Chapter-4

Methods of study

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4.1 Introduction

This chapter gives the overview about the materials and methods followed in the research work for the study of coal while the specific methodology has been discussed in details. The systematic methodology adopted for the coal characterization, qualitative and quantitative study of REEs in coal along with its recovery is shown in figure 4.1.

The research work begins with a component of extensive fieldwork in the study area. The coal samples were collected from the Dhanpuri opencast mine of Sohagpur Coalfield, Madhya Pradesh, India. Megascopic characterization of the samples was done according to Diessel's classification (1965). Furthermore, these samples were also used for the geochemical analysis to determine their proximate and ultimate analysis constituents. With the help of proximate analysis, moisture, ash, volatile matter and fixed carbon percentage were determined in coal samples. Ultimate analysis of samples determined the carbon, hydrogen, nitrogen, oxygen and sulphur percentage in samples. X-ray diffraction (XRD) was used to determine inorganic contents in samples, while functional groups present in coal samples were identified with the help of Fourier Transform Infrared Spectroscopy (FTIR). Surface morphology and elemental constituents of samples were determined by scanning electron microscopy with energy dispersive X-rays (SEM with EDX). Trace and minor elements were determined by inductive coupled plasma mass spectroscopy (ICP-MS) in samples. The analytical methods involved in the present study are being discussed in this chapter.

4.2 Methods of coal sampling

The idea of sampling is to take a representative portion of the bulk sample originally brought to the laboratory. The coal samples were collected from working seam faces of the opencast mine from the

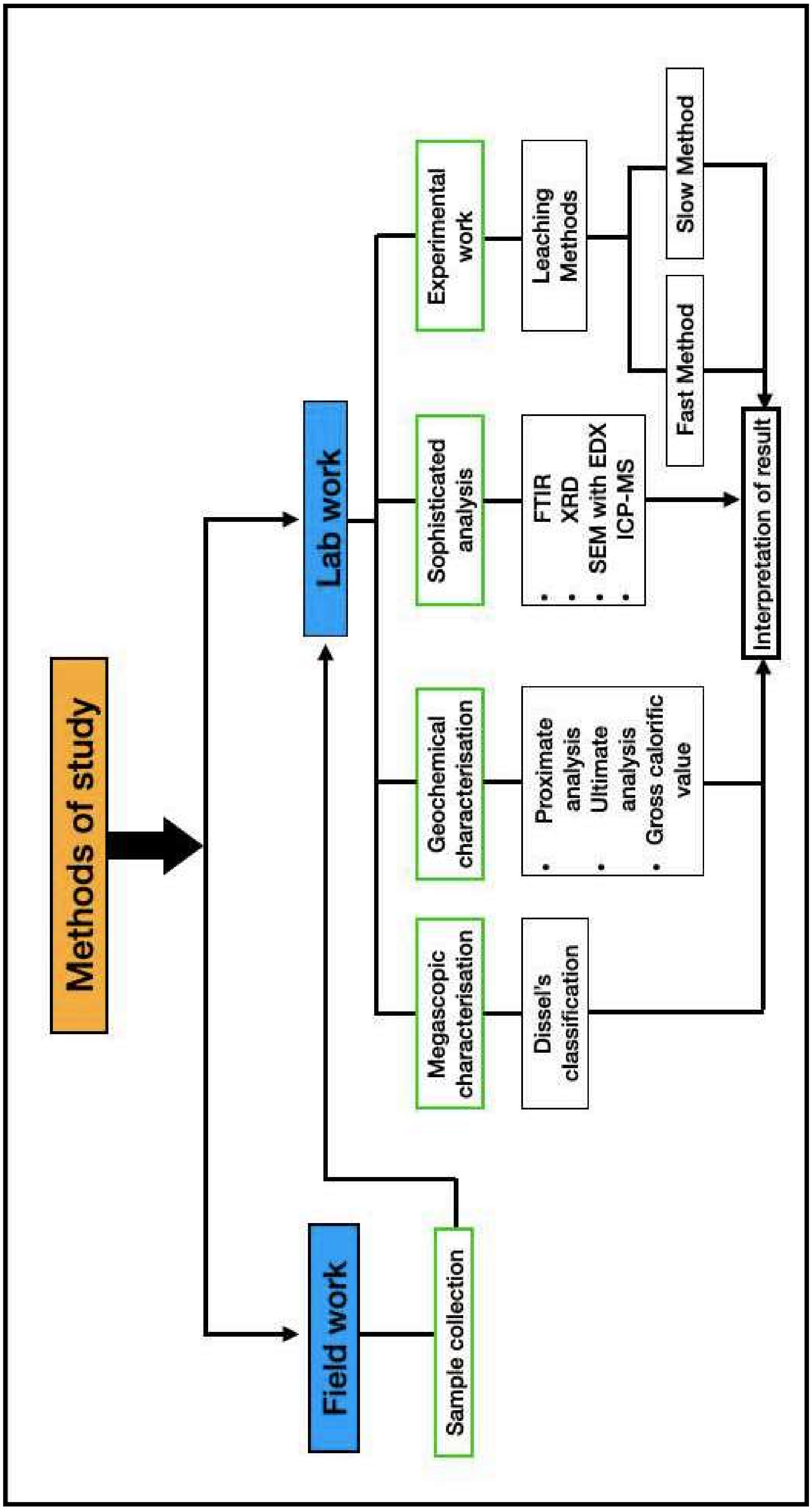

Fig. 4.1: Flow diagram representing the methodology

Fig. 4.2: Coal seam of Dhanpuri OCM of Sohagpur Coalfield

Dhanpuri of the Sohagpur coalfield, Madhya Pradesh, India (Fig 4.2 and 4.3). The samples were collected following the pillar sampling method, in such a way that the complete thickness of the seam could be reconstructed in the laboratory for macroscopic examination. That's why this method chosen to collect the samples from coalfield. All collected coal samples were put in ziplock plastic bags and sealed immediately to minimize oxidation and further contamination. Samples were brought to the laboratory for megascopic characterization in hand specimens. After this, the samples were crushed according to the mesh size required for analysis in the laboratory and experimental works.

