Chapter-3

Review of Literature

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3.1 Previous works

This chapter deals with the details of the previous work done by several researchers on various aspects of coal characterization, coal quality and qualitative & quantitative study regarding REEs in coal and coal by-products, along with recovery.

Coal meets a large part for energy requirements, and plays a very important role in mineral industry. It outranks all other sources of utilizable energy such as petroleum, natural gas, wood, water, power, solar and atomic energy. India's industrial development has been founded on the country's coal resources (Ministry of Coal, GOI 2022). A number of steps, taken to step up coal production have resulted in continuously upward trend in production touching 226 million tonnes in 1990-91 to 783 million tonnes in 2020-21 against world production of 4,738 million tonnes in 1990 to 8,000 million tonnes in 2020. Coal is a non-renewable fossil fuel that is combusted and used to generate electricity. Coal is essential for power industry in countries such as India and China (IEA 2020). Worldwide use of coal will continue to extend for the next several decades (Foreman et al. 2014).

Coal is a sedimentary deposit composed predominantly of carbon. Coal begins as peat, which consists of loosely consolidated layers of various mixtures of plant and mineral matter. Over millions of years, burial, compression by overlying inorganic sediments, and the effects of heat (from depth in the earth) cause peat to change to coal (USGS, 2003).

Coal is an organic-sedimentary rock that contains organic and inorganic materials. Due to the heterogeneous nature of coal, many analytical techniques were used to characterize coal. In recent years, many advanced techniques have been used in analysis. This sophisticated analysis helps to understand more about coal and its characterization.

To understand the behavior of coal, characterizing and understanding its physical properties is of paramount importance (Xie et al. 2015). Diessel's classification (1965) is significant for understanding the banding nature of coal (coal bands) in hand specimens. It also supports to understand the origin of peat formation during coalification and paleo-environment conditions (Stach et al. 1982). It is usually unfeasible to study the entire formation, hence representative sample have been collected to achieve the objectives of research work.

Selection of sample is an initial and crucial stage because that particular sample will represent the whole area of interest (Martínez-Mesa et al. 2016). The method of sample selection should be widely used and acceptable. Coning and quartering method is reliable and widely used because it does not require any apparatus or mechanical equipment. After carefully collecting samples from the field, they should be first divided by the coning and quartering method into four segments, the diagonally opposite of which are discarded. The coning and quartering method is extended till a proper sample volume is attained as requirements (Alakangas 2015). Hence, the selected sample will unveil the characteristics of coal in area of interest.

Qualitative and quantitative analysis of coal give a glimpse of geochemical parameters such as mineral matter, trace elements, calorific value, etc (Liu et al. 2005). All these useful information are helped to understand rank, grade and type of coal. It also provides a scope for the coal quality, coal characterization and other aspects of a particular mine. Geochemical data includes studies like proximate and ultimate analysis of coal. The proximate analysis of coal is presented as a group of test methods (ASTM

D3172; ASTM D3173; ASTM D3174; ASTM D3175; ASTM D5142; ISO 1171) that has been used widely as the basis for coal characterization. This analysis of coal is an assay of the moisture, ash, volatile matter, and fixed carbon as determined by a series of standard test methods (Earnest 1982; Earnest and Culmo 1983; Earnest 1984; Riley 2007). Moisture content in coal is very useful for coal combustion in thermal power plants.

There are several sources of the moisture that occurs in coal. All coals are mined with some moisture, such as (1) adventitious moisture, which consists of groundwater and other extraneous moisture (surface moisture), which can be evaporated, and (2) inherent moisture, which occurs within the pore systems of the coal and is analyzed quantitatively. These all constitute to moisture percentage in coal and it varies in different type and ranks of coal (Stach et al. 1982).

Ash is the non-combustible residue left after coal is burned and represents the bulk mineral matter after carbon, oxygen, sulfur, and water have been driven off during combustion. The test method is reasonably straightforward, with the coal thoroughly burned under specified conditions, and the ash yield is expressed as a percentage of the original weight (ASTM D3174; ISO 1171). The ash is composed primarily of oxides and sulfates, and it should not be confused with mineral matter which is composed of the unaltered inorganic minerals in coal (Given and Yarzab 1978; Speight 2013). There are two types of minerals in coal: (1) extraneous mineral matter and (2) inherent mineral matter. The extraneous mineral matter consists of materials such as calcium, magnesium, ferrous carbonates, pyrite, marcasite, clay, shale, sand, and gypsum. Inherent mineral matter represents the inorganic elements combined with organic components of coal that originated from the plant materials from which the coal was formed (Singh et al. 1983).

