Chapter-9

Discussion

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9.1 Introduction

Coal characterization and its relation for utilization are based on qualitative and quantitative data generated from a large number of coal samples collected from Dhanpuri OCM of the Sohagpur coalfield. The geochemical characterization is based on the various parameters of coal such as moisture, volatile matter, ash, fixed carbon, total carbon, hydrogen, nitrogen, oxygen and sulfur. Inorganic constituents are also part of the discussion along with their genesis in coal. All these parameters help in deciding the rank and grade of coal of the study area. Descriptive statistical methods were used and an attempt has been made to establish a correlation between various parameters. Various aspects of coal characterization and its relation to coal quality and occurrence of REEs concentration in coal and coal ash is discussed in this chapter in subsequent paragraphs.

9.2 Coal Characterization

Coal characterizations include petrology (megascopic characterization), geochemical characterization, trace elements and rare earth elements in coal samples. This requires a detailed understanding of the fundamental properties of coal, thus making the area of coal characterization of paramount importance.

9.2.1 Megascopic characterization

Under megascopic characterization, coal types were studied and its relation has been finding out with quality parameters. Megascopic characterization of 56 samples of coal collected from the study area has been done. Various bands have been identified in coal samples. Classification of these bands is based on the lithotypes. Each lithotype is defined as band when the thickness is 3 mm or more except fusain, which occurs in powdery soft mass (Singh et al. 1983). The preferred upward transition of clarain to durain and durain to fusain further indicates a reduction in toxic medium and lowering of the water table in coal samples of the study area. Similar interpretation for other coal basin has been made by some workers also (Tewari and Khan 2014). Based on the lithotypes, coal samples were classified according to Diessel's classification (1965) in hand specimen. Hence, Banded coal was found in most of coal samples and Dull coal was found in least coal samples in the study area. The details have already been discussed in chapter five.

9.2.2 Geochemical characterization

Geochemical characterization includes various parameters of proximate, ultimate analysis and mineral contents. Parameters of proximate analysis help in utilization coal as a source of energy. Moisture content helps in deciding the maturity (rank) of coal. It depends upon the rank of coal. Generally, the moisture content of lignite (low-rank coal) is higher than 20% . While in anthracite (highest rank), the moisture content is less than 2% (Grammelis et al. 2016). Coking coal also contains moisture less than 2% (Schweinfurth et al. 2009). The moisture content of coal has been studied. It may be observed from figures 9.1 and 9.2 that the average content of moisture in coal samples of study area is 3.32% with a variation from 1.74 to 7.3 percent. This study put the coal of study area into the bituminous rank of coal in maturity scale (Lou and Wang 2015).

From the buyer's point of view, high moisture content in coal is undesirable. This is because when coal is heated; endothermic reaction follows (which leads to smoke formation). However, sometimes free moisture is of added advantage specially for firing boilers. For optimal thermal efficiency, about 5% total moisture in coal is required including free and inherent moisture (Bhatt and Rajkumar 2015). So, if coal has moisture less than 5%, then it is advisable that some water is to be added to make up the total moisture content of about 5%. Hence, in coal of study area, it will be better to add some water for its optimum efficiency in thermal power plants (Wei et al. 2007; Wen et al. 2010; Salmi and Nuraini 2020). Another important geochemical parameter from quality point of view is inorganic content in coal.

Ash is obtained by the complete combustion of coal which is composed of organic and inorganic matter. The ash content of coal is summarized in table 6.1 and 6.2 in chapter six. It may be observed that there is wide variation in ash percentage in coal. It is ranging from 9.65 to 34.21 percent. The high percentage of ash content in a few coal samples is because of presence of dirt band (clay-inorganic bands) as shown in figure 5.1(d). However, the average ash content of coal in the study area is 16.95% which is indicator of good quality of coal.

The inorganic content in a coal seam may be of two types. The first inorganic content comes in contact with coal during the early stage of coal formation which is known as inherent mineral matter. It comes in coal from terrigenous matter and some of the parts of it are derived from peat forming plants. Second, inorganic content in coal may be adventitious or epigenetic in nature. This is deposited in the cleats, cracks and fissures through percolating water (Finkelman 1982; Groen and Craig 1994). Ash does not serve any useful purpose to the buyers; rather, it is a burden to them. As a consequence of coal combustion, the disposal of ash poses a great problem (Blissett et al. 2014; Cao et al. 2018). The mineral matter in coal increases the price of coal transportation. If coal contains 25% of ash, it means, roughly, for every four wagons of coal dispatched one wagon equivalent to ash is paid as a freight charge. Another important parameter of proximate analysis is volatile matter.

Volatile matter is also an important parameter to measure the coal rank for all practical purposes. Volatile matter in high rank coal (anthracite) is low and ranges from 3-10% and high in low rank coal (lignite) and ranges from 45 to 55% (Chen et al. 2006; Chen et al. 2015; Liu et al. 2007). Volatile matter decides the behavior of coal on combustion, carbonization and gasification (Stach et al. 1982). The volatile matter of the study area has been determined. The results are a tabulated in tables 6.1 and 6.2 in chapter six. It may be observed from tables 6.1 and 6.2 that the average volatile matter in coal of the study area is 27.50% (medium volatile matter bituminous coal, as per ASTM classification). This percentage suggests that if coking properties are present in such coal samples, it can be blended with prime coals with high volatile coal or semi-coking coal and the mixture can be used for steel making also (Miller 2017).

Fixed carbon is a very important factor in coal. For coal utilization, fixed carbon content is valued more than the volatile matter content in coal (Linares et al. 2000). The fixed carbon content increases with increase in rank of coal (Mackowsky 1982). Fixed carbon varies from 33.96 to 62.61 percent in coal samples of the study area. The average content of fixed carbon was 52.21% which depicts that it is a bituminous rank of coal in the study area (as per ASTM classification). The ultimate analysis of coal is also being used to characterize the quality of coal for coal utilization.

The ultimate analysis of coal involves the determination of the weight percent of carbon as well as hydrogen, sulfur, nitrogen, and oxygen (usually estimated by difference). It is very important from an evaluation point of view for major elemental concentration in coal. The carbon determination includes carbon present as organic carbon occurring in the coal substance and any carbon present as mineral carbonate (Speight 2015). The carbon percentage varies from 51.41-75.36% in coal samples. The average concentration of carbon was 63.05% in the coal samples of study area. Carbon in coal samples is mostly associated with organic carbon, as evidenced from XRD of coal samples of the study area (due to absence of any carbonate minerals in XRD graphs).

The hydrogen plays a greater role in determining the rank of coal, lower the hydrogen, greater the rank (Francis 1961). The hydrogen percentage varies from 3.13-5.98% in coal samples. The prime coking coals generally contain 4.8 to 5.3% of hydrogen (Khare and Baruah 2010), and coals in study area contain 4.37% on an average basis. Hence, the coal of the study area may be a high rank coal.

Source of nitrogen in coal may have been plant and animal protein. 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). Nitrogen is typically bound to the organic matter of coal (Gil 2002). Nitrogen varies from 0.414-0.856% in coal samples. The average concentration of nitrogen was 0.58% in coal samples of study area of Sohagpur coalfield. Nitrogen is mostly found in the organic fraction of coal. Upon combustion, it is liberated as nitrogen oxides (NOx) in the flue gas (emissions). Nitrogen oxides are an environmental concern because they combine with water vapour to produce nitric acid (HNO_3), which contributes to acid rain (EIA, 2001).

Sulfur is also one of the hazardous elements in coal. Sulfur is always there in coal in organic and inorganic form. Sulfur dioxide emitted during coal combustion is a principal source of acid rain (Glover 1980). It is desirable to know the occurrence of sulphur in coals and its behavior during coal utilization. It also tells much about depositional environments and the formation history of coals. Thus, sulfur in coals is an important parameter in the evaluation of coal quality (Chou et al. 2012). The major forms