4.3 Crushing of coal samples

After megascopic characterization, coal samples were crushed accordingly in the Mineral Processing and Beneficiation Laboratory, Department of Mining Engineering, IIT (BHU), Varanasi. For crushing, we used,

- Jaw Crusher
- Roll crusher
- Pulveriser

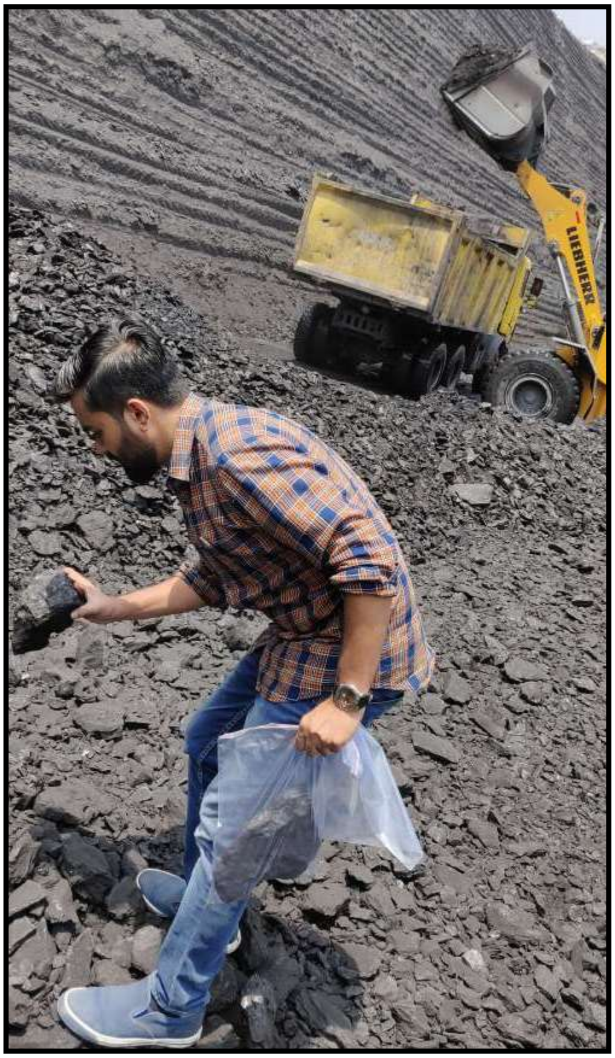

Fig. 4.3: Collection of coal samples from Dhanpuri OCM

Fig. 4.4: Photograph of Jaw

The photograph shows the crusher which was used in the crushing of coal samples (Fig. 4.4).

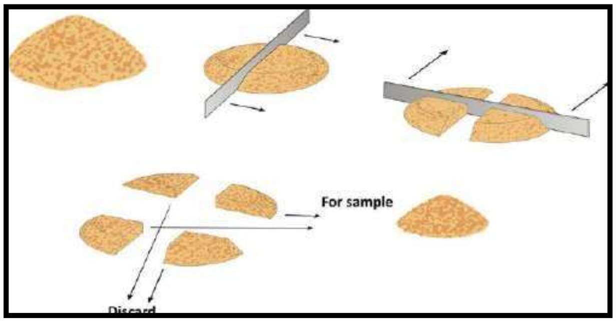

Fig. 4.5: The coning and quartering method can be used to first divide the sample into four segments, the diagonally opposite of which are rejected. Quartering is continued until a suitable sample volume is achieved. (Source: Quality guidelines of wood fuels in Finland VTT-M-04712-15)

4.4 Sample preparation

Coal samples were collected from the working seam faces of coal mines. The coal samples were numbered according to their position in the coal seam sections. Coal samples of a particular section were characterized macroscopically with the help of Diessel's classification (1965). After the megascopic characterization, samples were brought to the laboratory for the crushing accordingly. Coal samples were first crushed to -18 mesh size and with help of quarter and coning, fixed amount of samples were separated. In coning and quartering method the sample are mixed well and divided into four segments, the diagonally opposite of which are rejected. Quartering is continued until a suitable sample volume is achieved (Fig. 4.5). Coning and quartering method is chosen here due to easily availability and widely used (Alakangas 2015). It also doesn't require any sample divider or mechanical equipment. With the help of coning and quartering methods, samples were separated for crushing and pulverization. Samples were crushed into small parts first and then pulverized into tiny particles up to -72 mesh size for the geochemical characterization, sophisticated analysis and further experimental works (BIS 1975). This sample was used for further analysis as per requirements.

4.5 Geochemical analysis

Geochemical analysis includes the proximate analysis, ultimate analysis, x-ray diffraction, FTIR, SEM with EDX and ICP-MS. The samples were crushed down to -72 mesh size for the above analysis as per standards specified. A brief about proximate and apparatus used for various analysis is described below.

4.6 Proximate analysis

The proximate analysis of coal samples collected from field was conducted in the departmental laboratory by standard procedures. It includes the determination of moisture, volatile matter, ash and fixed carbon content (ASTM D3172). Few samples were also carried out by Thermogravimetric Analysis (TGA) in the Central Instrument Facility of Indian Institute of Technology (BHU), Varanasi. The analysis was performed by crushing the coal samples in suitable size and taking representative -72 mesh size coal only. The results of proximate analysis were used for assessing the grade of coal. The methods for the determination of individual components of proximate analysis are as follows:

4.6.1 Moisture

The weight loss due to moisture has been calculated by keeping the coal sample in oven as per standard procedure (ASTM method D3173-11). It requires a glass dish, an oven, a desiccator and an electronic digital balance. To determine the moisture content in coal samples, one gram of air-dried coal powder (-72 mesh size) was uniformly spread in a glass dish with the help of a nickel wire loop. It was then kept in an oven at a temperature of 108±2°C for one and half hours (Fig. 4.6). After heating, the dish was taken out and kept in desiccators for cooling. The coal powder was then weighted to know the weight loss, and the moisture percent was calculated.

The following calculation has been applied:

Let A = Weight of the glass dish

B = Weight of the glass dish + coal sample

C = Weight of the glass dish + sample after heating

Fig. 4.6: Photograph of Hot air oven

Then,

Moisture % by weight (Moisture %) = {B-C / B-A} X 100

By using above procedure and formula, all the 56 coal samples were analyzed for moisture content. The results are summarized in chapter five and discussions are given in chapter nine.

Fig. 4.7: Photograph of Muffle Furnace

4.6.2 Volatile matter

The volatile matter was also determined as per standard prescribed procedure (ASTM D3175). For determining the volatile matter, one gram of air dried coal (-72 mesh size) is heated under controlled conditions in a standard crucible with a lid. The crucible is placed in a furnace and heated at 900 ± 10°C for a period of seven minutes only. The loss in weight of coal sample after heating was calculated as per formula given below. This gives the percentage of moisture and volatile matter both. To obtain the percentage of volatile matter, the moisture content has also been determined at the same time at 105°C. The moisture content value was deducted from the total percentage loss obtained at 900°C to get the value of volatile matter percentage. The detail is described below:

Let,

A = Weight of the Crucible

B = Weight of the Crucible + coal sample

C = Weight of the Crucible + sample after heating

Then

Volatile Matter + Moisture, % by weight = {B-C / B-A} × 100

And

Volatile Matter % by weight = {(B-C / B-A)×100} – Moisture (wt.%)

By using above procedure and formula, all the 56 coal samples were analyzed for volatile matter content. The results are summarized in chapter five and discussions are given in chapter nine.

4.6.3 Ash

The ash was also determined by following standard prescribed procedure (ASTM D2795–95). One gram of air-dried coal powder (-72 mesh size) was taken in a silica crucible. It was placed in a ventilated muffle furnace at room temperature, and subsequently, the temperature was raised to 500°C for 30 minutes, and then the same sample was heated at 815±10°C for one hour (Fig. 4.7). After this, the crucible was taken out from the furnace and kept in the desiccators to cool down. Then, the weight of the sample/residue was taken.