Volatile matter in coal refers to the components of coal, except for moisture, which is liberated at high temperatures in the absence of air. Briefly, volatile matter consists of various paraffin-type hydrocarbons, aromatic hydrocarbons, and sulfur-containing (and other heteroatom-containing) compounds. The composition of the volatile matter evolved from coal is substantially different for the different ranks of coal, and the proportion of incombustible gases increases as the coal rank decreases (Stach et al. 1982).

Fixed carbon is the material remaining after determining moisture, volatile matter, and ash. The data produced should not be confused with the carbon content of coal as determined by ultimate analysis since some carbon is lost in hydrocarbons with volatile matter. The fixed carbon value is used to estimate the approximate yield of thermal coke from a coal sample, like the carbon residue produced from petroleum fractions (Speight 2014a, b). Fixed carbon is determined by subtracting the mass of volatiles, determined earlier, from the original mass of the coal sample (Speight 2015). The fixed carbon value is one of the values used in determining the efficiency of coal-burning equipment. It is a measure of the solid combustible material that remains after the volatile matter in coal has been removed. Determination of major elemental composition is also very important in coal.

Determination of ultimate analysis represents the elemental composition of the organic material in coal in terms of carbon, hydrogen, nitrogen, sulfur, and oxygen (White and Whittingham 1983). The carbon determination includes carbon content as organic carbon occurring in the coal substance and any carbon present as mineral carbonate. The hydrogen determination includes hydrogen present in the organic materials and hydrogen in all of the water associated with the coal. In absence of evidence to the contrary, all the nitrogen is assumed to occur within organic matrix of coal (Gil 2002). Oxygen is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, and sulphur from 100. The recommended test methods for elemental analysis include the determination of carbon, hydrogen (ASTM D3178), nitrogen (ASTM D3179), and sulfur (ASTM D3177; ISO 334; ISO 351).

On the other hand, sulfur occurs in three forms in coal: (1) organic sulfur compounds, (2) inorganic sulfides that are mostly the iron sulfides; pyrite and marcasite, and (4) inorganic sulfates (Chou 2012). The sulfur value presented for ultimate analysis may include inorganic sulfur and organic sulfur. Concentration and variation of sulfur in coal is closely related to the depositional environments of coal seams (Chou 2012).

Nitrogen occurs almost exclusively in the organic matter of coal. Very little information is available concerning the nitrogen-containing compounds in coal, but they appear to be stable and are thought to be primarily heterocyclic (Patnaik 2007). The main source of Nitrogen in coal is protein present in plant and animal. Plant alkaloids, chlorophyll, and other porphyrins contain nitrogen in cyclic structures stable enough to have withstood changes during the coalification process and thus have contributed to the nitrogen content of coal (Flaig 1968). Oxygen occurs in both the organic and inorganic portions of coal. It is determined by subtraction of all major elements from 100. Due to heterogeneous nature of coal, several analytical techniques are required for its characterization.

Many analytical techniques are involved in the assessment of coal in academics and industries. Sophisticated instruments are used such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), focused ion beam (FIB), high-resolution transmission electron microscope (HR-TEM) with selected area electron diffraction (SAED) and micro-beam diffraction (MBD), scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectrometer (EDS), and thermogravimetry (TG-DTG). Recent, most advanced studies for coal analysis help more to understand the coal quality and its relation with others (Saikia et al. 2016). XRD profiles support the presence of mineral contents in the coals.

Many minerals are found in coal which led to the contribution of coal ash. According to F. Reyes et al. (2003), in his studies, mineral phases identified are quartz, kaolinite, pyrite, gypsum, and sometimes dolomite and calcite in coal samples. XRD is used for the identification of mineral phases present in coal samples. The XRD analysis showed significant differences between the low-rank sapropelic and humic coals, although bituminous coals have a structure similar to that of humic coals of the same degree of coalification (Bodoev et al. 1996). It is also supported by the nature of bonding in functional groups present in coal.

FTIR plays a very crucial role in identification of functional groups and its bonding. Many functional groups can be identified in coal samples from FTIR. In the organic portion, oxygen is present in hydroxyl (–OH), usually phenol groups, carboxyl groups (-COOH), methoxyl groups ($–OCH_3$), and carbonyl groups (=C=O). In low-rank coal, the hydroxyl oxygen averages about 6–9%, while high-rank coals contain less than 1%. The percentage of oxygen in carbonyl, methoxyl and carboxyl groups average from a few percent in low-rank and brown coal to almost no measurable value in high-rank coal. FTIR analysis indicates the presence of aromatic hydrogen, aromatic carbon, aliphatic stretching, aliphatic bending, OH functional group within the organic matter and presence of kaolinite, quartz and carbonates within the studied samples (Varma et al. 2016).

