal and chemically treated coal ash was studied using EDS (energy dispersion x-ray spectrography). The chemical composition of ash obtained after every stage is represented in Table 1. Figure. 4.7 obtained from EDS of parent coal ash shows that aluminum oxide and silica oxide are present in major proportion. However, other compounds like calcium oxide, iron oxide, potassium oxide and sodium oxide are in presence in minor proportion. In the parent coal, Al_2O_3, SiO_2, Na_2O, FeO and CaO were present in the percentage of 18.43, 48.13, 2.58, 9.65 and 5.43% (by weight) respectively.

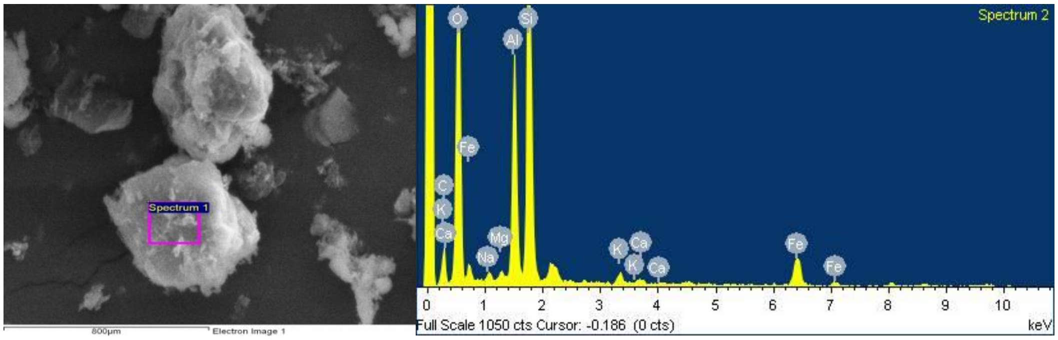

Figure 4.7: EDS image of ash retained from untreated coal

However the percentage of all ash constituents decreased with increase in NaOH concentration represented in Table 1. The chemical leaching treatment was successfully completed at the end of third stage. EDS image of 10% NaOH and 10% HCl is represented in Fig. 4.8(a) which reveals that percentage of Al_2O_3, SiO_2, CaO, FeO, K_2O and Na_2O was reduced to 10.54, 22.45, 3.46, 3.56, 1.42 and 1.34% respectively. From Fig. 4.8(b), it is noticed that ash constituents further undergo to formal decrease as 8.65, 16.54, 2.75, 2.13, 1.02 and 1.20% on treating with 20% NaOH and 10% HCl. Previous trend shows that the NaOH concentration significantly contributes in reduction of ash constituents which can also found in Fig. 4.8(c) and (d). As the After treating the coal samples with 30% NaOH and 10% HCl, percentage of ash constituents was observed as 5.46, 7.86, 1.90, 1.56, 0.78 and 0.97%. Ultra-clean coal was produced with 40% NaOH and 10% HCl and percentage of ash constituents was found as 1.56, 1.25, 0.98, 0.45, 0.35 and 0.67%.