The method has been applied for the calculation, is as follows:

Let,

A = Weight of the Crucible

B = Weight of the Crucible + coal sample

C = Weight of the Crucible + sample after heating

Then

Ash yield % by weight = {C-A / B-A} X 100

By using above procedure and formula, all the 56 coal samples were analyzed for ash content. The results are summarized in chapter five and discussions are given in chapter nine.

4.6.4 Fixed Carbon

To determine the fixed carbon content, the sum of moisture, volatile matter and ash content were subtracted from one hundred as given below formula:

Fixed carbon % by weight =100 – (Moisture + Volatile Matter + Ash yield)

Fig. 4.8: Photograph of Thermogravimetric analyzer (TGA)

For verification of results of proximate analysis, Thermogravimetric Analyzer has also been used in the research work. The Thermogravimetric Analysis (TGA) of coal samples was carried out in the Central Instrument Facility of Indian Institute of Technology (BHU), Varanasi, India. Model of TGA 50 was used for the analysis of M/s Shimadzu (Asia Pacific) Pvt. Ltd, Japan (Fig. 4.8). The protocol for the proximate analysis using TGA is described by some workers (Haines 1995; Donahue et al. 2009). The five steps involved are as follows: Steps 1–4 were performed under N_2 and step 5 in air: (1) hold for 4.0 min at 25 °C; (2) heat from 25 °C to 110 °C at 85 °C/min; (3) hold for 6 min at 110 °C; (4) heat from 110 °C to 900 °C at 80 °C/min; and (5) hold for 5 min at 900°C (ASTM E1131). The instrument software was used to determine mass percent loss of moisture, ash content and volatile matter as shown in figs. 6.1 and 6.2. Fixed carbon content was computed by summing these three quantities and subtracting the result from 100%.

4.7 Ultimate analysis

To characterize the coal of the study area, facility available in other departments of Banaras Hindu University has been utilized. The ultimate analysis of coal sample of the study area was carried out in the M. P. Singh Laboratory of Coal and Organic Petrology, Centre of Advanced Study, Department of Geology, Banaras Hindu University, Varanasi, Uttar Pradesh, India. The Ultimate study has been performed on an Elemental Analyzer, model Vario EL-III. Principally, the analyzer works as catalytic tube combustion in an oxygenated CO_2 atmosphere and high temperature (Fig. 4.9). Ultimate analysis was used to determine carbon, hydrogen, nitrogen and sulfur content in coal (ASTM D5373–08). While oxygen was calculated by the sum of carbon, hydrogen, nitrogen, and sulfur content, subtracting from one hundred. The combustion gases were made free from foreign gases. The desired measuring components are separated from each other with the help of a specific adsorption column. They are determined in succession with the thermal conductive detector. Helium acts as flushing as well as carrier gas.

Fig. 4.9: Photograph of Elemental Analyzer

4.8 Gross Calorific Value (GCV)

Gross Calorific Value is an important parameter to assess the heating value of any solid fuel including coal. Gross Calorific Value is described as per ISO standards as measuring heat value, the absolute value of specific energy of combustion for the unit mass of a solid fuel burned in oxygen in a calorimeter bomb under specific conditions (ISO 1928:2009). It consists of a base which supports the platinum crucible and is screwed to the body of the bomb. The top of the bomb carries an oxygen supply connection and a valve to release the product. One gram of powdered sample coal was taken for the test and the calorimeter was filled with approximately two litre of water. The sample was placed in the platinum crucible. The iron fuse wire which surrounds the sample of coal was connected to the lower end of the two electrodes. The electrodes extended through the base of the bomb and connected the fuse wire to an electric circuit. The coal was ignited by closing the electric circuit. The bomb was placed inside a copper vessel which contains water. There was a stirring device for agitating the water within the calorimeter. The calorimeter containing the bomb

Fig. 4.10: Photograph of Bomb Calorimeter

was placed in another container which acts as a heat insulator. The temperature of water in the calorimeter was measured by a thermometer. The oxygen cylinder was coupled to the bomb and oxygen was admitted to the bomb through the value until the pressure gauge in the cylinder indicates a pressure of 25 atmospheres. The fuel was ignited by passing a current through the fuse wire. The temperature of both starts increasing and the readings on the thermometer are taken at one minute intervals for 10 minutes, after the maximum intervals for 10 minutes, after the maximum temperature is reached. Thereafter the temperature starts falling slowly. When the temperature fall showed a steady rate the readings were taken at regular intervals for an additional five minutes.

Heat given by the combustion of coal + Heat given by the combustion of fuse wire = Heat taken by the water and calorimeter.

The bomb calorimeter (Parr 6100 model) was used available in the Department of Mining Engineering, Indian Institute of Technology (BHU), Varanasi (Fig. 4.10). The Parr 6100 Compensated Calorimeter takes advantage of the real-time, continuously corrected method originally developed by the Parr Instrument Company. This real-time correction can produce superior results. This feature will make it attractive for coal testing, waste and refuse disposal work, and other sample testing. The data obtained from this study are given in chapter five and discussed in chapter nine.

4.9 X-ray diffraction (XRD)

For further characterization of coal with reference to occurrence of minerals in coal the advance technique available was used. The X-ray Diffraction (XRD) is one such technique which is a rapid and powerful analytical technique primarily used for phase identification and mineralogical characterization of coal. It enhanced the broad view of the structure and composition of the material. It is also widely used for identifying unknown crystalline materials like minerals and inorganic compounds in samples. XRD analysis was carried out in the Central Instrument Facility of Indian Institute of Technology (BHU), Varanasi, India. For XRD analysis, coal samples were identified by Bench Top X-Ray Diffraction (BT-XRD), model name Rigaku Miniflex 600 Desktop X-Ray Diffraction System (Fig. 4.11) and made by RIGAKU Corporation Company, Japan.

Fig. 4.11: Photograph of X-ray diffraction

In this equipment also, first, coal sample (-72 mesh size) was placed in a sample holder tray that makes a very thin sample layer due to its square groove. Sample was then spread on the aluminium holder of the machine and enabled to rotate along with the X-ray beam. That sample holder was then placed inside the tube of the X-ray diffraction analyzer. The scanning was performed from 5° to 90° with using CuKα radiation 30 mA and 40 KV at a stepwise increase of 0.02° and a scanning speed of 0.5 (°)/min. Later, the photographs obtained from the scintillation counter were synchronized to obtain a single image. Various mineralogical compositions present in the samples were identified with the help of the Joint Committee on Powder Diffraction Standards files (Reyes et al. 2003). The graphs obtained from this study are given in chapter five and discussed in chapter nine.

4.10 Scanning electron microscope with energy dispersive X-rays (SEM with EDX)

For determining the elemental composition of coal and coal morphology, advanced technique has also been used. The analysis of coal samples by SEM was carried out by EVO-Scanning Electron

Microscope MA15 / 18 model, of Carl Zeiss Microscopy LTD, while EDX model is 51N1000–EDS System of Oxford Instruments Nanoanalysis for samples (Fig. 4.12). This is also available in the Central Instrument Facility, Indian Institute of Technology (BHU), Varanasi.