Different types of surface morphologies, different types of pores and pore shapes in the organic matter are identified by scanning electron microscope (SEM). SEM examination may detect some inorganic matter, especially amorphous materials that are not revealed by X-ray diffraction analysis (Wang et al. 1997). SEM analysis can be beneficial to see the properties of coal surface before and after the leaching effect on it for comparison. It may also unveil the matters (matrix or framework grains) involved in the leaching process (Guangyin and Youcai 2017).

A new characterization method is proposed to investigate the microscopic morphology of the intumescent fire retardant (IFR) char layer observed under a scanning electron microscope (SEM). The method consists of object segmentation extracting the object, color transformation, improving the recognition of subtle details, and statistical analysis to obtain the features (area, average, and standard deviation) of the object in the SEM images. It is a new method to study various materials with the help of SEM (Sun et al. 2020). Elemental and weight percentage is also detected by SEM-EDX. However, quantitative elements in coal is required some more investigations.

Coal contains most of naturally occurring chemical elements, and some of the elements are toxic (Orem and Finkelman 2003). These toxic elements are present in different contents and forms, depending on different geologic and geochemical processes that have occurred during peat and coal formation. As a result, their existence in coal is specific to where they are found. These toxic elements remain as such in coal waste (coal ash) after coal combustion.

Selected important elements such as copper, cadmium, zinc, nickel, chromium, lead, manganese, aluminium, iron and cobalt are also reported in lignite samples (Rajak et al. 2018). Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) is required to know the association of minerals with organic matter. The concentration of cobalt, nickel, cadmium, lead, sodium and potassium are also high compared to the world average and is the primary concern for environmental and health hazards in samples. The elements like iron, calcium, magnesium, zinc and lead have shown an increasing trend from top to bottom of the lignite seam with some fluctuations in the values in a few bands, whereas others do not follow a definite trend of variation along with the seam profile in previous studies of researchers (Singh et al. 2019). These elements are remained as such in coal ash (Jones 1995).

Coal ash, a by-product of coal combustion, is more enriched with several harmful trace elements compared to its parent coal-state due to the depletion of organic matter in coal during combustion (Fernandez-Turiel et al. 1994; Meij 1994; Baba et al. 2003; Jankowski et al. 2006). With the help of advanced studies and instruments, it is necessary to identify these elements in coal samples. Coal mining and processing led to the deposition of a clay mineral known as coal gangue (Li et al. 2013). Many developing countries are producing a massive amount of clay minerals; e.g. China produced 750 million tons in 2013. So, it has become one of the largest industrial solid wastes (Annual reports of China, 2014). Hence, it should be utilized in some other form to protect the environment.

The contributions on Indian coals are given by Mukherjee et al. (1982), Singh et al. (1983, 1985), Mukherjee et al. (1988); Singh (1991), Mukherjee et al. (1992) and Chandra and Singh (1994) in several coalfields. In their studies, source, concentration and accumulation of the trace elements in coals have been suggested through the following natural processes:

1. The elements absorbed by the plants from the soil or crust (concentrate mainly in biogenic ash).

2. The elements associated with the mineral matter (sediments) brought into the basin along with the vegetal matter through the natural transporting agencies (concentrate in terrigenous ash).

3. Metals contributed by the surface as well as underground circulating waters during the primary stages of coal formation. Most of these trace elements form organometallic complexes in coal.

4. Trace elements together with mineral matter deposited in the coal microstructures and deformational passages in the coal seams through surface as well as underground circulating waters.

5. Trace elements deposited through the hydrothermal solutions during the igneous activity in and around the coal basins.

The enrichment of trace elements in coal is mainly controlled by the following factors:

1. pH and Eh of the depositional basins,
2. Duration of supply of trace elements during the initial stages of coal formation,
3. Rate of maturity of coal (Time Vs Rank),
4. Intensity of circulation of solutions,
5. Quality and quantity of the prominent sorbents (humic substances),
6. Nature of ash,
7. Micro-structural framework of the coal seams,
8. Porosity of the overlying and underlying rocks, and
9. Rate of sedimentation and tectonics of the coal basin.