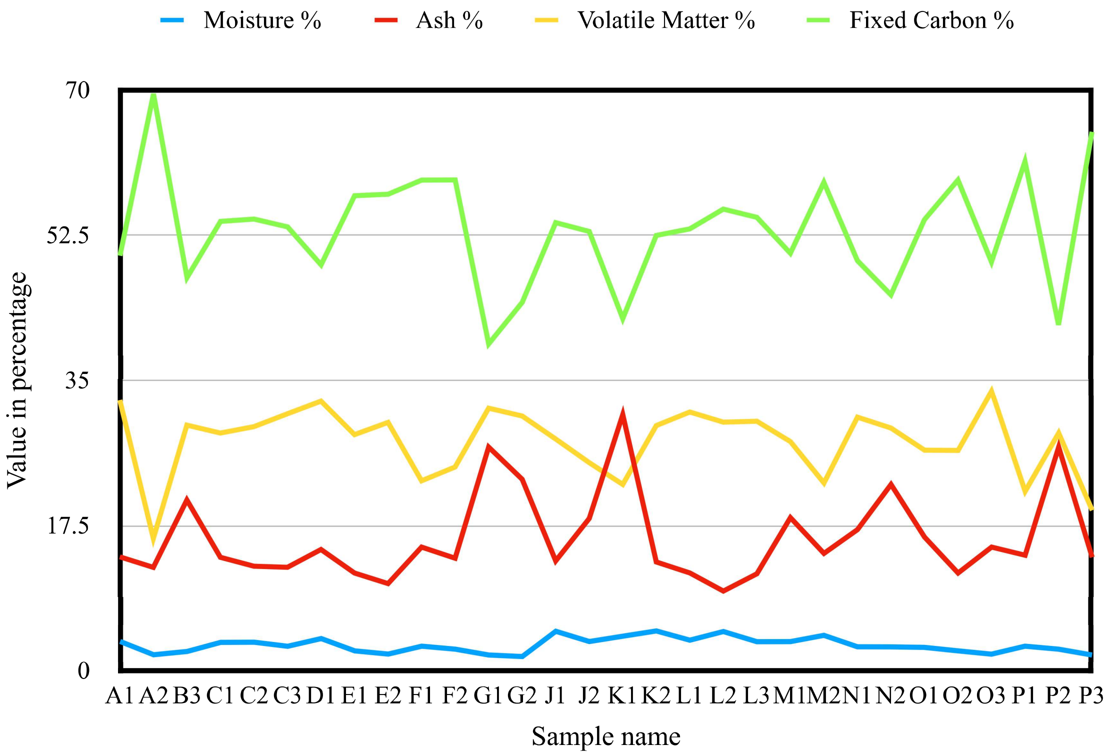

Fig. 9.1: Proximate analysis for all relative parameters of coal samples

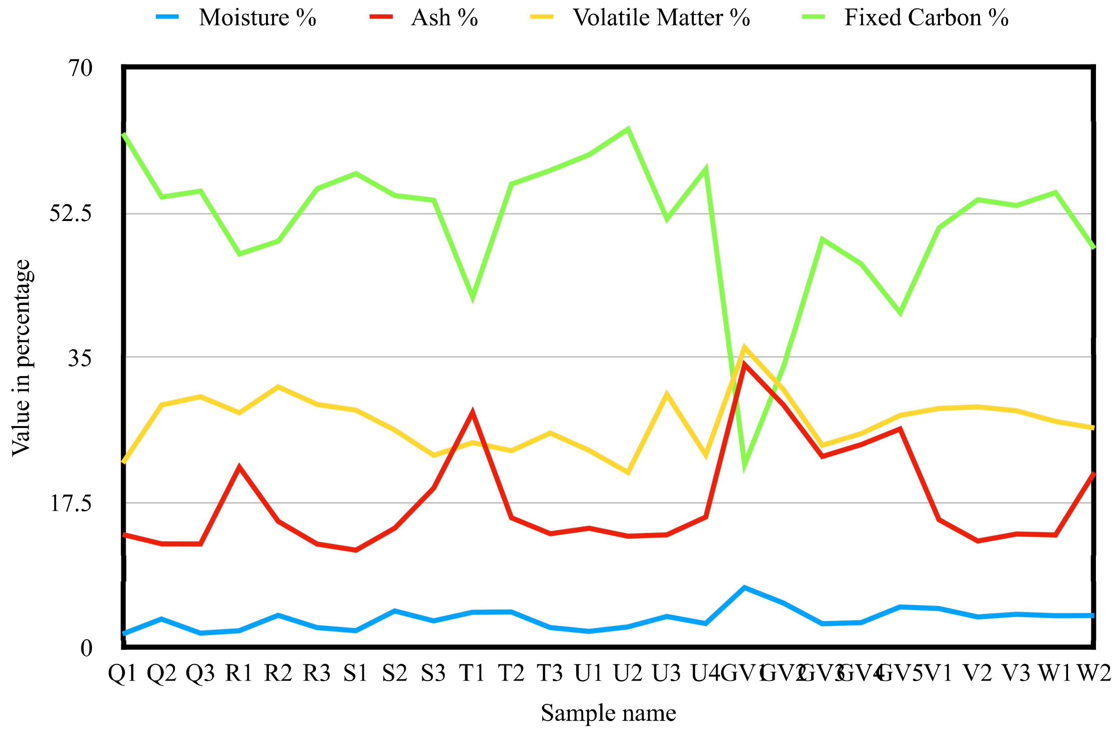

Fig. 9.2: Proximate analysis for all relative parameters of coal samples

of sulfur in coal are pyritic, organic, and sulfate sulfur. The sulfur content in coals globally varies considerably but is most commonly within the range of 0.5% to 5%. The coal with less than 1% sulfur is classified as low-sulfur coal. Coal with 1% to 3% sulfur is medium-sulfur coal. Coal with ≥3% sulfur is high-sulfur coal (Chou 2012). However, Indian Gondwana coal is having very low sulfur content. There is a clear indication of pyrite in the hand specimen (Fig. 5.1). However, average sulfur content in coal samples of study area is considered to be medium sulfur coal. Coals contain trace to minor amounts of sulfate sulfur. Sulfate minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) are found in non-marine coal (Gluskoter and Simon, 1968). Gypsum is reported in XRD graphs (Fig. 6.11, sample no. F1 and K1). Gypsum is generated by the reaction between calcite and sulfuric acid from pyrite oxidation (Rao and Gluskoter 1973).

The sulfur content in peat is closely related to its depositional environment. In general, peats accumulating under the influence of seawater have higher sulfur content than peats accumulating in a freshwater environment (Casagrande et al. 1977). Localized low-to-medium sulfur coal (1.0%–2.5% total sulfur) occurs in areas where the coal is overlain directly by non-marine shale. The non-marine shale, which may be interpreted as tidally influenced estuarine/deltaic deposits (Archer and Kvale 1993), acts as a barrier that keeps seawater from reaching the peat (Chou 1984). It is also discussed in the chapter two. Thus, the sulfur content in the coal samples of study area is closely related to the sedimentary environment immediately following peat accumulation.

Gross calorific value (GCV) of a coal is the quantity of heat liberated by the combustion of unit volume of coal (Francis and Peters 1980). The GCV of coal samples of study area is varying and ranging from 3438 to 6743 Kcal/Kg. The average GCV of coal of the study area is 5726.5 Kcal/Kg. Hence, according to the average content of GCV, the coal samples belonged to “G-6” grade of coal by Indian grading system

(Ministry of Coal, GOI 2014). The GCV of coal is a key-yard stick for many end users purchasing coal for combustion purposes. It provides a clear measure of the useful energy content of a coal (Kumari et al. 2019).

An attempt has also been made to establish a correlation among different geochemical parameters in coal samples of the study area (Table 9.1). A brief is discussed below.

Apart from carbon, hydrogen, oxygen, nitrogen and sulfur which are the major elements in coal, several other elements may be present in coal in the form of trace elements. These trace elements can be ranging up to about 1000 ppm. The highly variable occurrence of trace elements in coals is probably due to the variation in source rocks and also the tectonic set-up of the depositional basins (Finkelman 1999).

9.2.3 Pearson coefficient correlation of geochemical characterization

To avoid information overlapping from high dimensional data sets, statistical analysis, such as the Pearson correlation coefficient (Pearson 1920) was carried out by using IBM SPSS Statistics 16. Correlation may be described as the degree of association between two variables (Asuero et al. 2006). Pearson correlation coefficient (R) is based on linear regression and measures the strength of correlation between two variables. It varies between -1 to +1. Pearson coefficient correlation is divided into three parts: 1st is a strong correlation, 2nd is moderately, and 3rd is a low correlation. In strong correlation, one parameter is directly proportional to another parameter, which means that if the parameter increases, other parameters also increase and vice versa. Strong parameters are further divided into positive and negative correlations. The highest number, i.e. +1, signifies a strong positive linear correlation while -1 shows a strong negative linear correlation. A zero correlation value signifies a nonlinear correlation (Singh et al. 2020).

Correlation has been observed in among various geochemical parameters such as moisture, ash, fixed carbon, volatile matter, carbon, hydrogen, sulphur, nitrogen, oxygen, the ratio of hydrogen by oxygen, the ratio of oxygen by hydrogen and gross calorific value. Pearson coefficient correlations among various geochemical parameters are summarized in table 9.1. It may be observed from this table that there is a high correlation among various geochemical parameters. There is correlation between ash and fixed carbon; sulphur and ash; volatile matter and nitrogen; fixed carbon and sulphur; and carbon and gross calorific value. Ash and fixed carbon show a strong negative correlation (r 2 = −0.95), which indicates that with the increase of ash content in coal leads to decreases in fixed carbon content and vice versa (Table 9.1). It may also be observed from table 9.1 that ash content and sulphur shows a positive high correlation. Volatile matter and nitrogen also show a positive high correlation. Fixed carbon and sulphur show a strong negative correlation. Carbon and gross calorific values show a strong positive correlations (r^2 = 0.92). These correlations are helpful to relate each geochemical parameters in-between.