For this instrument also, coal sample and shaly coal powder (-72 mesh size) was used for the analysis on SEM with EDX with an airlock chamber. The focused electron beam was used for the scan in SEM, giving details about the topography and composition of the coal samples. EDX in SEM was used for the sample's elemental composition in microstructures. It is a non-destructive technique with high precision and accuracy which identifies the elements and their concentration in the samples. The SEM-EDX analysis provides the elemental/phase composition of a sample.

For assessing the texture, morphology and elemental composition of samples of coal from the areas of investigation, SEM-EDX was employed. The SEM operates by scanning an energetic, finely focused electron beam over a particular feature or field of features. The primary electron beam interacts with the specimen producing a variety of secondary signals that can be monitored with appropriate detectors. It provides detailed spatial and composition information of the samples collected (Willis et al. 2002). Approximately 1 KeV to 20-30 KeV is the energy range of the

Fig. 4.12: Photograph of SEM with EDX

primary electron beam for the sample analysis, enabling the instrument to visualize the image in a high resolution or X-ray microanalysis. Approximately 35 samples were investigated to determine the elemental analysis of coal along with morphological study also. Here, in this study, the samples were first crushed and dried to remove any moisture present in samples for 3-4 days. After this, it was passed through the sieve of 212 µm size, and then it was mounted over the aluminium stubs of the instrument.

The photomicrographs at various magnifications were taken by a secondary electron detector at 20 kV voltages, while the particles present in the samples were obtained at 15-30 kV. Therefore, it can be said that SEM-EDX is one of the most widely and accurate techniques for the evaluation of elemental determination of the coal.

4.11 Fourier transforms infrared spectroscopy (FTIR)

FTIR is also an advanced technique and utilized as a principal tool to understand the structure/ composition of minerals in coal. This method can be utilized to characterize a coal sample's inorganic and organic matter, mainly organic compounds in the coal samples. It provides information about the structure or composition of the functional groups present in the minerals of coal samples (Dun et al. 2013; Behera et al. 2018). The shape of all the FTIR spectra is very similar, and a slight change occurs in the intensities of the band related to the minerals, while no change is noticed in the corresponding organic compounds of coal. The principle of FTIR is based on the study of the interactions between infrared radiation and matter. The electric vector of light interacts with the molecules of the samples, which is to be characterized. This interaction of electromagnetic radiation with the matter under study forms the basis for absorbing a particular Infrared frequency. The relationship used for calculating the energy of a photon is given by,

$$E=h\nu \text{ (Planck's equation)}$$

Where,

E=energy in Joule, h=Planck's constant = 6.6X10-34 and ν = frequency of photon (s-1).

However,

$$c=\nu\lambda$$

Where,

c = speed of light $=3\text{x}10^8$m/s and λ=wavelength of the light.

Therefore, energy and light can be related as

$$E = hc/\lambda \text{ and since } 1/\lambda = \bar{\upsilon}$$

Therefore,

$$E=hc\bar{\upsilon}$$

where $\bar{\upsilon}$=wavenumber

By these above equations, it can be established that frequency and wavenumber are directly proportional to energy, indicating that the higher the photon's energy, the higher its frequency will be (Sahoo et al. 2015). Thus, the infrared spectrum of FTIR has been plotted as intensity v/s wavenumber (Szymanki et al. 1964). Hence, it is plotted from high $\bar{\upsilon}$ to low $\bar{\upsilon}$ from left to right in

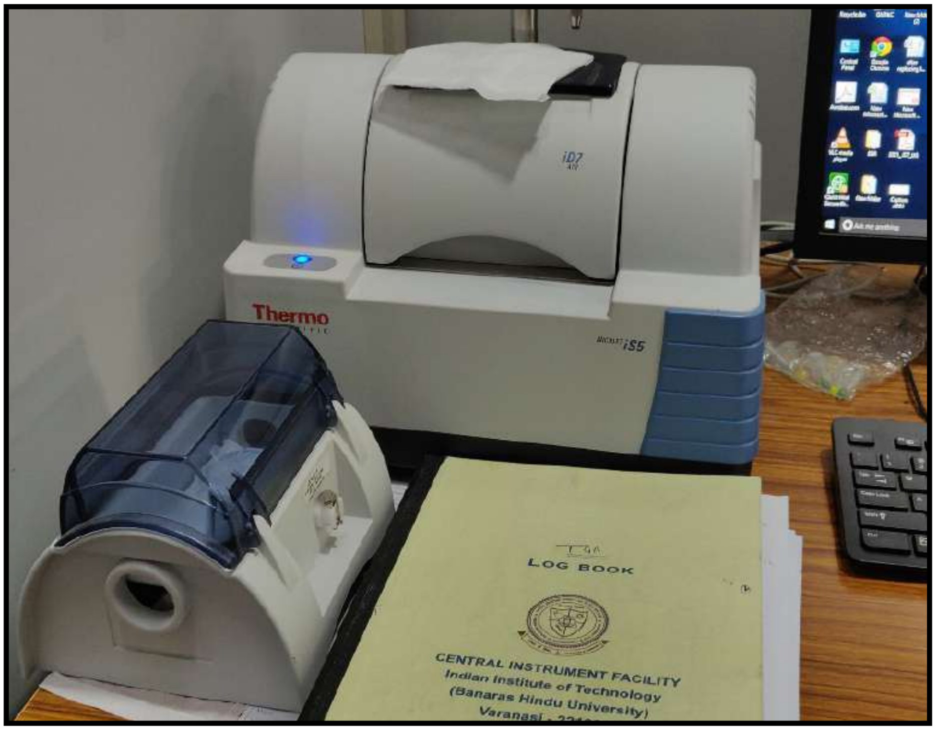

Fig. 4.13: Photograph of FTIR

the mid-infrared region of 4000 to 400 cm^{-1} indicating high to low energy distribution for organic molecules (Doshi 1998). The basis of FTIR quantitative analysis is Beer's law which is as follows:-

$$A = \varepsilon l c$$

Where,

A = absorbance, ε = absorptivity (proportionality constant between concentration and absorbance), l = path length and c = concentration.

The samples were carried out in the analytical facility of the Central Instrument Facility, I.I.T. (BHU), Varanasi, India (Fig. 4.13). This analysis was done by the Nicolet iS5 model and company name THERMO Electron Scientific Instruments LLC. One gram of a powdered coal sample (-72 mesh size) was mixed with ten mg of KBr powder to get a homogeneous mixture. The samples were prepared by the K-Br method. A sample was mixed with the K-Br for making pellets and then pressed by the eight ton hydraulic pressure. After that, the sample was placed in the compartment of the sample holder. Infrared Rays of the analyzer were passed from the sample, and then graphs were plotted between the transmittance and wave numbers of that sample. To provide an adequate characterization of a mineral by infrared spectroscopy, the spectrum was recorded in the range of 4000-400 cm^{-1}. FTIR instrument and spectra of each collected sample were observed by using the software for accessing the presence of various functional groups present in the samples. The graphs obtained from this study are given in chapter five and discussed in chapter nine.