These trace elements remains as such in coal (in coal fly ash) after its combustion. Hence, disposal of coal fly ash (CFA) may lead to severe and long-lasting environmental issues by conventional methods, but CFA is a valuable industrial solid waste. The study of technologies for CFA recycling has been a significant concern, while the harm caused by CFA is only partially understood, limiting its reuse (Wang et al. 2020). According to statistics, the amount of CFA produced globally annually is approximately 600-800 million tons (Jayaranjan et al. 2014). USA and Europe contribute 10% of this, while India and China account for nearly 18% of global production (Jana et al. 2017; Wang et al. 2018). Currently, CFA is stockpiled in landfills, monofills (landfills in which only CFA is disposed of), and ponds or is disposed of by simple stack (Valeev et al. 2019). However, these disposal methods are not environmentally friendly because they can lead to various types of contamination by leaching, radioactivity and toxicity of CFA.

Researchers started investigating appropriate techniques for the reuse of CFA in the 1970s, which could be used to avoid CFA contamination in the environment (Fleming et al. 1979). In the 1980s, pozzolanic reactivity was first discovered when the possibility of using CFA as a raw material for construction was realized (Sybertz 1988). CFA started to be used in constructing roads, roadbeds, pavements, landscaping, and embankments, among others, and large amounts of CFA were reused (Turner 1997). However, the amount of CFA reused is still less than the amount generated (with only < 30% reused) (Jayaranjan et al. 2014; Larsen et al. 2016). Therefore, the methods mentioned for the reuse of CFA can only relieve the pressure of excessive production in terms of environmental pressure, and pollution is still unavoidable. Based on the physicochemical properties of CFA, it contains a high abundance and wide variation of valuable elements

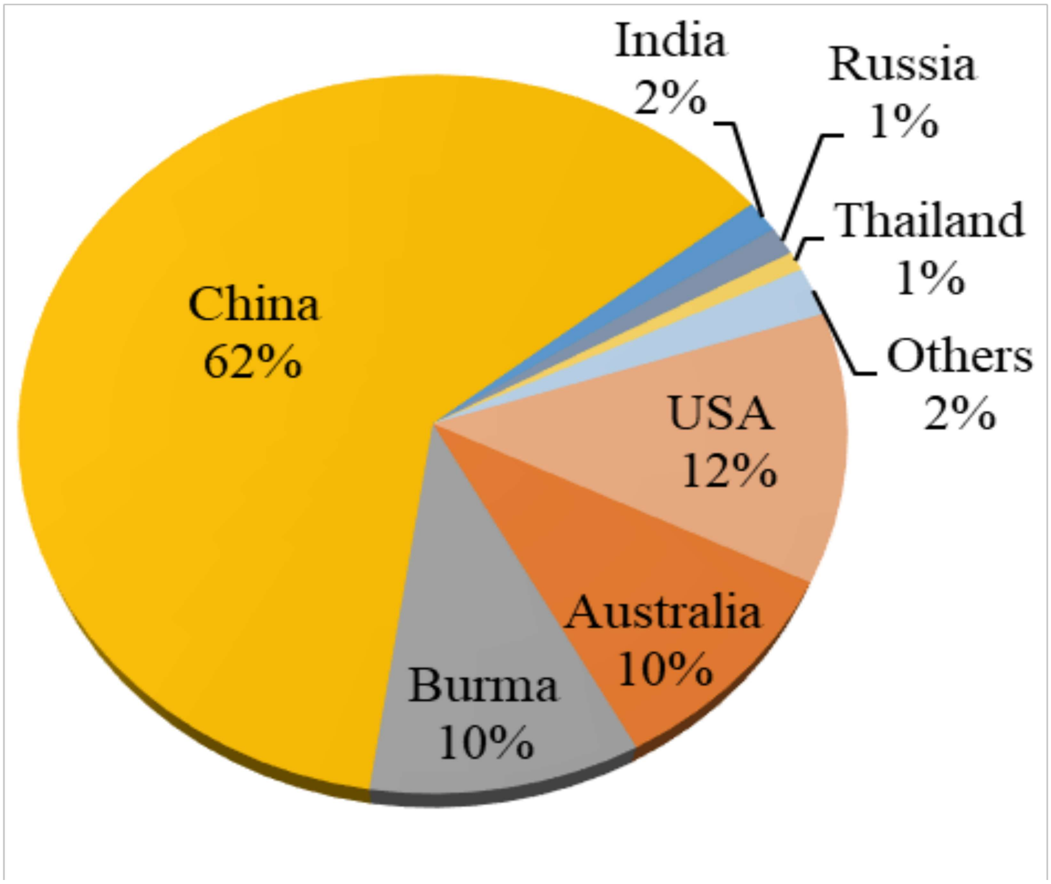

Fig. 3.1:REEs production by different countries.