With the increase of carbon percentage in the coal, the GCV also increases (C vs GCV: 0.926). While ash has a strong negative correlation with fixed carbon (−0.953), which signifies that with the increase of fixed carbon, ash in the coal reduces (Bilen 2019). Moreover, sulphur has a positive moderate correlation with ash (0.75), which manifested that if ash content increases in coal, sulphur content also increases and vice versa. Similarly, nitrogen has a positive moderate correlation with volatile matter (0.732) also. The significance of these correlations helps in making of prediction model based regression.

	M	A	VM	FC	C	H	N	O	S	H/C	O/C	GCV
M	1											
A	0.267	1										
VM	0.231	-0.017	1									
FC	-0.383	-0.953	-0.281	1								
C	-0.559	-0.366	0.393	0.273	1							
H	-0.388	-0.081	0.404	-0.014	0.672	1						
N	0.357	0.314	0.732	-0.529	-0.157	0.119	1					
O	0.490	0.069	-0.289	-0.013	-0.373	-0.536	-0.109	1				
S	0.362	0.757	0.311	-0.822	-0.092	0.241	0.378	0.107	1			
H/C	0.187	0.145	0.073	-0.170	0.273	0.529	-0.127	0.080	0.221	1		
O/C	0.408	-0.103	-0.496	0.209	-0.649	-0.708	-0.220	0.603	-0.408	0.033	1	
GCV	-0.370	-0.339	0.657	0.159	0.926	0.721	0.198	-0.374	-0.020	0.284	-0.661	1

Table 9.1: Pearson coefficient relation between coal characterization parameters

9.2.4 Mineral contents in coal

The silicates are the largest, most complex, and generally the most abundant group of minerals in coal (Finkelman et al. 2019). Not surprisingly, the silicates are the hosts of many elements found in coal, particularly of major elements including silica and aluminium, and to a lesser extent, potassium, calcium, sodium, magnesium, and iron. The silicates include the clay minerals, the most diverse and generally most abundant mineral group along with quartz in coal. Other important silicates are micas, analcime and various feldspars (Finkelman 1988; Wang et al. 2018).

A few important minerals were identified in coal samples with the help of X-Ray Diffraction (XRD) and supported by Fourier Transform Infrared Spectroscopy (FTIR). Phyllosilicate clay (kaolinite) was identified in coal samples of the study area. Kaolinite has been observed almost in all coal samples studied under XRD and FTIR. A brief is also discussed in the chapter two (2.6). It is probably formed by syn-depositional or early diagenetic process in coal (Ward 2016). Kaolinite is the most common minerals in coal samples. Illite (phyllosilicate-clay) in coal is also common in nature (Ward et al. 1999). It usually negatively charged in nature, have a high surface to volume ratio, which enables

Minerals	**Samples**
Kaolinite	A1, A2, B1, C1, F1, F2, K1, G2
Andalusite	B1, C1, F1
Illite	A1, A2, B1, C1, F1, F2, K1
Monazite	G2
Quartz	A1, A2, B1, C1, F1, F2, K1, G2
Hematite	B1
Graphite	F2
Gypsum	F1, B1

Table 9.2: Mineral contents in coal samples

trace elements, usually positively charged, to be adsorbed on its surface. Also, some clay has interlayer space, where cation exchange may take place (Finkelman et al. 2019). So, this can be the reason for the higher concentration of some trace elements in coal. Quartz (tectosilicate-silica minerals) will be found in majority of coal, it also leads to association with arsenic and mercury. Arsenic is found in coal samples of the study area. Quartz is formed in coal by detrital origin (Dai et al. 2014). Silicate is also associated with clay minerals commonly. Hematite (oxide) is also reported in some coal which is generally uncommon (Silva et al. 2011). Pyrite undergoes an exothermic reaction, and burns due to the interaction of its sulphur with oxygen and an iron oxide residue is formed (Ward et al. 2016). Depending on the oxidation/reduction conditions, the iron oxide minerals produced from these phases may be represented by hematite (Valentim et al. 2016). The occurrence of monazite is also found in coal of the study area (Table 9.2). The presence of monazite in coal is important because it is an ore of REEs. Monazite contains several rare earth element such as cerium (Ce), lanthanum (La), neodymium (Nd), praseodymium (Pr), and samarium (Sm). Sometimes thorium is also reported in monazite (Peelman et al. 2016). The concentration of rare earth elements in coal has been determined by using advance instruments like ICP-MS.

9.2.5 Surface morphology of coal

With the help of scanning electron microscope (SEM), various sizes of non-uniform irregular flakes with uneven texture were found on the surface structure of coal samples. Characterization of surface morphology of coal samples will also help in interpretation after leaching experiments. It (characterization of surface morphology) can also help in the fabrication, plotting and designing of experimental work in future studies. Surface morphology helps in the leaching experiments, as higher the surface area, higher will be the reactions with chemical constituents in coal samples. Rounded and smooth surface leads to the low surface area, which further leads to lower chemical reactions with coal particle (Habhashi 1978; Bafghi et al. 2013; Ruan et al. 2019). Calcinations also lead to removal of organic matter which further creates new pores, void spaces and crack in samples and leads to increase in surface area (Ahmed et al. 2008).

Apart from carbon, hydrogen, oxygen, nitrogen and sulfur which are the major elements in coal, several other minerals and elements are present in coal. These trace elements can be ranging up to about 1000 ppm. The highly variable occurrence of trace elements in coals is probably due to the variation in source rocks and also the tectonic set-up of the depositional basins (Finkelman 1999).

9.2.6 Trace elements in coal

Several studies (Swaine 1990; Swaine and Goodarzi 1995; Raask 1995; Huggins et al. 2000; Kolker et al. 2000) have shown that distribution of trace elements differ significantly between coals from different sources and even between coals from the same seams. In order to have a realistic assessment of the release of these trace elements during the coal utilization process, such as combustion and gasification, it is vital to have knowledge about the variations of trace elements in different coals (Vejahati et al. 2010). Majority of the trace elements in coal have a harmful effect. When coal is burnt, some of the volatile trace elements escape into the atmosphere. However, most trace elements remain in coal ash. Hence, escape to the atmosphere and dumping coal ash in ponds or landfill leads to the concentration of toxic elements exceeding certain limits and due to this, the atmosphere is polluted (Finkelman 1999). A detailed trace elements analysis has been done by ICP-MS and the results are discussed in chapter six. It may be observed from table 6.5 given in chapter six that there is wide variation in concentration of trace elements in coal. The average concentration of chromium is 78.91 ppm, manganese is 55.32 ppm, cobalt is 14.42 ppm, nickel is 19.42 ppm, copper is 7.82 ppm, zinc is 26.02 ppm, arsenic is 8 ppm, molybdenum is 11.96 ppm, cadmium is 0.070 ppm, hafnium is 1.06 ppm, and lead is 16.92 ppm in coal samples of study area. The concentration of trace elements in the coal samples of the study area have been compared with the Clarke values (WCHC). The concentration of trace elements and Clarke value are given in table 6.7 in chapter six. It may be observed from this table that chromium is much higher than the Clarke value (four times), along with other elements such as cobalt, nickel, molybdenum and lead.

Some elements are highly toxic to the plants and animals even at a relatively low level, these elements are molybdenum and lead, which is higher in coal samples of the study area. The precise distinction between the organic and inorganic associations of most of the trace elements is rather difficult. Cobalt is normally associated with sulphides and also with clay minerals and organic matter (Finkelman 1994). Arsenic and several other elements are considered to be the most abundant minor elements in iron-disulphide (pyrite) in coal (Kolker 2012). Such pyrite usually contains elevated arsenic content which may be deposited from the hydrothermal fluids or metal rich basinal brines or compaction-driven fluids (Kolker 2012). Sometimes, there is preferential enrichment of nickel in framboidal pyrite also. Manganese is usually associated with carbonates and clay minerals (Swaine 1990). However, carbonate minerals are not detected in coal samples of the study area. Hence, clay minerals may be a source of manganese in coal samples. The occurrence of rare earth elements in coal is discussed in subsequent paragraph.