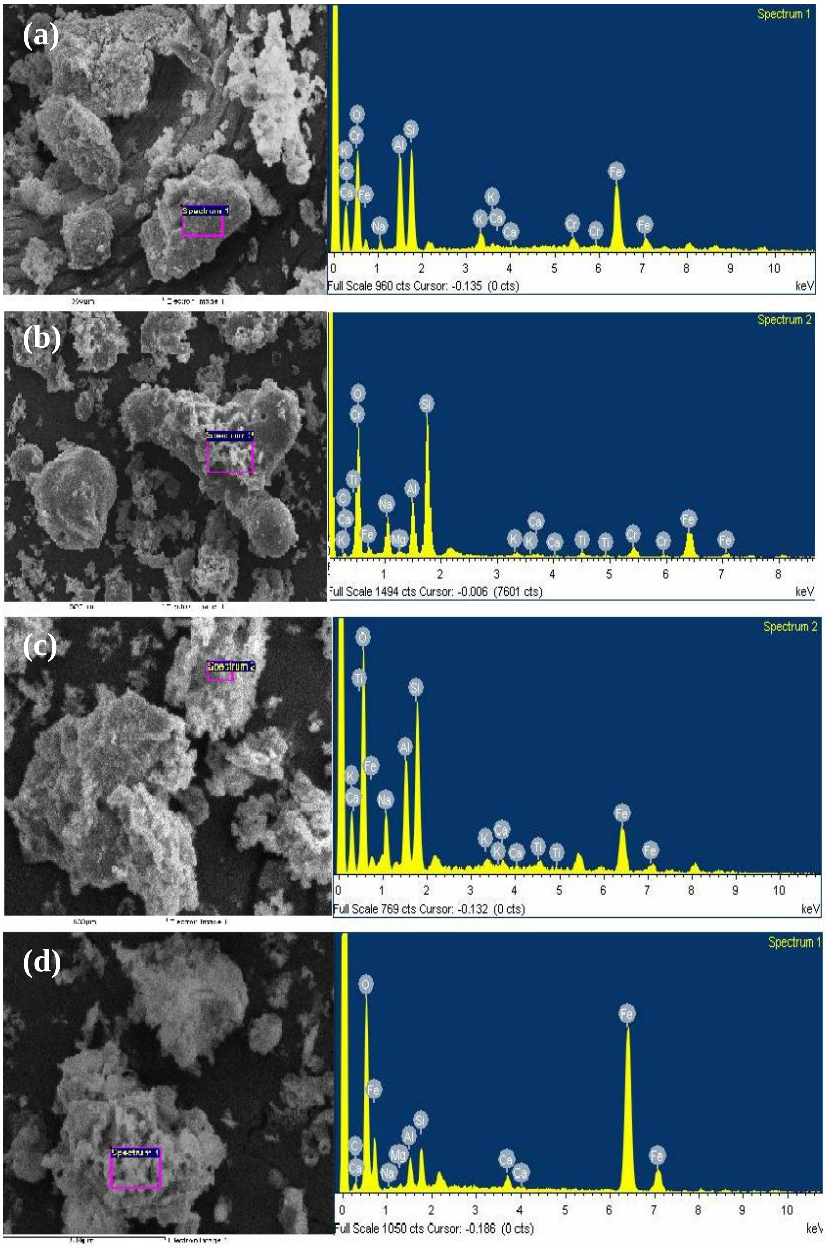

Figure 4.8: EDS image of ash retained from coal treated by 10% HCl and NaOH of (a) 10%, (b) 20%, (b) 30% and (b) 40%

Table 4.1: Effect of chemical leaching on ash constituents and calorific value

Stages	Coal samples	Ash constituents (wt.%)							Calorific Value (kcal/kg)
		Al_2O_3	SiO_2	CaO	FeO	K_2O	Na_2O	Unburnt Carbon	
Initial	Untreated coal	18.43	48.13	5.43	9.65	2.86	2.58	7.56	5057.55
First	10%NaOH + 10%HCl	15.34	40.56	5.34	7.56	2.32	2.12	6.8	6019.34
	20%NaOH + 10%HCl	14.02	36.28	4.32	6.08	1.94	1.93	4.98	6069.56
	30%NaOH + 10%HCl	12.38	28.56	3.45	5.23	1.50	1.67	3.54	6184.65
	40%NaOH + 10%HCl	9.98	10.98	2.65	3.98	1.28	1.51	1.56	6342.15
Second	10%NaOH + 10%HCl	12.56	32.65	4.54	5.78	1.96	1.95	5.22	6159.65
	20%NaOH + 10%HCl	9.87	28.54	3.95	4.65	1.21	1.53	3.10	6198.53
	30%NaOH + 10%HCl	7.23	20.95	2.45	3.45	1.08	1.26	2.56	6298.76
	40%NaOH + 10%HCl	5.90	4.95	1.54	2.43	0.89	0.98	0.92	6457.80
Third	10%NaOH + 10%HCl	10.54	22.45	3.46	3.56	1.42	1.34	3.54	6210.76
	20%NaOH + 10%HCl	8.65	16.54	2.75	2.13	1.02	1.20	2.86	6269.56
	30%NaOH + 10%HCl	5.46	7.86	1.90	1.56	0.78	0.97	1.4	6384.65
	40%NaOH + 10%HCl	1.56	1.25	0.98	0.45	0.35	0.67	0.56	6542.15

Chapter 5

Optimization of experimental data using ANOVA variance

Taguchi approach is used in present study for optimizing process parameters and also to find out the optimal combination of experimental factors. The input parameters/variables used in present study are also discussed earlier in this chapter, on the basis of that an orthogonal array is made as given below.