4.12 Inductive coupled plasma mass spectroscopy (ICP-MS)

The advance analytical technique of reputed national laboratories was also availed. The Agilent 7700 ICP-MS of Birbal Sahni Institute of Palaeosciences, Lucknow, Uttar Pradesh, India was used to analyze the coal and associated samples for trace and rare earth elements (Fig. 4.13). The Agilent 7700 ICP-MS produces unparalleled accuracy and precision in high-matrix samples, with the help of redefining cell performance in helium mode with a revolutionary 3rd generation cell design, the

ORS3. Microwave digestion and inductively coupled plasma mass spectroscopy were used to determine REEs' and trace elements concentrations in the samples (ASTM D6357–11). In this equipment digested samples are required. Coal and coal ash samples were digested by a mixture of aqua regia and hydrofluoric acid, and finally dissolved in 1% nitric acid. Coal combustion residues were digested. 20 samples in total were analyzed by this instrument.

The leachate obtained after coal leaching under different leaching conditions were also analyzed for trace and rare earth elements. USGS standards were used (SGR-1B, SCo-1 for shale samples, and CLB-1 for coal) for analysis of the samples.

Fig. 4.14: Photograph of ICP-MS

4.13 Leaching experiment on coal (Experiment 1 - Slow method)

4.13.1 Materials

Leaching test is a standard method for study of metal migration from coal and other material (Townsend et al. 2003). Acrylic sheets were used in the model box with a funnel and a collector to collect percolated solutions from above (Fig. 4.15 and 4.16). The model box dimension was 40 cm * 18.5 cm * 12.5 cm with 0.5 cm (5 mm) thickness of the acrylic sheet. Coal blocks filled up to 30 cm in height in the model box. First, ultra-pure de-ionized (D. I.) water (i.e., resistivity > 18 MU-

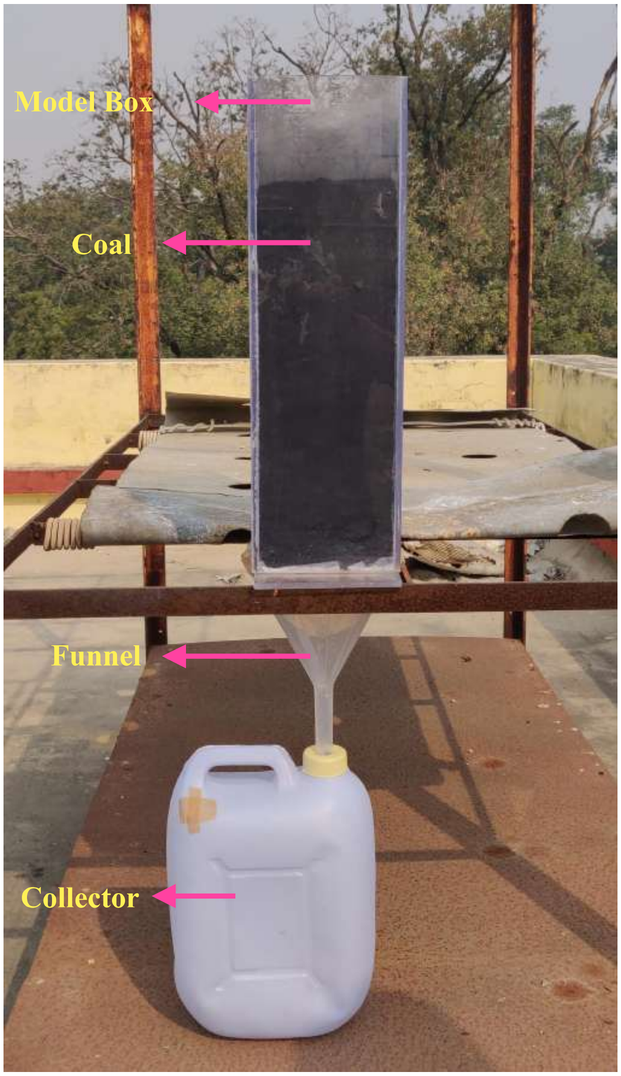

Fig. 4.15: Experimental model of leaching column system

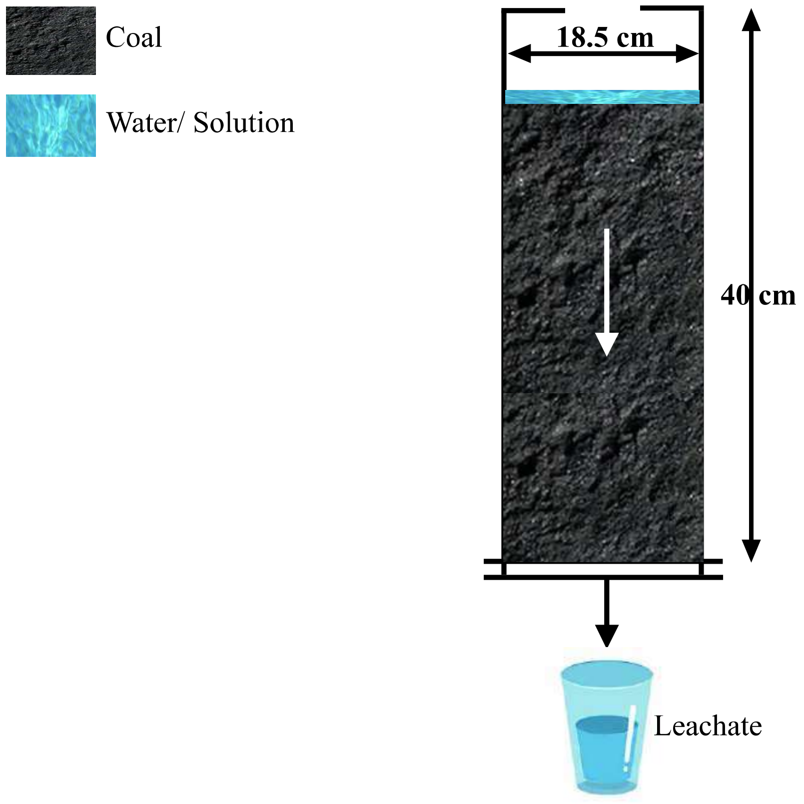

Fig. 4.16: Schematic representation of the laboratory column for leaching experiment

cm) were utilized during the leaching experiments (Type I water per the ASTM D1193-06 standard).

The pH of water was 7.05 at 22°C. At the same temperature, conductivity was 36 µS/cm of water. After water, acid (i.e., nitric acids) was used for conducting the experiment through leaching. The nitric acid was of trace metal grade, used in all experiment work.

4.13.2 Experimental methods

This experiment was conducted in the Department of Mining Engineering, Indian Institute of Technology (BHU), Varanasi, India. The setup was put in a place on the roof of the department in presence of sunlight. The recorded temperature were varied from 15°C to 25°C during the entire experiment for optimum recovery as discussed in chapter three. The setup was capped from top with silver foil to minimize the evaporation and contamination from surroundings. It took around 90 days for completion. That's why it is called 'slow method'.