9.3 Occurrence of rare earth elements in coal

Coal has been investigated as a preferred host of rare earth elements (Hower et al. 2015). Rare earth elements include many elements of lanthanide series including scandium and yttrium. Rare earth elements are important in modern technological world, because they are used in a variety of products used every day, including televisions and cellphones, etc. The occurrences of these elements as ore are rare. Hence, there is a need to search new sources of these elements to meet the demand (Ramasamy and Repo 2017; Cao et al. 2021; Pavon et al. 2021).A detail investigation has been done to determine the occurrence of these elements in coal, shaly coal and its ash. The results are given in table 7.2 in chapter seven. As discussed in chapter seven, coal contains higher REEs concentrations as compared to crustal average, however much lower than obtainable in traditional mining scenario. The enrichment of REEs in coal may be due to the chelating ability of humic acid that existed significantly during the initial coalification process (Mishra et al. 2019). Coal and its ash are showing a wide variation in concentration of REEs. It is nearly three times higher in ash than coal samples on average as given in table 7.2 of chapter seven. The maximum concentration of cerium was found in coal (58.15 ppm) and also in its ash (187.37 ppm).

The occurrence of REEs in the coal seams have been studied by many researchers (Crowley et al. 1989; Seredin and Dai 2012; Hower et al. 2016), broadly four genetic types of REE accumulation have been proposed, i.e., terrigenous, tuffaceous, infiltration, and hydrothermal. Some studies have given evidence of REEs in coal that these are associated with the minerals present in coal. The REEs are associated with pyrite as reported by some workers (Dai et al. 2014; Hower et al. 2015; Pan et al. 2018). Concentration of light REE (LREE) is higher in coal samples due to association of clay

	45 Sc	89 Y	139 La	140 Ce	141 Pr	146 Nd	147 Sm	153 Eu	157 Gd	159 Tb	163 Dy	165 Ho	166 Er	169 Tm	172 Yb	175 Lu	232 Th	238 U
45 Sc	1																	
89 Y	0.9970	1																
139 La	0.9667	0.9833	1															
140 Ce	0.9933	0.9974	0.9827	1														
141 Pr	0.9797	0.9895	0.9890	0.9958	1													
146 Nd	0.9828	0.9894	0.9813	0.9967	0.9988	1												
147 Sm	0.9834	0.9935	0.9940	0.9963	0.9987	0.9962	1											
153 Eu	0.9736	0.9870	0.9959	0.9809	0.9801	0.9723	0.9887	1										
157 Gd	0.9865	0.9961	0.9947	0.9949	0.9931	0.9893	0.9975	0.9954	1									
159 Tb	0.9809	0.9900	0.9881	0.9810	0.9738	0.9676	0.9838	0.9976	0.9936	1								
163 Dy	0.9762	0.9862	0.9880	0.9755	0.9696	0.9625	0.9808	0.9975	0.9905	0.9990	1							
165 Ho	0.9760	0.9868	0.9900	0.9772	0.9721	0.9648	0.9827	0.9985	0.9921	0.9994	0.9998	1						
166 Er	0.9877	0.9954	0.9911	0.9887	0.9832	0.9789	0.9909	0.9969	0.9969	0.9982	0.9974	0.9976	1					
169 Tm	0.9829	0.9916	0.9888	0.9830	0.9761	0.9703	0.9856	0.9976	0.9946	0.9999	0.9989	0.9992	0.9988	1				
172 Yb	0.9711	0.9789	0.9766	0.9638	0.9539	0.9466	0.9677	0.9911	0.9808	0.9958	0.9980	0.9968	0.9925	0.9953	1			
175 Lu	0.9633	0.9702	0.9641	0.9524	0.9379	0.9300	0.9538	0.9839	0.9716	0.9920	0.9930	0.9918	0.9849	0.9909	0.9974	1		
232 Th	0.8050	0.8229	0.8477	0.7877	0.7727	0.7516	0.8034	0.8833	0.8387	0.8922	0.9012	0.8984	0.8681	0.8871	0.9189	0.9345	1	
238 U	0.4675	0.4686	0.4848	0.4153	0.4043	0.3903	0.4395	0.5173	0.4605	0.5263	0.5606	0.5468	0.5227	0.5247	0.5990	0.5904	0.7016	1

Table 9.3: Pearson coefficient relation between REEs of samples

minerals in coal. Geological studies on coal have also reported that LREE are more likely associated with clay minerals relative to Heavy REE (Eskenazy 1987; Seredin 1996). Eskenazy (1987) found in his studies that coals especially the low-ash coals, were relatively enriched in REE. The ratio of LREE to HREE is lower in coal samples and concluded that the majority of the REEs might be strongly bound to the organic matter. The average ratio of LREE/HREE in coal samples of the study area is ranging from 11 to 14 as explained in detail in chapter seven (Para 7.8) which suggests that REEs are associated with both, organic and inorganic contents in coal samples (Wang 2015). The relation of REEs is further correlated by Pearson coefficient correlation.