Table 5.1: Parameters and their levels

S No.	Parameters	Level 1	Level 2	Level 3	Level 4
1	Temperature(˚C)	25	40	55	70
2	Concentration (% by volume)	10	20	30	40
3	Particle size(µm)	53-75	75-106	106-150	150-250

ANOVA (Statistical analysis of variance) is performed in present study to find out the influence of experimental parameters for the erosion process. Motive of the study is to find out optimal combinations of parameters to minimize erosion for all the three materials.

5.1 Analysis of results

In Taguchi's approach results are analysed on the basis of three basic quality characteristics.

1. The bigger the better
2. The nominal the better
3. The smaller the better

The bigger the better is used where our prime motive is to maximize the output, the nominal the better is used when output should be nominal and the smaller the better is used when to minimize the output is primary concern. The output of nine experiments given by orthogonal array is recorded and results are obtained according to the quality characteristic the smaller the better because here minimum erosion of specimens is requirement. Mean standard deviation and signal to noise ratio is calculated by using the following equations.

$$\mathrm{MSD} = \frac{1}{\mathrm{n}}\sum_{\mathrm{i}}^{\mathrm{n}}(\mathrm{E_w})^2 \qquad (5.1)$$

Where n represents the repetition of experiment and E_w represents the erosion of specimens. Then S/N ratio of performed experiments was calculated by using the following equation.

$$\frac{S}{N} ratio = -10\log(MSD) \qquad (5.2)$$

S/N ratio is a generalized term which denotes the output to error ratio. So to have the minimum erosion output, an experiment must produce the highest S/N ratio.

5.2 DESIGN OF EXPERIMENT

Taguchi approach is powerful analysis tool for design of experiment (DOE) and analyzed influence of control factors on performance output. It helps to provide an efficient and systematic way to optimize designs for high quality output data at lower cost. The basic principal of optimal design is to develop high quality data by minimizing the effect cause by variable with elimination. During experimental investigation there are number of uncontrolled and controlled variable which effect outcome or results. In Taguchi method, the term ‘signal’ represents the desirable data (mean) for the output characteristic and ‘noise’ represents the undesirable data for the output characteristic. The S/N ratio is used to measure the quality characteristic and the significant erosion parameters. S/N for lower is better can be expressed as

$$\frac{S}{N} = -10\log\left[\frac{1}{n}\sum y_i^2\right] \qquad (5.3)$$

Where i = 1, 2, 3, 4, 5, ……………………

Where “n” is the number of test run and “y_i” Observed performance characteristic data in the i^{th} experiment. The information of contribution to each individual parameter is important for describes the nature of process. In the Taguchi method, orthogonal array is used to determine the relative importance of influence parameters and identity the best suitability of their response. There are several arrays available for S/N ratios which depending on the nature of performance characteristics. Lower is better array is used for expresses ash content after chemical cleaning in term of S/N ratios. It is calculated in logarithmic transformation of ash content. L_{16} orthogonal array has been chosen as there are three input parameter and each parameter has four levels. The design of experiments of the chemical treatment process includes factors and levels are mention in Table 5.2. In order to shorten the leaching test time and cost, three factors, i.e., coal particle size in the range of 53-75, 75-106, 106-150 and 150-250 µm, temperature 25, 40, 55 and 70 ˚C and acid concentration of 10, 20, 30 and 40% (by volume) respectively was examined in three-factor, three-level, orthogonal array. It is clear from the Fig. 5.1 as the temperature increases from 25 to 70˚C S/N values are also increases from -19.82 to -9.84. It represents that as the temperature increases the ash content in the coal decreases. Also, with the increase in the concentration from 10-40% the value of S/N ratio increases from -19.07 to -10.34. However S/N value decreases from -12.06 to -16.85 with the increase in particle size of coal ranging from 53-75µm to 150-250µm.