Leaching experiments were conducted on the coal samples using a common acid (i.e., HNO_3) to assess the acid effects on coal seams in the laboratory. Parameters and conditions were used or plotted here to mimic the natural conditions as much as possible. Water leaching and acid leaching were plotted to break the glassy phases due to silica-containing in coal and remove water-soluble and acid-soluble products to improve REEs recovery with other valuable elements from coal correspondingly (Pan et al. 2021). A basis assumption in leaching is that the distribution of the leaching solution is uniform and that all particles were exposed equally to the leachant solution. This will also help to see the movements or mobility of toxic elements from coal in the surrounding formations.

To break the glassy phase of coal samples, mostly in ash form (by containing silica), it is needed to make it porous with the help of water through the leaching. The solid to liquid ratio was 1:10 in this experiment. This ratio was chosen as per literature review and findings from researchers with little modifications. For this, first water leaching took place 14 times in sunlight conditions. Approximately 1300 ml of water was used every time for leaching in the coal sample, and a total of 18,200 ml (≈ 18.2 litre) of water was used to make coal porous and for leaching. The solutions (water or acid) were poured in coal sample drop wise from the top. After water leaching, coal samples went through acid leaching 10 times with increasing acidic conditions every time (increasing molarity of solution). The molarity of acidic solution varies from 1.8 *M* (lowest) to 2.5 *M* (highest). These molarities were chosen so that it can be applied on industrial scale in future with minimal disturbance and contamination to environment. It is also found in studies that ponds nearby coal mines lead to acidic in nature. These kind of pond can be having a pH of varies from 4.5 to 1.5 on pH scale (Cravotta III et al. 1999).

In short, leaching took place in the experiment with the help of water and an acid solution. The solution percolated through the coal seam in the model box and went to bottom, passing through the tiny pores and collecting in the collector with the help of funnel (Fig. 4.15). After reaching into the collector, the solution was collected every next morning. It was filtered using 2.5 µm pore size filter paper and stored in a dry and cool place at a constant temperature for future analysis. Basic parameters were calculated immediately including the pH of leachate which will be further discussed in coming chapters of eight and nine.

4.13.3 Standard test method

The standard available techniques have been used for laboratory experimentation and analysis. This leaching method is a standard laboratory procedure for generating aqueous leachate from materials using standard dimension of the apparatus. The methodology is almost similar to the standard operating procedure used (ASTM D4874-95). As a result of leaching, received leachates are used to analyzed for major elements, rare earth elements and trace elements. The column leaching apparatus was designed and constructed of material non reactive with solution. Analysis of leachate provides information on the leaching characteristics of material under the conditions used in the experiment. This test method provides for the passage of an aqueous fluid through material of known mass in a saturated down-flow mode. The sample used for this experiment was properly prepared as per standard sampling procedure. It is intended that the sample used in the procedure be physically, chemically, and biologically representative of the material. This test method does produce results that may be used as the sole basis for (1) engineering design of a leaching column, and (2) the characterization of coal based on their leaching characteristics. However, a few limitations of this method are discussed in last conclusion chapter.

4.13.4 Analysis method

Minerals in the coal samples were identified by Carl Zeiss EVO - Scanning Electron Microscope MA15 / 18 with Energy Dispersive X-Ray (SEM-EDS) analysis. The Agilent 7700 Inductivity Coupled Plasma Mass Spectroscopy (ICP-MS) analyzed the elemental content of coal samples. The Agilent 7700 ICP-MS produces unparalleled accuracy and precision in high-matrix samples, with the help of redefining cell performance in helium mode with a revolutionary 3rd generation cell design, the ORS3. Trace elements grade acids (i.e., hydrofluoric (HF), HNO_3, and HCl acids) were used for sample digestions of water samples for elemental analysis by ICP-MS (ASTM D6357–11).

4.14 Leaching experiment on coal (Experiment 2-Fast method)

4.14.1 Materials

The experiment conducted on direct coal and calcined material samples in the laboratory through leaching. The leaching experiment was conducted in the departmental laboratory in room temperature conditions. Polypropylene bottles, funnels, and collectors were used to conduct this experimental work. Polypropylene bottles are chemical resistant and suitable for leaching experiment, were used. The samples were taken approximately 50 g in polypropylene bottles of 272-micron size. The solid to liquid ratio was 1:10 in this experiment. These bottles have numerous apertures at its bottom, from which solution passed from powdered samples and collected in the collector with the help of funnel in between the bottle and the collector (Fig. 4.17). The gaps in the apparatus were sealed properly to minimize the oxidation or contamination from outside in between the junction of experimental setup. These tiny apertures took around 24-72 hours to pass all the solution from bottle to collector. It is a static extraction tests (single addition). There was no shaking of samples or bottle during leaching. After collecting leachate sample, it was filtered using 2.5 µm pore size filter paper. Samples were put into another polypropylene bottle at a constant temperature and for further analysis.

4.14.2 Calcination of samples

The mineral phases change as a result of calcination process in coal samples as reported by some researches (Li et al. 2017; Li et al. 2015; Zhang et al. 2013; Zhang et al. 2014). Calcination treatment of coal led to the significant removal of organic matter (Hower et al. 2016), thus increasing the surface area (Li et al. 2006). It’s seen that pre-heating treatment at 600 °C for 120 min, coal samples resulted in a remarkable increase in REEs recovery which is ranging from

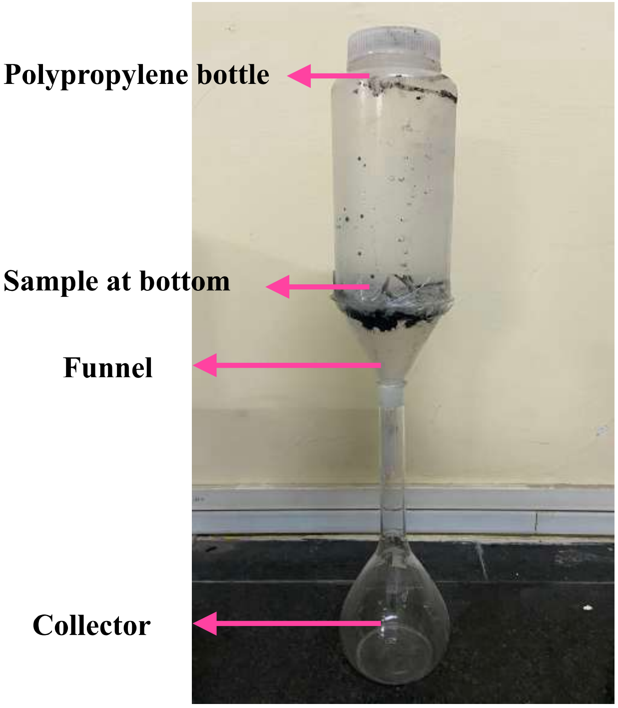

Fig. 4.17: Experimental model of leaching column system

20-80% for coal sources. Comparatively, REEs recovery is higher on 600 °C and 750 °C than 900 °C calcined samples (Honaker et al. 2019).