9.3.1 Pearson coefficient correlation between rare earth elements

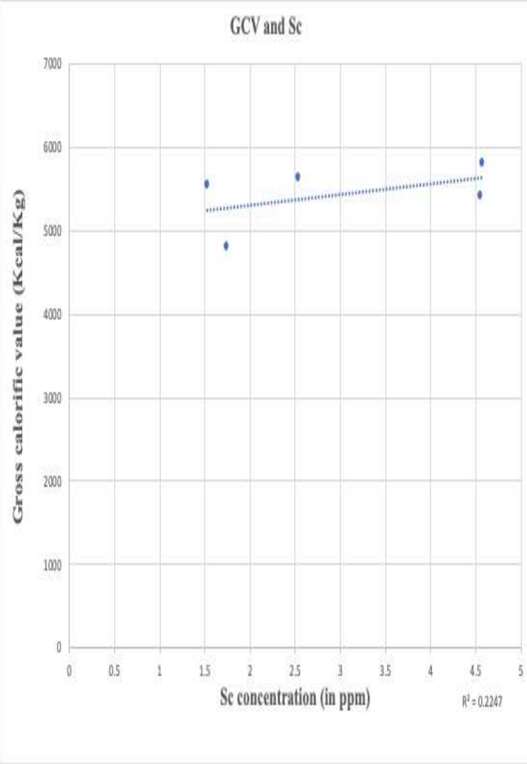

Fig. 9.3: Relation between GCV and scandium content in coal samples

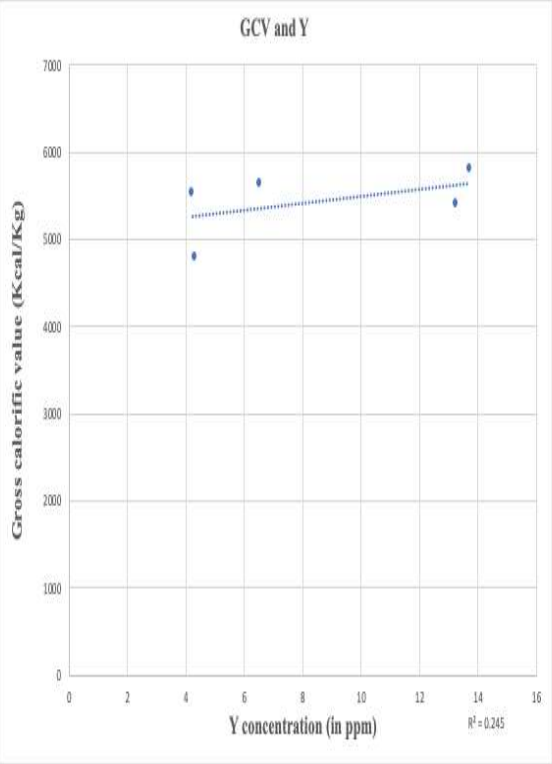

Fig. 9.4: Relation between GCV and yttrium content in coal samples

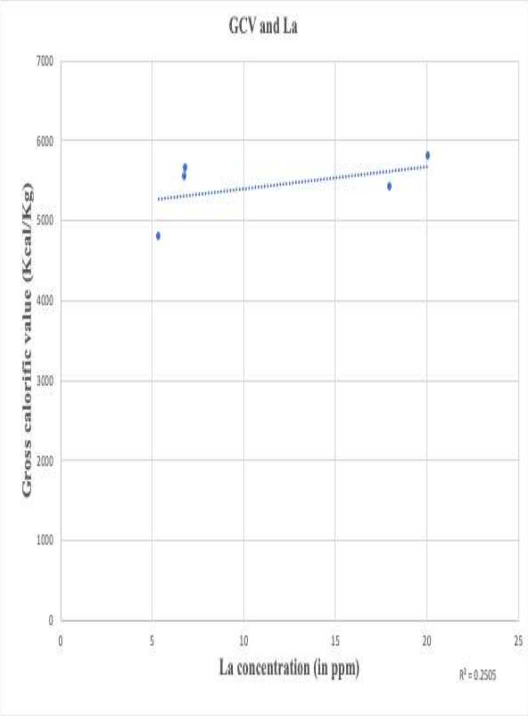

Fig. 9.5: Relation between GCV and lanthanum content in coal samples

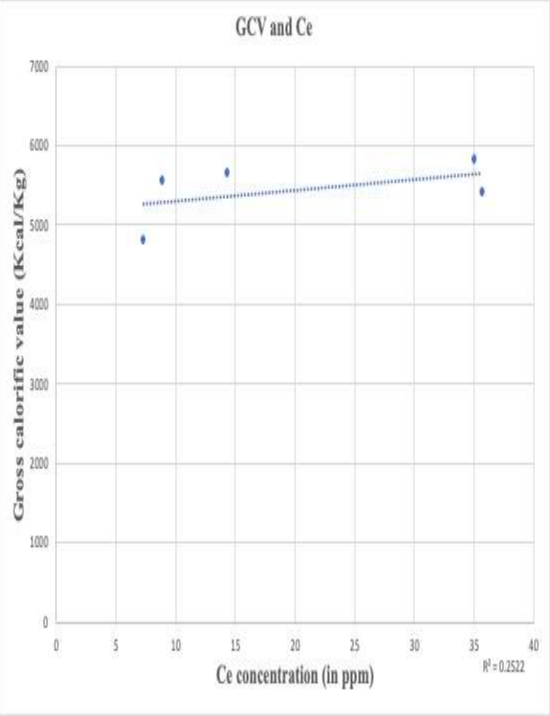

Fig. 9.6: Relation between GCV and cerium content in coal samples

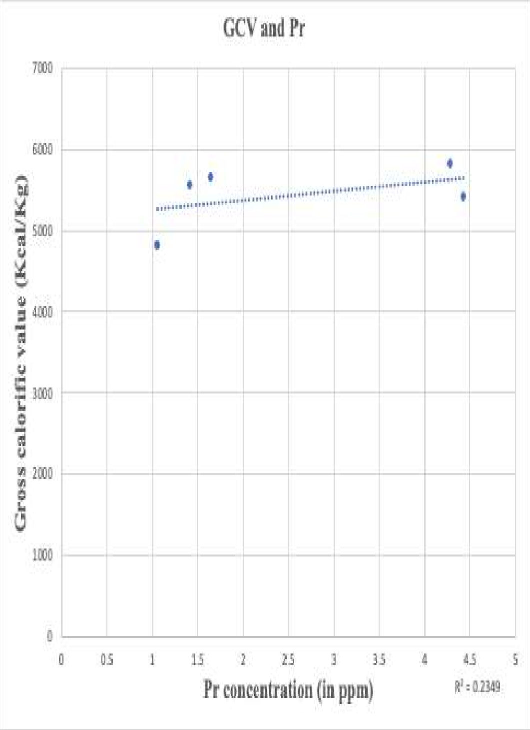

Fig. 9.7: Relation between GCV and praseodymium content in coal samples

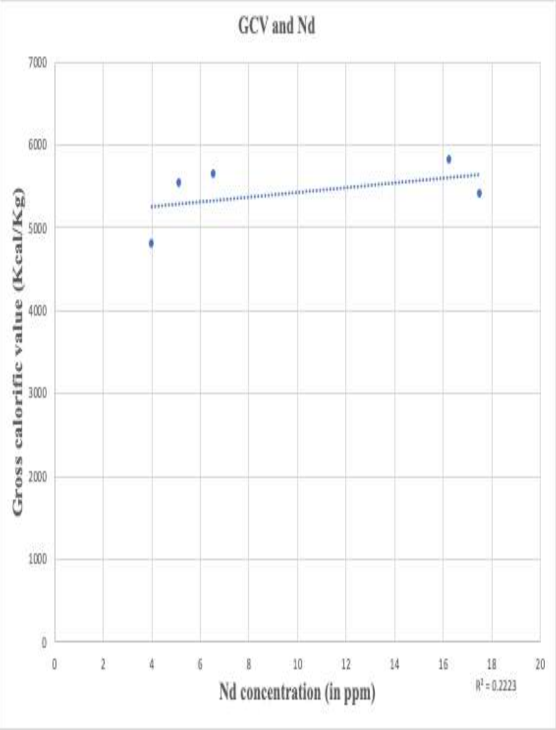

Fig. 9.8: Relation between GCV and neodymium content in coal samples

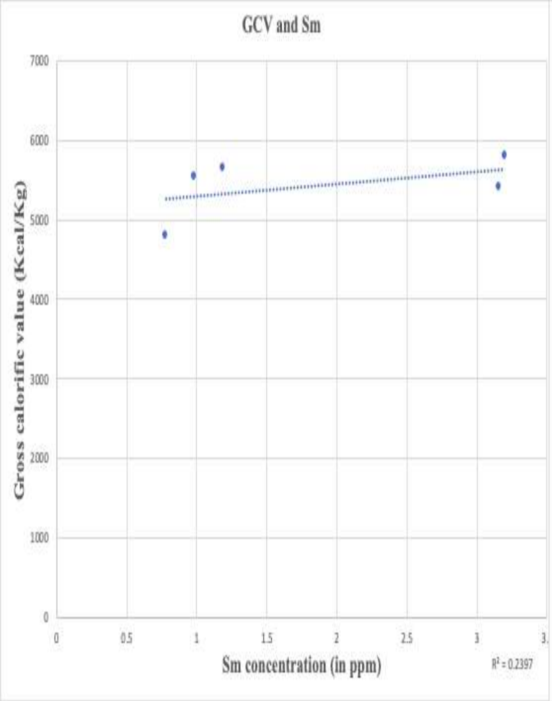

Fig. 9.9: Relation between GCV and samarium content in coal samples

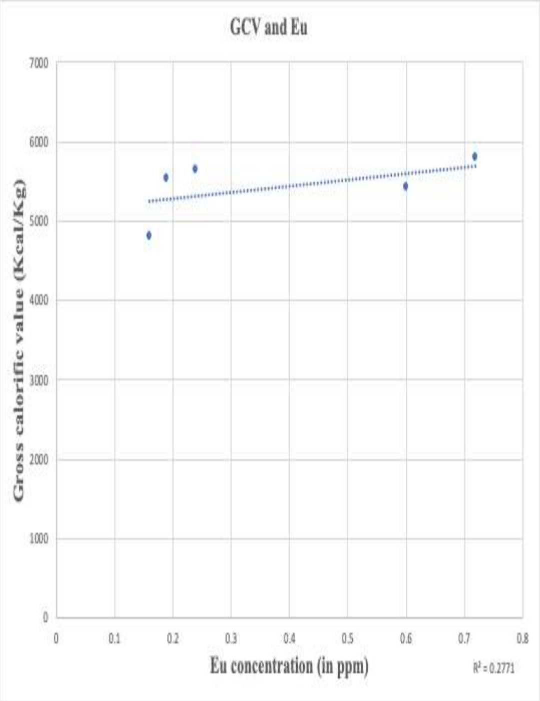

Fig. 9.10: Relation between GCV and europium content in coal samples

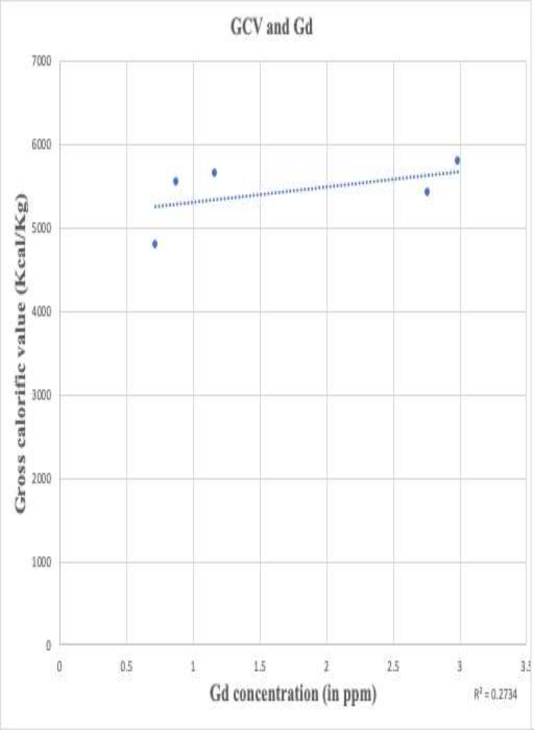

Fig. 9.11: Relation between GCV and gadolinium content in coal samples

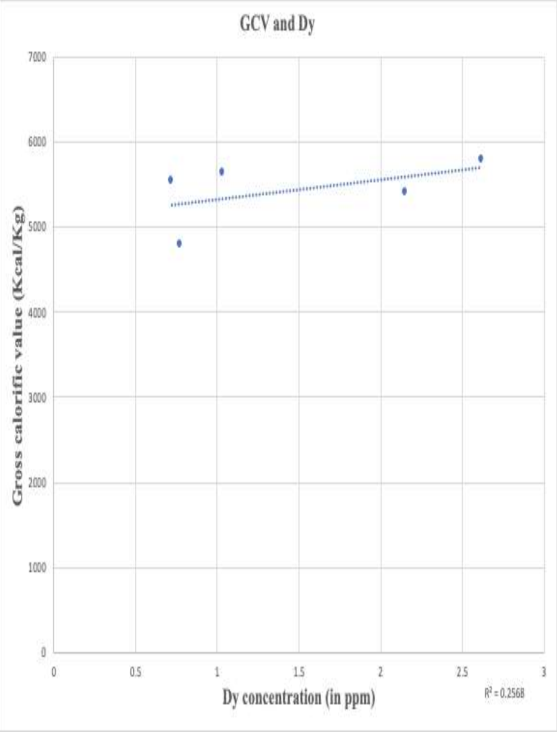

Fig. 9.12: Relation between GCV and dysprosium content in coal samples

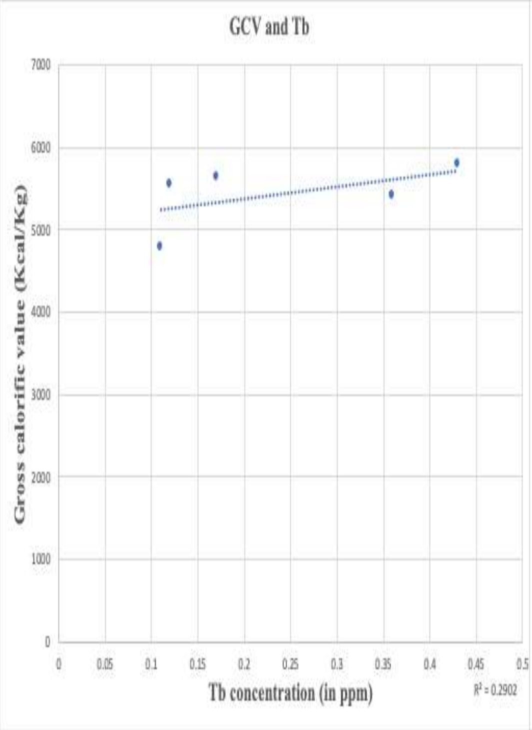

Fig. 9.13: Relation between GCV and terbium content in coal samples

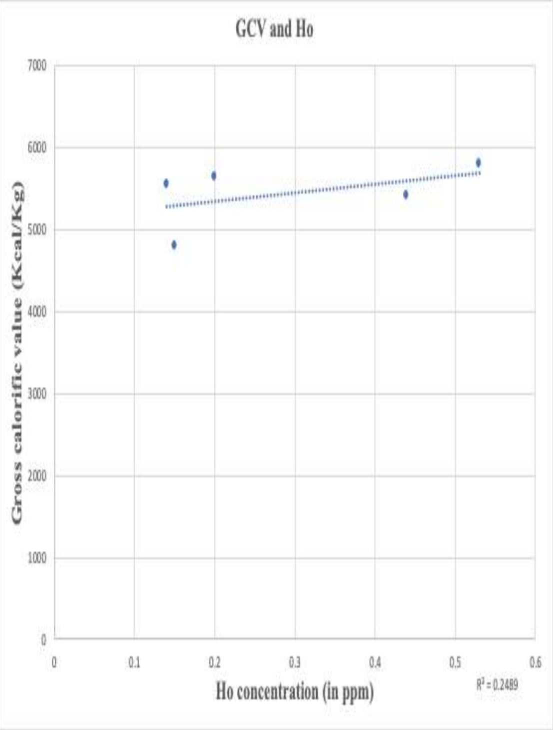

Fig. 9.14: Relation between GCV and holmium content in coal samples

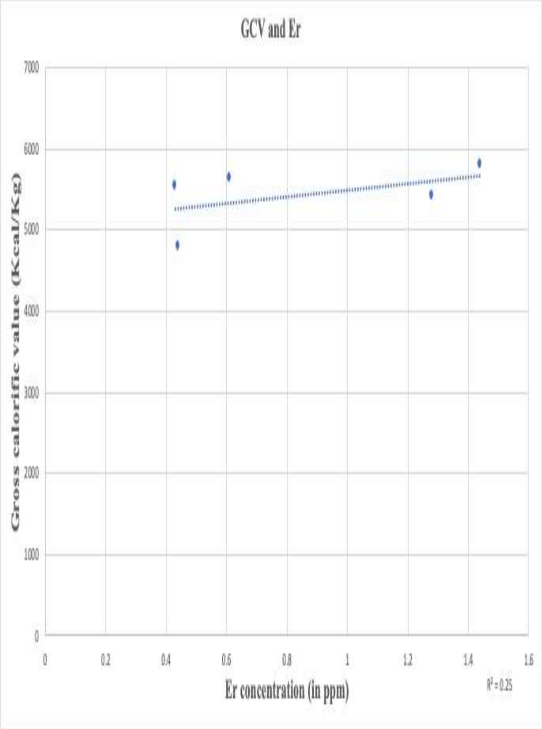