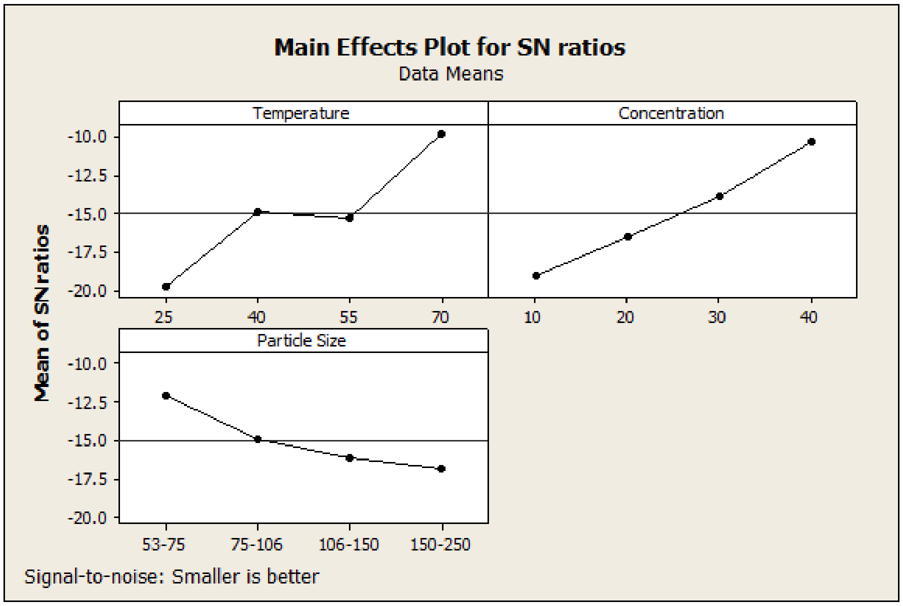

Figure 5.1: Effect of SN ratio with temperature, concentration and particle size

Table 5.2: Experimental layout using L16 array for uncoated materials

Experiments	Parameter level			Ash Content (% by weight)	S/N ratio
	Temperature (˚C)	Concentration (% by volume)	Particle size (µm)		
1	25	10	53-75	11.41	-21.1457
2	25	20	75-106	10.63	-20.5307
3	25	30	106-150	10.21	-20.1805
4	25	40	150-250	7.45	-17.4431
5	40	10	53-75	8.61	-18.7001
6	40	20	75-106	4.96	-13.9096
7	40	30	106-150	6.01	-15.5775
8	40	40	150-250	3.54	-10.9801
9	55	10	53-75	8.67	-18.7604
10	55	20	75-106	6.87	-16.7391
11	55	30	106-150	4.32	-12.7097
12	55	40	150-250	4.54	-13.1411
13	70	10	53-75	7.65	-17.6732
14	70	20	75-106	5.31	-14.5019
15	70	30	106-150	2.34	-7.3843
16	70	40	150-250	0.65	-1.7981

5.3 VALIDATION STUDIES BY ANOVA (ANALYSIS OF VARIANCE)

The results obtained from Taguchi method for optimization of linseed oil methyl ester production were statistically verified by ANOVA (analysis of variance). The term variance ratio, which is ratio of variance of factor to error variance, distinguishes the more significant factors from less significant. More than 9 variance ratio for a factor represents that the factor is having an erosion of specimens and tables below shows the analysis of variance using S/N ratios of performed experiments for all parameters.

The various terms of ANOVA that are used for the calculation are given below in the series of small equations:

$$C.F. = \frac{T^2}{n} \tag{5.4}$$

$$S_T = \sum_i^n y_i^2 - C.F. \tag{5.5}$$

$$S = \frac{A_1^2}{N_1} + \frac{A_2^2}{N_2} + \frac{A_3^2}{N_3} - C.F. \tag{5.6}$$

$$V = \frac{S}{f} \tag{5.7}$$

$$F = \frac{V}{V_e} \tag{5.8}$$

$$S_P = S - f \times V_e \tag{5.9}$$

Where T is total of all the weight loss obtained, n is total number of experiments, A_1 is sum of all the S/N ratios under level 1 of any parameter, N_1 is number of experiments having level 1 of any parameter, A_2 is sum of all the S/N ratios under level 2 of any parameter, N_2 is number of experiments having level 2 of any parameter, A_3 is sum of all the S/N ratios under level 3 of any parameter, N_3 is number of experiments having level 3 of any parameter, f is the degree of freedom of parameter and V_e is the error variance.