(such as Si, Al, Fe, Mn, Zn, and Cu) (Mashau et al. 2018). Hence, CFA has the potential for other resources or elements that must be studied.

With the depletion of primary materials (high-grade ore), the secondary resource (materials) become the primary source to encounter the future growing requirements (Barik et al. 2012). For example, the shortage of bauxite and the alternative demand for it (Guo et al. 2013 and Li et al. 2014). Coal and coal ash also contain considerable amount of valuable elements (Dai et al. 2016a). These valuable elements are also important strategically.

There is a wide range of applications of REEs in defense, and national security fields, some of the elements are listed as strategic or critical materials because of the uncertainties in supply and prices (Fan et al. 2020). The global production of REEs was

210,000 metric tons of REO in 2019 (Sangine 2019). Productions of REEs in different countries are shown in figure 3.1. REEs have been coded as critical materials by several international institutions and governments due to their supply risks and importance to the clean energy industry, advanced military applications, and many commodity items in high-tech industries (Binnemans et al. 2013, Chu 2011, DoI US 2018; European Commission 2015). For this reason, it has become essential to search for alternative resources for supplying REEs, including unconventional resources. Coal and coal by-products are identified as a particular candidate among them with a strong incentive (Dai et al. 2016b).

The REEs within coal sources have received recent attention due to the abundance of coal sources and the need to diversify the supply base (Dai et al. 2008 and Hower et al. 1999). The forms of REEs in coal may include different types of minerals and associations, such as accessory minerals (allanite, monazite, xenotime, etc.), resistant minerals (florencite, zircon, etc.), and clay minerals (illite, kaolinite, etc.) (Zhang and Xu 2015).

REEs are, in fact, abundant in the earth's crust. However, the mode of occurrence and the complex circuitry needed to concentrate the REEs makes economic recovery challenging (Oudenhoven et al. 2016). For most of the rich deposits worldwide, REEs primarily exist in mineral form in which the concentrations are measured in percent of total weight. Secondary resources typically have low REE concentrations measured in parts per million and include those associated with ion adsorbed clays (Peelman et al. 2014).

As per studies, based on earth crust normalization cobalt, nickel, arsenic, selenium, molybdenum, zinc, lead, uranium and REEs (except Pr and Er) are enriched in the low grade coal ash; molybdenum, zinc, caesium, lead thorium, uranium, lanthanum, cerium and lutetium in the refuse ash; and molybdenum, zinc, strontium, caesium, lead and lutetium in the biomass. Quartz is the most abundant mineral species in this context (Ram et al. 2011). Other minerals are mullite, hematite, gehlenite, anhydrite, and calcite in the lignite ash; orthoclase in the refuse ash; albite, sanidine, gehlenite, anhydrite, and calcite in the biomass ash. Most rare earth-bearing minerals, especially carbonates and phosphates, are rich in light REEs (LREEs), i.e., cerium, lanthanum, neodymium, promethium, samarium, and scandium (Jha et al. 2016). The genesis of rare earths is heterogeneous and complex. They are found in various host minerals, such as halides, oxides, phosphates, and silicates (Rim et al. 2013; Suli et al. 2017).

Certain studies have given evidence of REEs in coal, but it also associated with the minerals. Many studies have reported that some REEs are associated with pyrite contained in coals (Dai et al. 2014; Hower et al. 2015; Pan et al. 2018). Pyrite was converted to hematite after calcination, and thus the REEs originally associated with pyrite likely reported to the iron oxides in an ion-substitution form. Kolker et al. (2017) found that Fe-oxide magnetospheres in fly ash also contained REEs using a SHRIMP-RG ion microscope, which agrees with the conclusion of their study. Coal geological studies have also reported that LREEs are more likely associated with clays relative to HREEs (Eskenazy 1987; Seredin 1996).