Fig. 9.15: Relation between GCV and erbium content in coal samples

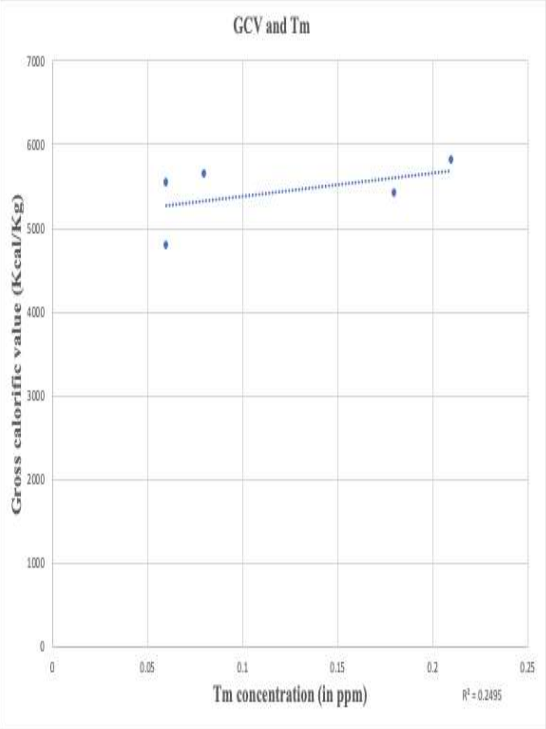

Fig. 9.16: Relation between GCV and thulium content in coal samples

Statistical data is correlated by the Pearson correlation coefficient (PCC). It is an invariant correlation that measures the linear correlation between any two parameters. The correlation value varies between −1 to +1. The highest number, i.e., +1, signifies a very strong positive linear correlation while −1 shows a strong negative linear correlation. A zero correlation value signifies a nonlinear correlation (Singh et al. 2020). All elements of REEs show a strong positive correlation except uranium (Table 9.3). Uranium is showing a moderate to low, positive correlation with every element. The highest correlation is showed by the holmium element with terbium, dysprosium, and thulium. The lowest correlation is showed by the uranium element with neodymium, praseodymium and cerium elements. Linear correlation is higher in light rare earth elements than heavy rare earth elements as concluded by others also (Viral 2020). Furthermore, high correlations

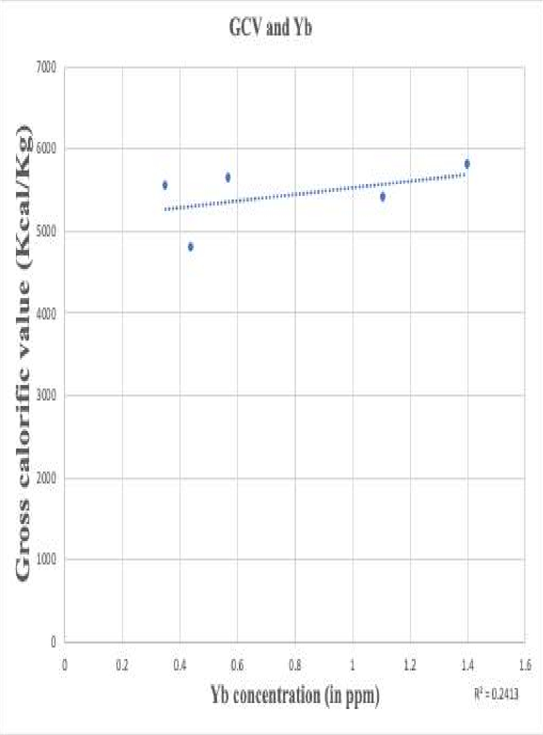

Fig. 9.17: Relation between GCV and Ytterbium content in coal samples

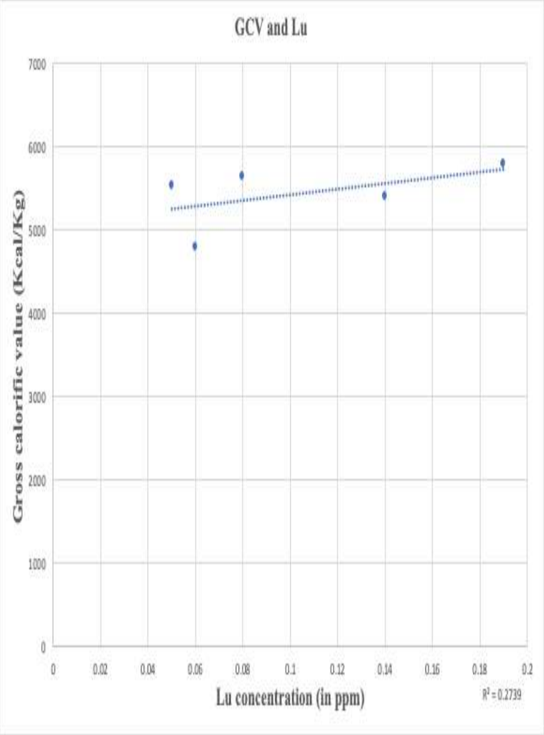

Fig. 9.18: Relation between GCV and lutetium content in coal samples

lead to prediction of certain elements with the help of regression model which may be reduced the cost and time of analysis.