Analysis of variance (ANOVA) statistic is most commonly applied on the experiment data to establish the relationship between experimental parameters and output data. The main purpose of the ANOVA is to determine the most influences parameter which affects to reduce the ash content of the coal. The number of levels (4) subtracted 1 gave the degree of freedom 3. The sum of squares (SS) was determined by following relation.

$$SS_i = \left((M_{1i}\text{-}M)^2 + (M_{2i}\text{-}M)^2 + (M_{3i}\text{-}M)^2 + (M_{4i}\text{-}M)^2\right) \times 3 (i = A \times B \times C) \tag{5.10}$$

Where SS_i sum of square, M is mean of ash content of experiential data, i= number of factors i.e. A= temperature, B= Concentration, C= Particle Size. The variance was determined as the ratio of sum of squares to degree of freedom. In order to determine the significance of different factors like temperature, concentration and particle size influence on ash content of coal sample, variance analysis was performed on the experimental data.

Table 5.3: Analysis of Variance for Means

Source	D.O.F	Seq SS	Variance ratio	Adj MS	F
Temperature	3	72.71	13	24.23	43.12
Concentration	3	52.85	9.45	17.61	31.34
Particle Size	3	5.59	1	1.86	3.32
Error	3	5.59			

The Table 5.3 indicates the variance results with F and P ratios. This analysis was taken with the significance level and confidence interval of ± 5% and 95% respectively . The minimum value of SS_i is consider as error of variance i.e. 5.54. The variance ratios was calculated by ratio of sum of square to the error. The variance ratio of temperature, concentration and particle size was determined as 13, 9.45 and 1 whereas 43.12, 31.34 and 3.32 were F value found respectively (Table 2). The variation of ash content with temperature and concentration is represented in Fig. 5.2. From result data it is clear that reduction in the ash content can be increased by treating the coal with higher alkali concentration and temperature. From the variance analysis it is clear that temperature and concentration are the principal factors for removal of ash content from parent coal. According to this approach temperature has a dominating factor for ash removal followed by concentration and particle size.

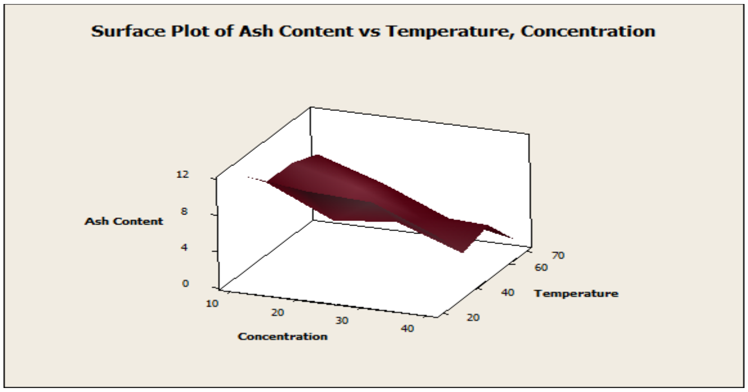

Figure 5.2: Variation of ash content with temperature and concentration

Chapter 6

Conclusion and future Scope

In this work, investigations are carried out to evaluate the effect of chemical leaching of coal and coal ash. The experiments were performed to reduce ash content from pulverized coal. The coal was leached with NaOH and HCl solutions to reduce the ash content from it. The concentration of alkali, shaking speed, particle size, temperature and time duration were found as highly influencing parameter for reduction of ash content in coal.

- Ultra-clean coal was produced with 40% NaOH and 10% HCl having percentage of ash constituents Al_2O_3, SiO_2, CaO, FeO, K_2O and Na_2O as 1.56, 1.25, 0.98, 0.45, 0.35 and 0.67%.
- The calorific value of the ultra-clean coal was found as 6542.15 Kcal/Kg.
- The ultra-clean coal was produced after three stage chemical treatment and leads to reduction in ash content from 35.33 to 0.98% (by weight) with 40% volume concentration of NaOH.
- Experimental influence parameters were optimized using Taguchi method. The result indicates that the temperature contribute the most dominants factor followed by acid concentration and particle size.
- According optimum condition was obtained as, particle size range 75-106µm, temperature 70˚C and concentration of NaOH 40% respectively.

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