Calcination of samples was performed in a muffle furnace. The samples were put into the several crucibles (approximately five gm per crucible) as per required (amount) for experiments and placed into a muffle furnace. After putting samples into muffle furnace, the temperature was elevated from room temperature to 600°C at a ramping rate of 10°C/min. This process was lasted for two hours, after which the muffle furnace was cooled down to room temperature. The calcined material was collected from crucibles and uniformly mixed before the leaching experiments.

4.14.3 Experimental methods

For experimental leaching, coal samples were divided into two groups, the first was only raw samples (coal and shaly coal), and the second was calcined samples (Fig. 4.18). The experiment was carried out at room temperature between 25 °C to 45 °C to get the optimum recovery of rare earth elements (Guo et al. 2015). Under normal conditions, the experiment was carried out in a few

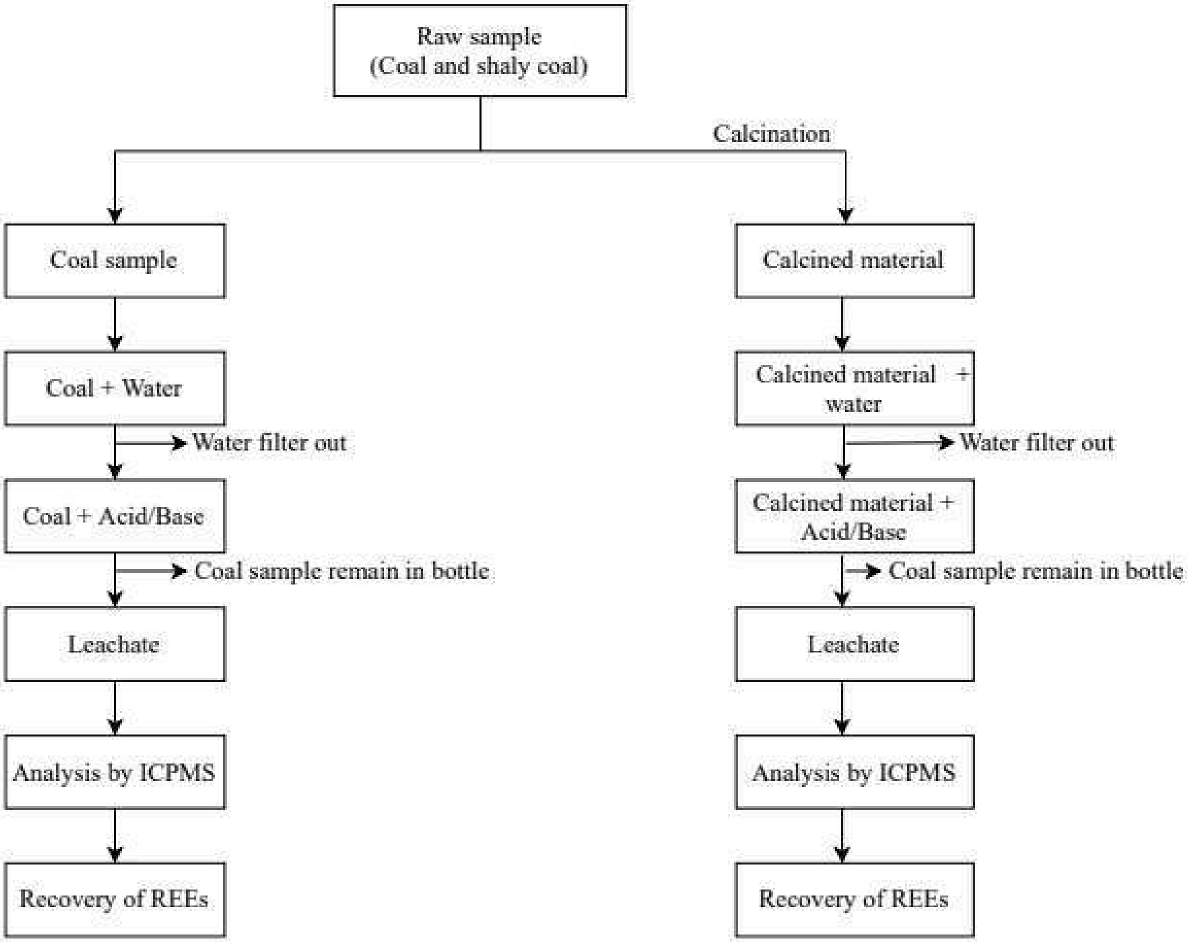

Fig. 4.18: Program diagram of leaching experiment

stages, first leaching with de-ionized water in all samples and second stage with acidic/basic solution (Pan et al. 2020 and Ye et al. 2012). Water leaching results were plotted to reveal the release of various elemental constituents dissolved during leaching. This includes rare earth elements and other valuable elements present in coal. Water leaching results were plotted to reveal the release of various elements present in coal. Water leaching and acid leaching was done to break the glassy phases due to silica-containing in coal and remove water-soluble and acidic/basic-soluble minerals (Wang et al. 2018) to improve REEs recovery and other valuable elements from coal, correspondingly (Pan et al. 2021). To break the glassy phase of coal samples (mostly in inorganic form containing silica), it is needed to make it porous with the help of water through the leaching, for this water leaching was allowed to take place in the absence of sunlight. Known amount of water were allowed to percolate through samples as shown in figure 4.17. After water leaching, the same coal samples were subjected to acidic/basic leaching with a constant molarity of solution. Molarity (*M*) of acidic/basic solution was 2 *M*. In short, leaching was taken place in the experiment with the help of water followed by acidic solution and in some samples with basic solution. The solution was allowed to percolate through the samples in the polypropylene bottle and went to the bottom, where it passes through the tiny pores and ultimately collected in collector with the help of funnel. After reaching into the collector, solution was collected every next morning and stored in a dry and cool place at a constant temperature for further analysis. The exact processes were followed for calcined samples also.

So, seven bottles and samples were used in the experiment. The three samples were chosen and marked as A1 (I), B2 (I) and C3 (I). Sample A1 (I) and C3 (I) were the bituminous coal of G6 grade coal, according to the Indian grading system of coal. B2 (I) was a shaly coal sample. A1 (I) was gone through three experiments of leaching. First one was gone through with basic leaching, the second one was gone through acidic leaching, the third one was gone through a calcined material conversion, and then acidic leaching. The collected solution samples (leachates) were known as recovered and named as A1(R)-B, A1(R)-A, A1(CR)-A. For B2 (I), which is a shaly coal samples as said earlier, was gone through with basic solution leaching and calcined basic solution leaching experiment. Its collected solution samples (leachate samples) were known as B2(R)-B and B2 (CR)-B. The third sample, C3 (I) was converted into calcined material, and then it was gone through with acidic and basic leaching. Its collected solution samples (leachate) were known as C3 (CR)-A and C3 (CR)-B. So a total of seven experimental setups were gone parallel. The program diagram of the leaching experiment is shown in figure 4.18. Standard operating procedure was followed same as discussed for the experiment number one (ASTM D4874-95) previously.