9.3.2 Rare earth elements (REEs) correlation with gross caloric value (GCV)

Correlations based on regression are also evaluated between GCV and REEs in coal samples of the study area. REEs were showing a moderate correlation with the gross calorific value (GCV) as shown in figure 9.19. REEs concentration varies from sample to sample. Sometimes, it is associated with inorganic content, sometimes it is associated with organic content and sometimes with both (Lin et al. 2017b). Every element of REEs is showing a positive correlation with GCV, it means that with the increase of GCV, concentration of REEs also increases in coal samples of the study area (Figs. 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, 9.10, 9.11, 9.12, 9.13, 9.14, 9.15, 9.16, 9.17 and 9.18). Hence, it may be concluded that the minerals of REEs are associated with the organic content (GCV) in the coal samples of the study area.

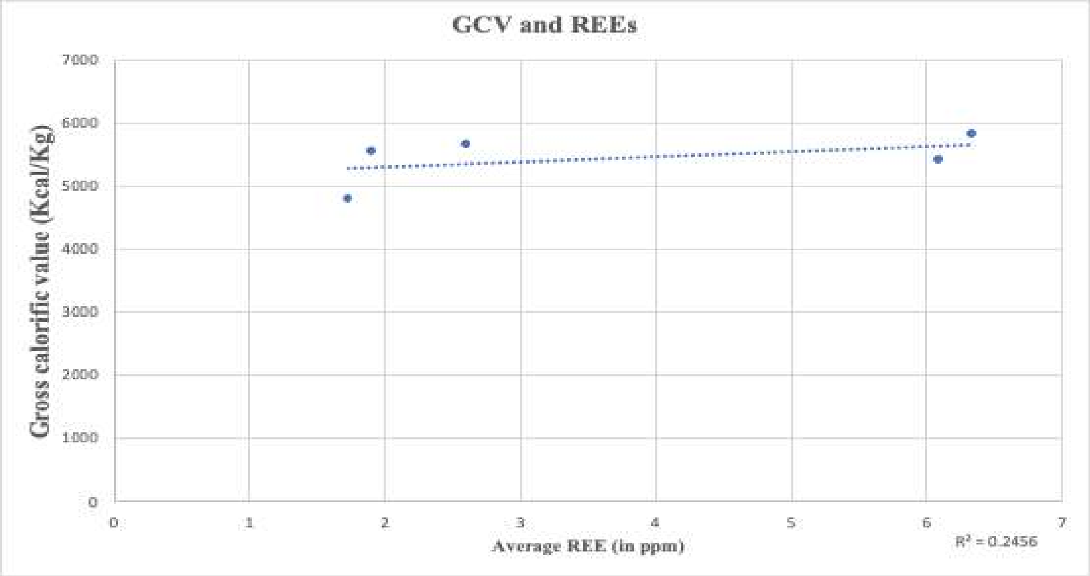

Fig. 9.19: Relation between GCV and average REEs content in coal samples

9.4 Recovery of trace elements and rare earth elements from coal (Experiment 1)

Coal and its by-product are considered to be a promising resource for the critical and rare earth elements (Hower et al. 2016). Numerous research methods have tried to recover these valuable REEs from coal; however, these methods have complications to apply on an industrial scale. The recovery of REEs from coal by simple leaching set-up at laboratory scale has been done. The detail experimentation, methodology and result are discussed in chapter four and eight. It may be observed from the results (Table 8.5) that as a result of leaching of coal there is recovery of REEs more than 50% and some other metals, the recovery percentage goes up to 90% also. Recovery of REEs from coal as a result of leaching are ranging from element to element such as for praseodymium it is 89%, neodymium 97%, samarium 85%, europium 90%, gadolinium 95%, erbium 89%, thulium 90% and uranium 72% respectively. It has been also observed from microscopic images of SEM that the size and shape of coal particles also changed after leaching of coal samples (Figs. 8.6 and 8.7).

This experimental work also helps to recover the trace elements from coal to leachate samples. Samples of leachate also show the mobility of trace elements, which may harmful to the environment. However, the migration of trace elements from coal to water was not much, and some workers have also made a similar interpretation (Cabon et al. 2007). Manganese is alkaline earth metal ions which remove (mobility) very easily (Sracek et al. 2021). Thereby, manganese shows a higher concentration in water leachate samples. Furthermore, it is observed that the concentration of these elements were more in acidic solution (in leachate samples), which might be attributed due to their more significant mobilization in acidic solution than in water. It can be seen that the

	Cr	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Mo**	**Cd**	**Hf**	**Pb**
Cr	1										
Mn	0.577	1									
Co	0.458	0.805	1								
Ni	0.699	0.844	0.921	1							
Cu	0.502	0.609	0.610	0.629	1						
Zn	0.848	0.522	0.714	0.820	0.463	1					
As	0.257	-0.228	-0.370	-0.231	-0.505	0.084	1				
Mo	-0.699	-0.849	-0.525	-0.717	-0.507	-0.485	0.030	1			
Cd	0.527	0.848	0.925	0.876	0.639	0.671	-0.285	-0.685	1		
Hf	0.691	0.479	0.537	0.580	0.214	0.751	0.351	-0.285	0.436	1	
Pb	0.209	-0.482	-0.045	-0.001	-0.094	0.455	0.163	0.456	-0.220	0.306	1

Table 9.4: Pearson correlation coefficient relation in trace elements water samples collected from experiment no. 1

	Cr	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Mo**	**Cd**	**Hf**	**Pb**
Cr	1										
Mn	0.934	1									
Co	0.834	0.973	1								
Ni	0.921	0.996	0.980	1							
Cu	0.992	0.924	0.832	0.918	1						
Zn	0.953	0.966	0.921	0.968	0.951	1					
As	0.995	0.902	0.793	0.888	0.993	0.936	1				
Mo	0.392	0.067	-0.153	0.028	0.361	0.178	0.433	1			
Cd	0.947	0.998	0.962	0.994	0.943	0.971	0.920	0.096	1		
Hf	0.898	0.688	0.522	0.668	0.905	0.769	0.930	0.685	0.724	1	
Pb	0.991	0.925	0.832	0.920	0.998	0.948	0.991	0.366	0.943	0.898	1

Table 9.5: Pearson coefficient correlation in trace elements acidic water collected from experiment no. 1

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Sc	1																	
Y	0.836	1																
La	0.842	0.997	1															
Ce	0.850	0.998	0.998	1														
Pr	0.865	0.995	0.993	0.997	1													
Nd	0.846	0.997	0.996	0.998	0.992	1												
Sm	0.862	0.995	0.992	0.995	1.000	0.990	1											
Eu	0.859	0.997	0.995	0.997	0.998	0.993	0.998	1										
Gd	0.856	0.997	0.996	0.997	0.997	0.992	0.998	1.000	1									
Tb	0.827	0.994	0.997	0.995	0.993	0.989	0.994	0.994	0.995	1								
Dy	0.841	0.998	0.994	0.996	0.997	0.991	0.998	0.999	0.999	0.995	1							
Ho	0.826	0.998	0.996	0.997	0.996	0.992	0.997	0.998	0.998	0.997	0.999	1						
Er	0.817	0.995	0.996	0.995	0.993	0.990	0.994	0.995	0.996	0.999	0.997	0.999	1					
Tm	0.833	0.997	0.993	0.995	0.997	0.990	0.998	0.998	0.998	0.996	1.000	0.999	0.997	1				
Yb	0.834	0.997	0.996	0.996	0.996	0.992	0.997	0.998	0.999	0.998	0.999	0.999	0.999	0.999	1			
Lu	0.832	0.997	0.996	0.996	0.996	0.991	0.997	0.998	0.998	0.998	0.999	0.999	0.998	0.999	1.000	1		
Th	0.996	0.825	0.834	0.840	0.849	0.840	0.844	0.844	0.842	0.813	0.825	0.811	0.803	0.815	0.819	0.816	1	
U	0.983	0.894	0.902	0.906	0.908	0.908	0.903	0.905	0.903	0.882	0.889	0.880	0.873	0.881	0.885	0.883	0.988	1