According to Cunliang Zhao et al. (2016), the conclusions of their study are based on new data and evidence that suggest the considerable enrichment of Ga-Rb-Cs-REEs and Y in the No. 6 coal of the Iqe Coalfield may be a hidden treasure with yet to be realized additional economic potential if such rare metal enrichment is proven across the whole area of Iqe Coalfield. The No. 6 Coal is enriched in Al_2O_3, SiO_2, Na_2O, MgO,

P_2O_5, K_2O, TiO_2, Rb, Cs, Ga, Sc, V, Cr, Cu, Ba, W, Pb, Th, and REY, especially in Ga, Rb, Cs and H-REY, compared to world coals. The average contents of Ga, Cs, Rb, and REY are 3.1, 12.3, 6.0 and 3.5 times higher than those of world bituminous coals. Gallium may occur in clay minerals (e.g., kaolinite), particularly in potash-rich clay minerals (e.g., illite), which are thought to be derived from the Qilian Mountain Range. These minerals are probably the hosting phases for rubidium and caesium in the coal studied. REEs and yttrium in the coal are more likely to be associated with phosphates. The combustion products (e.g., fly and bottom ash) derived from those coals may be further enriched in these valuable rare metals and have economic potential in the recovery of gallium, rubidium, caesium, REEs and yttrium, providing additional economic value to this coal deposit. This kind of research works in global context encourages to look for valuable elements in Indian coals.

The presence of rare earth elements and yttrium (REY) in northeast Indian coal, mine overburden, and fly ash samples is also reported for the first time by Saikia (Saikia et al. 2014). Identifying these components may be significant from an economic point of view. Some Northeast Indian fly ashes, with REE oxides up to 1580 ppm on an ash basis, might represent sources for recovering REEs. Four genetic types of REE accumulation in coal have been identified: terrigenous, tuffaceous, infiltration, and hydrothermal (Crowley et al. 1989; Seredin 1996; Seredin and Dai 2012; Hower et al. 2016).

Rare earth elements were also reported in coals collected from Gondwana basin in India. The area of a basin is comprised of two coal-bearing formations, i.e., Karharbari and Barakar formations. Samples collected from one borehole were analyzed by X-ray diffraction, X-ray fluorescence, electron microprobe and inductively coupled plasma mass spectrometry (ICP-MS). The coals are medium to high volatile, with high ash and low sulphur. The rare earth elements and yttrium (REY) of the 34 coal samples vary from 29.6 ppm to 179.4 ppm, averaging 91.0 ppm. So, Indian coals also have the REE content in them. Coal naturally contains REEs at concentrations above crustal averages due to the chelating ability of humic acids that existed significantly during the initial coalification process (Mishra et al. 2019).

As earlier said that there is evidence of metal concentration in coal and CCPs. It is a big question, how these elements react with water. When coal and coal ash come in contact with water, their hazardous constituents may be leached or dissolved out and contaminate surface water, groundwater, and soil in different proportions (PSR 1995; Baba et al. 2003). Many trace elements that are typically mobilized as cation were also more abundant in leachate from the co-fired fly ashes. It is due, most likely, to the more acid pH conditions involved. Mobility of trace elements also depends upon the mineral and elemental characteristic of coal ash (Silva et al. 2010). It can affect the surrounding habitat due to mobility.

The Sohagpur coalfield area is located in one of the most environmentally sensitive areas since it is surrounded by rivers used by the local community for domestic, municipal, fishery, livestock raising, and irrigation purposes. Therefore, leaching hazardous elements from coal and coal ash could cause enormous problems for the local community. Consequently, it is crucial to understand the leaching of toxic trace elements. It is also important to recover the valuable elements from coal with the help of leaching.

According to Wencai Zhang et al. (2015), coal is a valuable resource not only for its energy content but also for the metals enriched within it. Many have realized the potential value of REEs in coal, and the increasing demand for REEs continues to drive the exploration of REEs recovery from coal. So, according to Zhang et al. (2019), studies on coal provides a review of the abundance, mode of occurrence, and recovery methods of rare earth elements in coal and coal by-products. The feasibility of using established REEs extraction and recovery technologies is discussed, along with issues associated with their use of coal resources. It is increasingly essential to recover critical materials from alternative and secondary resources due to their important role in critical areas (e.g., clean energy and advanced electronic technologies) and an uneven production distribution worldwide. The findings from several attempts to recover rare earth elements (REEs) from coal-related materials have been reported in several recent publications (e.g., coal, coal refuse, coal ash, and coal mine drainage). Leaching of the tungsten material (infiltration input), detrital mineral input into the peat, and subtle hydrothermal fluid from the south-east side also caused the enrichment of REEs in the upper and lower benches of the coal seam.

Fractionation of the REEs in coal seams occurred due to the different genetic types and chemical nature of REEs. The findings of several studies report that heavy REEs (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) are more likely enriched in low-ash content coals than high-ash coals (partings, roof, floor, etc.) due to its affinity towards organic matter in coal (Harrar et al. 2022).

