Chapter-7

Rare earth elements (REEs) in coal

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7.1 Introduction

The increasing demand of REEs in newer advanced technology has elevated many folds. To fulfil this demand, there is a need to look for new resources base substances having REEs concentration. The existence of rare earth elements (REEs) in coal has been in a new fancy study over the past decade. Despite its (REEs) importance, very limited studies have been carried out on methods to recover and refine the REEs in Indian coals and their existence usually known as lanthanide elements (Varma et al. 2018; Mishra et al. 2019). REEs is a group of 15 elements which we call the lanthanide elements (atomic numbers 57-71), and two transition metal elements, i.e., yttrium and scandium. Promethium (atomic number 61) is extremely rare and is generally considered not to exist in nature. Increasing applications for REEs started in the 1960s when developments were in the process technology allowed their purification at a commercial scale (Huffine 1960).

China is the world's largest producer, consumer and exporter of rare earths, controlling more than 90 percent of the global supply base with a virtual monopoly (Mancheri et al. 2019). China is leading in REEs for reserve and in future exports. Various applications in several industries have stimulated the scarcity of REEs (Fig. 7.1). Demand for rare-earths is likely to increase between 7–8% annually (Kingsnorth 2016).

Category	**Elements**
Light Rare Earth Elements (LREEs)	La, Ce, Pr, Nd, Sm
Heavy Rare Earth Elements (HREEs)	Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Critical Rare Earth Elements (CREEs)	Nd, Eu, Tb Dy, Y

Table 7.1: Rare Earth Elements category: Lanthanide series including Yttrium and Scandium

This condition has created to search for assured sources of these strategically and valuable, essential elements in countries.

Coal and coal by-products contain valuable elements (Hower et al. 2016a). Coal ash is the material produced after coal combustion, mostly in coal-fired power plants, including fly ash and bottom ash. Coal combustion by-products (CCPs) is a significant industrial waste having adverse impacts on the surrounding environment and human health because of its abundance and potential to free toxic elements by natural leaching at the dumping/disposal sites in mines. However, coal ash is also an economically promising resource for the extraction of certain critical metals, including Ge, Ga, rare earth elements and Y (REE + Y or REY), Nb, Zr, V, Re, Au, Ag, and base metals such as Al (Seredin and Dai 2012; Dai and Finkelman 2018; Dai et al. 2018). An alternative source for REY globally was triggered by a short-lived supply crisis in 2010 and the REY price spike in 2010-11 (Alonso et al. 2012; Massari and Ruberti 2013; Dai et al. 2018). It led to the

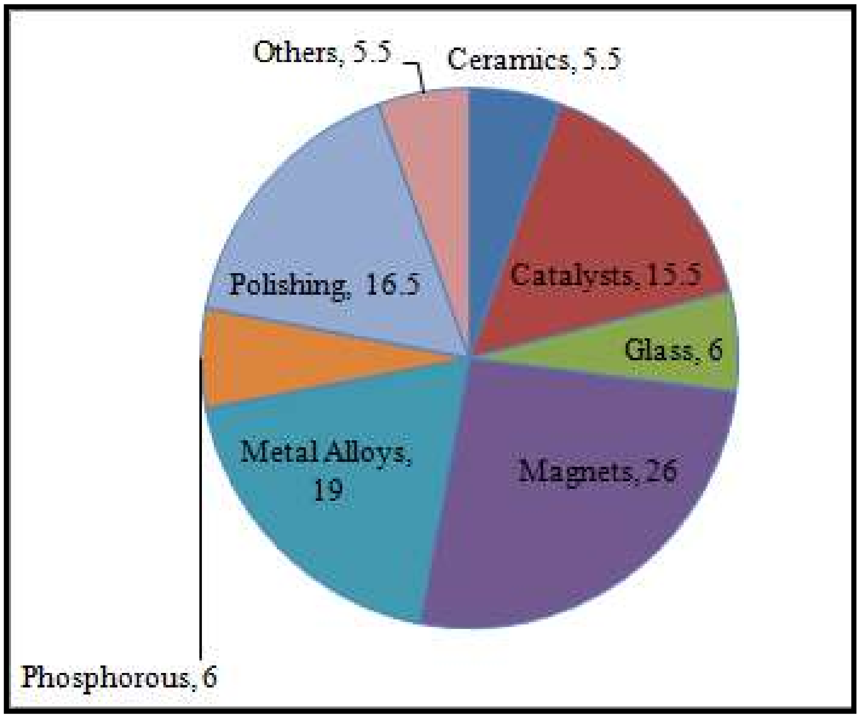


Fig. 7.1: Use of REEs worldwide

investigation of sources of REY increased significantly. Conventionally, REY is commercially extracted from rare earth deposits containing REY-bearing minerals such as bastnaesite, monazite, and xenotime, among others (Haxel et al. 2002: Jordens et al. 2013).