Table 9.6: Pearson coefficient relation of rare earth elements for acidic water solution collected from experiment no. 1

mobilization of manganese is highest in trace elements. It was directly proportional to the acidic concentration (molarity) or low pH value of solution used for leaching. Comparatively, the average concentration of trace elements is higher in acidic leaching than in water leaching in experiment. There is wide differences of the elemental concentration in water and acidic leaching samples. The concentration of elements in leachate samples were much higher in acidic leaching than water leaching such as for lead (2393 times), chromium (2106 times), copper (495 times), nickel (148 times), cobalt (90 times), manganese (90 times), zinc (89 times), cadmium (89 times), arsenic (47 times), and hafnium (24 times). It is also inferred from the experiment that heavy metals were more sensitive and soluble in acidic solution than in water. Hence, these trace elements need to be removed before burning of coal in thermal power plants for safe disposal of coal waste.

There is negligible movement of REEs in water leaching. However, the mobility of REEs were high in acidic leaching. LREE shows higher recovery than HREE. REEs are entrapped and associated with particular minerals. Xenotime is a major mineral of HREEs (Xu et al. 2017) which is not found in the coal samples of the study area. While monazite, which is a major mineral for LREEs, can lead to a higher concentration of LREEs in coal and leachates (Lazo et al. 2018). So, this experimental method does the recovery of REEs and trace elements simultaneously.

9.4.1 Pearson correlation coefficient (PCC) of trace elements in water samples

Correlations were evaluated by PCC for trace elements in leachate samples after water leaching. Chromium and zinc shows a moderate positive correlation (r^2= 0.85) while chromium and molybdenum shows moderate negative correlation (r^2=-0.70). Manganese and cadmium shows moderate positive correlation (r^2= 0.85) while it shows moderate negative correlation (r^2=-0.85) with molybdenum. Cobalt and cadmium shows strong positive correlation (r^2= 0.925). Nickel and cadmium shows a moderate positive correlation (r^2= 0.88) while it shows moderate negative correlation (r^2=-0.72) with molybdenum (Table 9.4).

9.4.2 Pearson correlation coefficient (PCC) of trace elements in acidic water samples

For PCC of trace elements in acidic leachate samples, almost all elements show a strong correlation (Table 9.5), specially chromium and manganese. Chromium and arsenic show a strong positive correlation (r^2= 0.995). Manganese and cadmium also show a strong positive correlation (r^2= 0.998). Cobalt and nickel show a strong positive correlation (r^2= 0.980). Nickel and copper show a strong positive correlation (r^2= 0.998). Zinc and cadmium show a strong positive correlation (r^2= 0.971). Arsenic and lead show a strong positive correlation (r^2= 0.991). Cadmium and lead show a strong positive correlation (r^2= 0.943).

9.4.3 Pearson correlation coefficient (PCC) of rare earth elements in acidic water samples

Pearson correlation coefficient of rare earth elements (REEs) showed the highest correlation, which showed only a positive correlation (Table 9.6). There was no negative correlation between REEs. Praseodymium (Pr)-samarium (Sm), europium (Eu)-gadolinium (Gd), dysprosium (Dy)-thulium (Tm), ytterbium (Yb)-lutetium (Lu) pairs (Table 9.6) show the highest positive correlation (r^2=1) (Table 9.5). We can also see that HREE have high correlation than LREE.

9.5 Recovery of rare earth elements through leaching by different chemicals

(Experiment 2)

Recovery of REEs from alternative resources has become essential, due to the increasing criticality of REEs. For recovery of coal without affecting the heating value of coal an experiment was designed and fabricated at laboratory scale. This experimental work was conducted due to importance of REEs and their extraction from coal, shaly coal, and calcined material by leaching method. A detailed methodology is given in chapter four and results are summarized in chapter eight. The objective of this experiment was to recover the REEs from raw samples (coal samples and shaly coal samples) and calcined samples by interaction with acid and base solution. The sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used to conduct experimental work.

After leaching with these reagents, in leachate several REEs were found. The concentrations of various REEs are given in table 8.7. It may be observed from this table that the most leachable REEs is cerium and maximum concentration of cerium was 73 ppm in the collected leachate. It may be further observed that the average concentration of TREEs was 12.71 ppm in the leachate. To enhance the recovery from coal, calcined coal samples were used in leaching experiment. It may be observed that calcined samples have given better recovery (one and half times more than non- calcined samples). It may be observed from graph (Fig. 6.11 in chapter six) that monazite and other minerals are present in coal. These minerals are reacting with sulphuric acid more effectively than sodium hydroxide. The calcined samples are susceptible to leaching as explained by some researchers also. Minerals containing REEs are more soluble after the thermal treatment

(Ji and Zhang 2021). Further, there may be two possibilities pertaining to the considerable increases in solubility of REEs as explained by other workers also: (1) Insoluble REEs may be transformed into soluble forms after thermal treatment for two hours up to temperature of 600^{O}C and; (2) REEs-bearing minerals disintrigated during thermal treatment and particles are being liberated from samples (Zhang and Honaker 2019; 2020).

The maximum recovery is shown by A1 (CR)-A, which is collected from calcined sample. After this, leachate sample A1(R)-A also shows the recovery of REEs, but it is less than the A1(CR)-A sample. Leachate sample C3 (CR)-A has the lowest recovery of REEs by acidic solution despite the calcined material sample. Calcination material leads to loss of organic matter, which creates void space and an increase in surface area, by which acidic solution gets room to interact within inter- and intra-spaces of particles. The leachate samples collected by the basic solution are A1 (R)-B, B2 (R)-B, B2 (CR)-B and C3 (CR)-B. The C3 (CR)-B leachate sample showed the highest recovery, which is calcined material (calcined sample). After this, B2 (R)-B and A1 (R)-B were almost equal recovery of REEs from samples to leachate. Acidic and basic leaching experiments were performed on both raw and calcined samples. Recovery of REEs was notably improved in calcined material samples. However, recovery of REEs was comparatively low without calcination, up to 30% only.

REEs in coals can be classified into organic and inorganic associations (Wang et al. 2008; Zhang, Yang, and Honaker 2018). Two factors may provide the enhanced recovery after calcination: (1) the organically and inorganically associated REEs were liberated after calcination, which might be more leachable (e.g., REEs on the surfaces and entrapped within the inner layer of micro dispersed clays) (Lin et al. 2017; Stuckman et al. 2018), and (2) high-temperature calcination transformed the REEs into more leachable forms such as rare earth oxides. So, this is the significance of material calcination for more recovery of REEs.

The highest recoveries were shown by cerium, lanthanum and neodymium elements from sample to leachate. It is also noticed that the mobility of LREE was higher than HREE from samples to leachate. The significance of this research will further enhance utilization of coal as a resource of REEs and it also provide environment-friendly disposal of coal waste with low concentration of REEs and other toxic metals. This kind of recovery can lead to coal as a secondary resource for REEs than the traditional ones It may be concluded from this experiment that that the recovery of REEs, especially LREEs, may be improved by using acidic leaching. It also depicts that the most effective recovery of REEs is from calcined coal sample by acidic leaching. However, proper technique is required for utilizing acid and base for leaching and safe disposal of it after leaching of coal sample.

As seen from experimental works, acid (sulphuric acid) can recover most of the REEs from coal samples, and now it needs to be required to see the concentration of REEs in acid mine drainage water with pyrite inclusion in coal samples. Due to its chemical composition, pyrite forms sulphuric acid in coal mines. Pyrite can lead to acidic concentration in the coal mine, and it may lead to the mobility of REEs from the coal mine. So, this acidic condition may mobilize the REEs and collect them to nearby water resources or ponds.

Recovery of REEs from coal may be economically viable and provide additional income to mining companies and, in some cases, may have sufficient value to justify REEs production without coal production. The challenge to encounter the need for rare earth elements will keep on increasing in the long run, in line with the developments in fast proceeding green technologies and high-tech devices.

Coal and its by-products from Dhanpuri OCM of Sohagpur coalfield have a considerable concentration of REEs. Its recovery from coal and coal by-products is adding value to this research work because it did not only identify its value but also attempted to recover through several treatments and processes. Concentration and recovery from coal and its by-products will lead to the alternative of the strategic metal resources than traditional resources and will add more significance to strengthen the country in future.