4.14.4 Acidic and basic leaching experiments

There are two main processes that may enhance recovery after calcination. The acid leaching was performed by taking common lixiviants such as sulphuric acid (H_2SO_4) (Seferinoglu et al. 2003). To convert in particular molar solution, ultra-pure de-ionized (D. I.) water (i.e., resistivity > 18 MU-cm) were used during the leaching experiments (Type I water per the ASTM D1193-06 standard). The bottles from the top were covered by aluminium foil and the cap to minimize evaporation. In basic leaching experiment (base leach test), it was performed by taken the sodium hydroxide (NaOH) solution. The solution of NaOH was made up of dissolving the NaOH pellets into the ultra-pure de-ionized (D. I.) water.

4.14.5 Analysis method

The elemental content of samples was analyzed by the Agilent 7700 Inductivity Coupled Plasma Mass Spectroscopy (ICP-MS). The Agilent 7700 ICP-MS produces unparalleled accuracy and precision in high-matrix samples, with the help of redefining cell performance in helium mode with a revolutionary 3rd generation cell design the ORS3. Trace elements grade acids (i.e., HF, HNO_3, and HCl acids) were used for sample digestions of coal samples and shaly coal samples for elemental analysis by ICP-MS. The samples were digested according to the ASTM D6357-11 method. The element in samples and solution samples (leachates) collected after the acidic/basic leaching experiment were analyzed by ICP-MS. It is done in the Geochemistry lab, Birbal Sahni Institute of Palaeosciences, Lucknow, India.

Samples were also analyzed by Carl Zeiss EVO-MA15/18 scanning electron microscope (SEM-EDX). SEM-EDX instrument helps in producing the detailed high-resolution images of sample by rastering a focused electron beam across the surface and detecting secondary or backscattered electron signals. It is done in the Central Instrument Facility of the Indian Institute of Technology (Banaras Hindu University), Varanasi, India.

The powder samples' XRD analysis was performed on Rigaku Miniflex 600 Desktop X-Ray Diffraction System with Cu-Kα radiation as a source. The XRD pattern has been recorded over a 2θ interval of 3-70°, with a step size of 0.0167° in theta configuration.

4.14.6 Experiment samples

For the experiment, we have chosen three samples, A1, B2 and C3. These are known as initial samples (raw samples). Rest is the recovered solution (leachate) after leaching. The sample number is based on experimental and leaching solution methods, for e.g. in A1 (I) sample number, where in bracket alphabet 'I' stands for initial or raw sample, before the leaching, while 'R' stand for recovered solution (leachate), after the leaching. In the same way, the alphabet 'A' stands for acid/ acidic, while 'B' stands for base/basic and 'CR' stands for calcined recovered samples, collected sample (leachate) after leaching. Initial (I) means, concentration of REEs in hard sample (raw sample), while recovered (R) or calcined recovered (CR) means, concentration of REEs in collected solution samples (leachate) after leaching.

4.15 Factors affecting leaching

Several factors may affect the leaching process in samples. These factors include the physical factors and chemical-biological factors. Factors influencing chemical leaching from coal material may include pH, complexation with organic or inorganic chemicals, leaching (or contact) time, common ion effect, etc. Factors influencing physical leaching from coal material may include particle size, surface morphology, contact time, homogeneity, liquid to solid ratio (L/S ratio), porosity, sorption, partitioning, temperature, and type of flow (Townsend et al. 2003). These factors may cause the errors associated with leaching. So, it required to take precautions for minimal errors to these factors.

4.16 Statistical data calculation

In statistics, the standard deviation measures the amount of variation or dispersion of a set of values (Bland and Altman 1996). The main part of the calculation of a standard deviation consists of finding the sum of squares of deviations about the mean (Hill 1979). A low standard deviation indicates that the values tend to be close to the mean of the set, while a high standard deviation indicates that the values are spread out over a wider range. In science, it is widely used to know the variance in data samples for significance. Here standard deviation is calculated for the samples from the formula as follows:

$$\sigma = \sqrt{\frac{\sum(x_i - \mu)^2}{N}}$$

Where,

σ= Samples standard deviation

N= The size of the samples

x_i=each value from the samples

μ= the samples mean

Photographs of crushing, measuring and drying of coal related to laboratory work

Fig. 4.19: Photograph of pulverisation of coal samples

Fig. 4.20: Photograph of weighting of coal samples

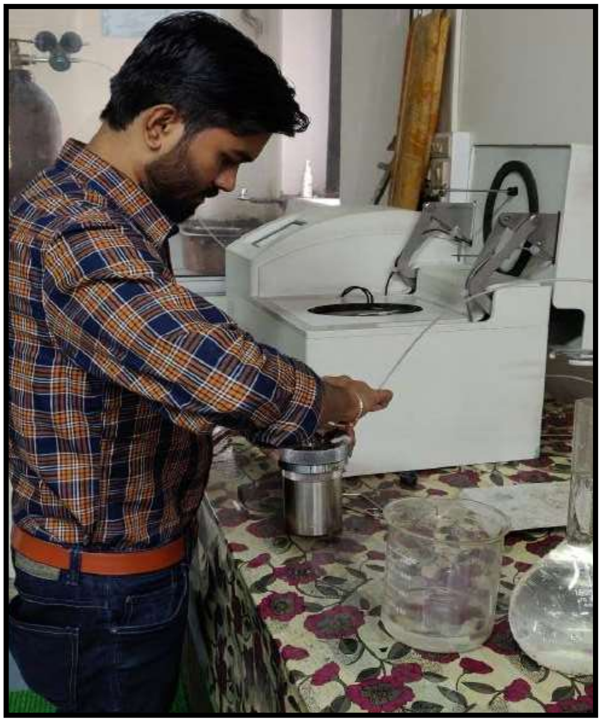

Fig. 4.21: Photograph of operating Bomb calorimeter

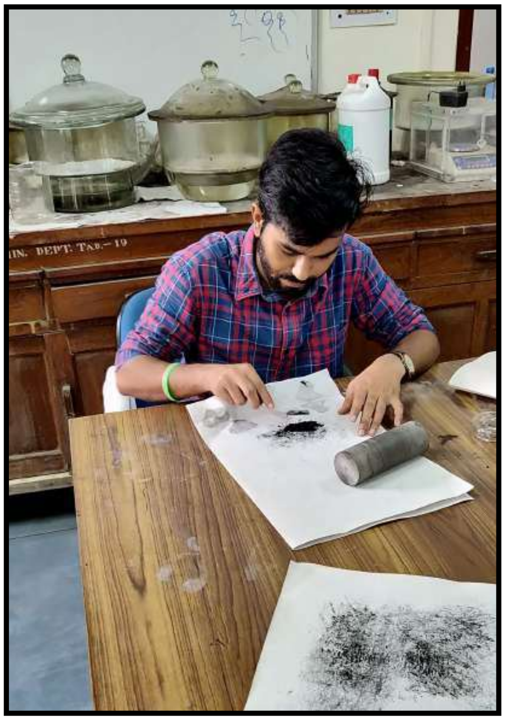

Fig. 4.22: Photograph of drying coal samples