7.2 Occurrence of REEs in coal

Coal, shaly coal and its ash (made in the laboratory) were analyzed with the help of inductive coupled plasma mass spectroscopy (ICP-MS). The analysis is given in table 7.2. Graphs were plotted between REEs and their concentration among coal samples, shaly coal and its ash (Fig. 7.2). The LREEs are more in all samples compared to HREEs. In coal samples, the concentration of scandium (Sc) varies from 1.53 ppm to 21.25 ppm, and the average concentration is 7.88 ppm. Yttrium (Y) varies from 4.21 ppm to 32.47 ppm, and the average concentration is 15.11 ppm. Lanthanum (La) varies from 5.38 ppm to 85.56 and the average concentration is 30.18 ppm. Cerium (Ce) varies from 7.31 ppm to 175.47 ppm and the average concentration is 58.15 ppm. Praseodymium (Pr) varies from 1.06 ppm to 18.79 ppm and the average concentration is 6.57 ppm. Neodymium (Nd) varies from 4.01 ppm to 69.15 ppm and the average concentration is 24.61 ppm. Samarium (Sm) varies from 0.78 ppm to 12.63 ppm and the average concentration is 4.52 ppm. Europium (Eu) varies from 0.16 ppm to 2.19 ppm and the average concentration is 0.84 ppm. Gadolinium (Gd) varies from 0.72 ppm to 10.26 ppm and the average concentration is 3.80 ppm. Terbium (Tb) varies from 0.11 ppm to 1.36 ppm and the average concentration 0.46 ppm. Dysprosium (Dy) varies from 0.72 ppm to 7.35 ppm and the average concentration is 3.02 ppm. Holmium (Ho) varies from 0.14 ppm to 1.35 ppm and the average concentration is 0.58 ppm. Erbium (Er) varies from 0.43 ppm to 4.08 ppm and the average concentration is 1.67 ppm. Thulium (Tm) varies from 0.06 ppm to

Elements	A1	A2	B1	B2	B3	D1	C1	Average	AA-1	BA-1	BA-2	Average
Sc	1.53	2.54	18.98	21.25	1.75	4.55	4.58	7.88	32.07	20.58	24.87	25.84
Y	4.21	6.51	31.37	32.47	4.29	13.23	13.72	15.11	64.62	27.98	61.86	51.49
La	6.79	6.84	66.61	87.56	5.38	18.01	20.09	30.18	122.98	77.38	84.44	94.93
Ce	8.92	14.38	130.21	175.47	7.31	35.71	35.06	58.15	237.73	152.11	172.28	187.37
Pr	1.42	1.65	14.34	18.79	1.06	4.44	4.29	6.57	26.71	16.75	19.72	21.06
Nd	5.15	6.57	53.59	69.15	4.01	17.55	16.26	24.61	100.00	61.89	76.13	79.34
Sm	0.98	1.19	9.70	12.63	0.78	3.16	3.20	4.52	18.67	10.87	14.00	14.51
Eu	0.19	0.24	1.78	2.19	0.16	0.60	0.72	0.84	3.47	1.99	2.61	2.67
Gd	0.88	1.17	7.85	10.26	0.72	2.76	2.99	3.80	16.22	8.70	12.47	12.46
Tb	0.12	0.17	1.13	1.36	0.11	0.36	0.43	0.46	2.26	1.16	1.71	1.71
Dy	0.72	1.03	6.53	7.35	0.77	2.15	2.62	3.02	12.84	6.50	9.94	9.76
Ho	0.14	0.20	1.25	1.35	0.15	0.44	0.53	0.58	2.40	1.17	1.99	1.85
Er	0.43	0.61	3.47	4.08	0.44	1.28	1.44	1.67	6.29	3.10	5.40	4.93
Tm	0.06	0.08	0.48	0.51	0.06	0.18	0.21	0.23	0.84	0.43	0.74	0.67
Yb	0.35	0.57	3.15	3.24	0.44	1.11	1.40	1.47	5.07	2.65	4.59	4.10
Lu	0.05	0.08	0.45	0.46	0.06	0.14	0.19	0.20	0.72	0.37	0.68	0.59
Th	1.83	2.33	26.59	33.28	2.12	2.85	4.90	10.56	31.23	30.40	24.80	28.81
U	0.63	0.81	4.89	7.27	1.44	1.07	1.61	2.53	7.27	4.89	5.73	5.96

Table 7.2: Rare earth elements concentration (in ppm) distribution in the coal and coal ash along with shaly coal of Sohagpur coalfield

Note: Critical rare earth elements= in blue font; Ash= in red font and yellow cells

0.51 ppm and the average concentration is 0.23 ppm. Ytterbium (Yb) varies from 0.35 ppm to 3.24 ppm and the average concentration is 1.47 ppm. Lutetium (Lu) varies from 0.05 ppm to 0.46 ppm and the average concentration is 0.20 ppm. Thorium (Th) varies from 1.83 ppm to 33.28 ppm and the average concentration is 10.56 ppm. Uranium (U) varies from 0.63 ppm to 7.27 ppm and the average concentration is 2.53 ppm. Thorium and uranium were also identified with REEs in samples of the study area.

The graphs were plotted on the linear and logarithmical axis scale to see the REEs variations. Variation of concentration is unable to find on the linear axis scale, that is why the logarithmical axis scale is also plotted here. The highlighted font in sky-blue of table 7.2 shows the critical rare earth elements (CREE-Y, Nd, Eu, Tb, Dy).