The coal-fired power plant generates mass production of coal combustion by-products such as fly ash and bottom ash (Kamal et al. 2019). The leaching of heavy metals fluxes may contribute to adverse environmental and health impacts due to bioaccumulation in soft tissues, toxicity at a certain level of concentration and period of exposure (Malakahmad et al. 2015; Khan et al. 2017; Khan et al. 2016; European Parliament and council 2008).

When coal is used for power generation, the REEs are enriched in ash by-products (fly ash and bottom ash) due to carbon and volatile matter removal. Several studies have been performed to recover REEs from coal ash material (Lin et al. 2018; Taggart et al. 2018; King et al. 2018). It has been reported that most REEs are homogeneously distributed in a glassy amorphous matrix (Hower et al 2013; Ward and French 2005; Pan et al 2018; Wang et al 2019). Strong acidic and basic solutions are required to dissolve the REEs from the fly ash material (King et al 2018; Wang et al 2019). Most leaching studies focus on the acid leaching behavior for the higher mobility of metal elements (Peng et al 2018; Yue and Zhao 2008; Wang 2014; Zhang 2013; Yang 2016). The temperature may promote the water-rock interaction according to the thermodynamics laws (Dash 2015). According to Mohammad Rezaee et al. (2021), the majority of rare earth elements (REEs) in coal fly ash (CFA) are associated with the aluminosilicate glassy phase, hindering their solubility in the acid leaching process. Their study developed a sequential chemical roasting, water leaching, and acid leaching processes to recover REEs from CFA. This process significantly enhanced the REE recovery by using NaOH and Na_2CO_3 roasting, respectively, compared to 20% REE recovery in baseline acid leaching.

Even in India, currently, almost 55% of the power generation is still met by coal. However, Indian coals are low-grade because of the high ash contents (Meshram et al. 2015). The ash contents in Indian coals vary from 5% to as high as 55%, most Indian coals with an average ash content of 35%.

Battsengel et al. (2018) have reported REEs recovery in their research article. They recovered the rare earth elements from an Apatite ore sample by using sulphuric acid leaching, solvent extraction, and precipitation processes. Results showed that the most effective dissolutions of light REEs (> 85%) and heavy REEs (> 89%) from the

Apatite ore sample were achieved with a dilute sulphuric acid solution (1 *M* H_2SO_4) at a temperature of 20 °C in an hour. There are several REE extraction methods which are still in process. Hydro-metallurgical extraction of REEs from rare earth-bearing minerals usually involves strong acid/alkaline, salt or oxidant roasting followed by acid leaching (Kumari et al. 2015; Kemp and Cilliers 2016; Wood et al. 2005).

Laboratory test programs are being done to recover REEs from coal-based resources. Honaker et al. (2014, 2017) found in their studies that the medium density fractions (e.g., 1.8–2.2 specific gravity) of several bituminous coals had the highest contents of REEs with above-average leachability characteristics (Yang et al. 2018; Zhang et al. 2018). Several methods have been explored for the recovery of REEs.

Calcination of coal products can be crucial for recovery. According to Honaker and Zhang (2019), the modes of occurrence associated with rare earth elements (REEs) in bituminous coal sources were evaluated along with their potential recovery by calcination treatment followed by sequential extraction. They collected coal samples from three different resources, i.e., Fire Clay, West Kentucky No. 13, and Illinois No. 6 seams. Sequential extraction tests indicated that most REEs in the calcined samples occurred as metal oxides, especially for the West Kentucky No. 13 calcined material (54% of total REEs), which is distinct from untreated coal and combustion by-products from pulverized coal boilers reported in the literature. In addition, heavy REEs were more likely associated with easily dissolvable forms (i.e., ion-exchangeable, carbonates, and metal oxides). The calcined samples were leached under weak acidic conditions with and without adding ammonium sulfate to recover REEs. About 13%, 24%, and 20% of the REEs were extracted from the Fire Clay, West Kentucky No. 13, and Illinois No. 6 materials by leaching at pH 4.0. Adding 1 *M* ammonium sulfate further increased the recovery values to 18%, 45%, and 32%, respectively. In addition higher percentage of HREEs were extracted from the West Kentucky No. 13 calcined material under this condition. A significant portion of the REEs can be easily extracted from the samples obtained by calcining the coals at 600 °C. The REE concentration in the leachate was analyzed using an ICP-OES. So it can be concluded that calcination of samples can play important role in recovery of REEs.

According to Honaker et al. (2018), the existence of rare earth elements (REEs) in coal sources at elevated concentrations has been the focus of several studies over the past decade. However, limited research has been conducted on methods to recover and refine the REEs. They also report the results of a detailed study into the potential of selectively recovering REEs in an Illinois basin coal source by leaching. Leaching characteristics are obtained for several segments obtained from a core sample and three different reject materials collected at a coal processing plant. Using a 1.2 mol/L sulfuric acid solution at 75 °C, over 60% REE recovery is achieved from the direct floor and an inner parting material and the coal-rich core segments pretreated by low-temperature plasma oxidation to obtain access to the micro-dispersed mineral matter. In the leachable parting material, fluorapatite is detected by XRD analysis, one of the more soluble phosphate minerals with a documented association with REEs. For the three plants reject samples, the leaching recovery values obtained for the heavy REEs are higher than those obtained for the light REEs under the standard leaching conditions and when 0.1 mol/L $(NH_4)_2SO_4$ was used to extract REEs by an ion-exchange mechanism. Thermal activation by roasting or chemical activation by pretreatment using 8 mol/L NaOH solution increases the total REE recovery with significantly higher gains obtained for the light REEs. However, significantly higher recovery values were realized when treating mixed-phase (middling) particles existing within the coarse reject material. However this method is a little complicated.

According to Jinhe Pan et al. (2019), the growing demand for rare earth elements (REEs), which play vital roles in the production of technologically advanced products, has stimulated the development of original processes to recover REEs from secondary resources. Coal fly ash (CFA), the main by-product of coal combustion, enriches REEs in some areas of the world. They developed a two-stage hydro-metallurgical process (alkali fusion-acid leaching) to recover REEs from CFA. The CFA was firstly roasted at high temperature with Na_2CO_3 addition, followed by the leaching step. The effects of parameters of the alkali fusion and acid leaching on REEs extraction were investigated. Results indicated that the two-stage method was more efficient than the direct leaching method. Optimum conditions of alkali fusion were 1:1 (mass ratio of CFA/Na_2CO_3), heating at 860 °C for 0.5 h. The 72.78% leaching REEs efficiency can be obtained in the optimal operation conditions: leaching time (2 hours), stirring speed (400 rpm), the HCl concentration (3 mol/L) and the solid-liquid ratio (1:20). This study should help develop a strong theoretical foundation and technological support for the enrichment and extraction of REEs.

According to Honaker et al. (2019), high-temperature pretreatment of coal-based mineral matter in an oxidizing environment significantly enhances the leaching characteristics of rare earth elements (REEs). A research study has found that the temperatures used in fluidized bed combustion (FBC) of coal to produce electricity are near optimum for pretreating the associated mineral matter before leaching to maximize critical materials' recovery. The results showed that pretreatment at 600°C for few hours significantly increased REE recovery for all coal sources. The leaching kinetics is characterized by a quick release of rare earth elements within the first few minutes of the process.

Direct acid leaching is the most powerful method to reduce the metal content of whole coals since low pH destabilizes many inorganic parts. A few compounds are dissolved in caustics, but low pH is generally favourable for metal ion solubilization. Treatment in strong acids followed by filtering and washing of the solid residue, is an effective way to achieve low concentrations of trace elements (Sloss and Smith 2000; Davidson and Clarke 1996; Spears et al. 1994). Certain compounds, notably metallo-organic chelates and sulfide inclusions are less affected by acid treatment alone (IEA 1991 and Rousaki et al. 2000).

There are several methods to recover the REEs, but it may be complicated on an industrial scale. It needs to find a simple extraction method for these valuable REEs from coal and CCPs from Indian coal samples. Extensive studies of these literatures and its findings have helped in understanding the problems of study area during the research work.

3.2 Research Gap

Most of earlier researchers were focused on the coal classification, genesis and paleo-environmental conditions. There is a little work done on studies of coal characterization. Furthermore, there are a few studies on the future context of coal and coal waste utilization particularly in India. It was perhaps due to lack of holistic approach for proper utilization of organic and inorganic content in coal. Some work has been done on the coal characterization and study on REEs in coal along with fly ash, coal by-products. There is need to do comprehensive studies of REEs in coal and coal by-products along with recovery from coal. Therefore, there is a research gap emerges in qualitative and quantitative investigation of rare earth elements in coal. Thereby, recovery of these valuable elements from coal is also not getting due attention. Thus, the present work focuses on a holistic approach to coal characterization, coal quality, study on REEs concentration in coal and its by-products, along with developing techniques for its possible recovery.