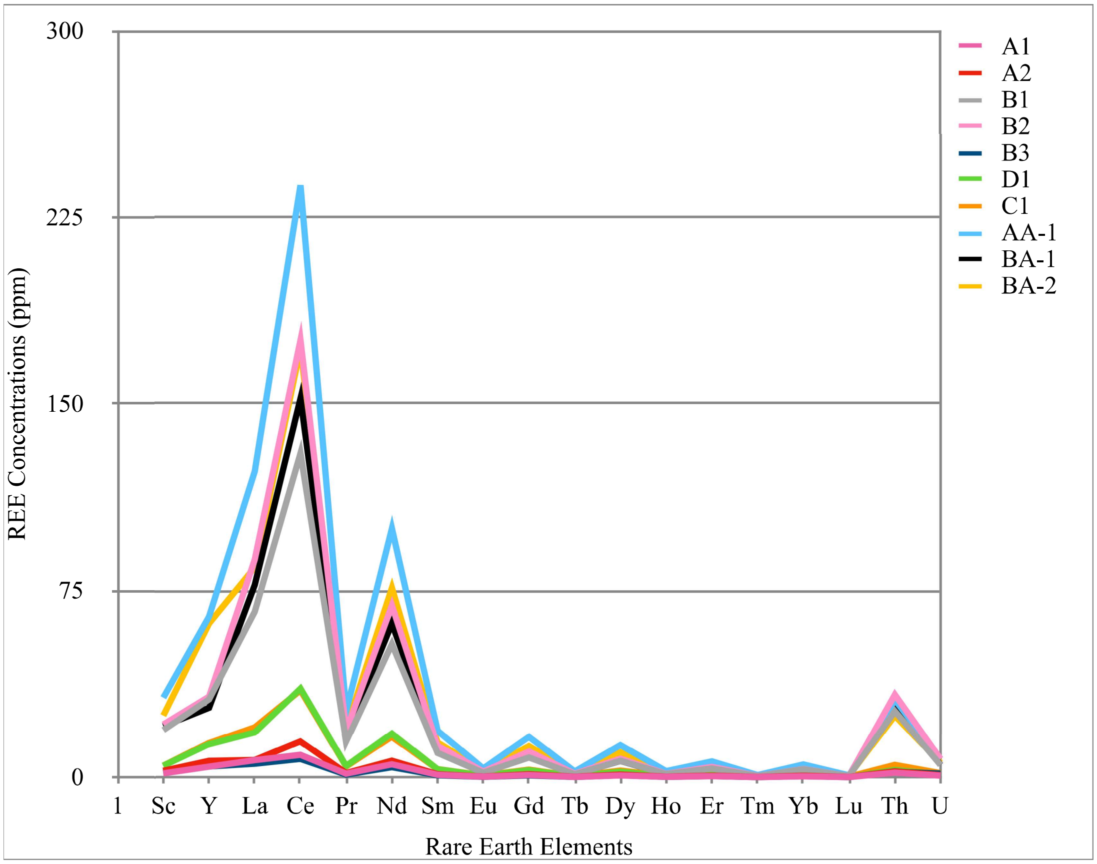
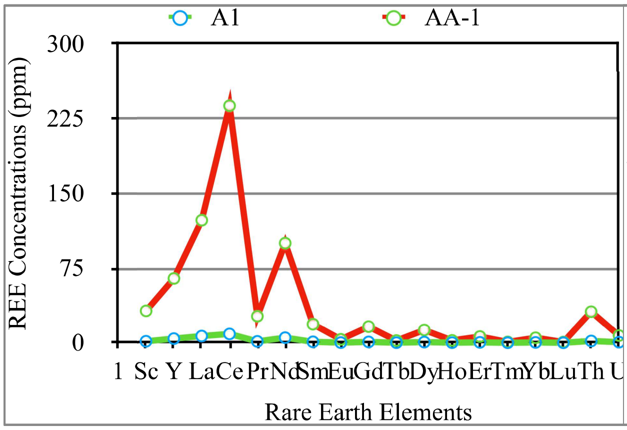


Fig. 7.2: Graphical representation of coal samples and ash samples with respect to REEs concentration



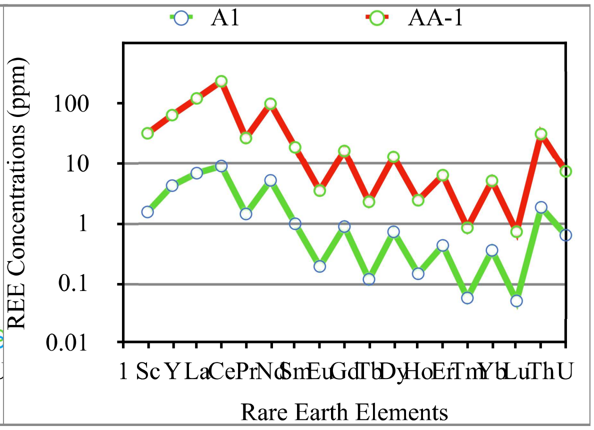
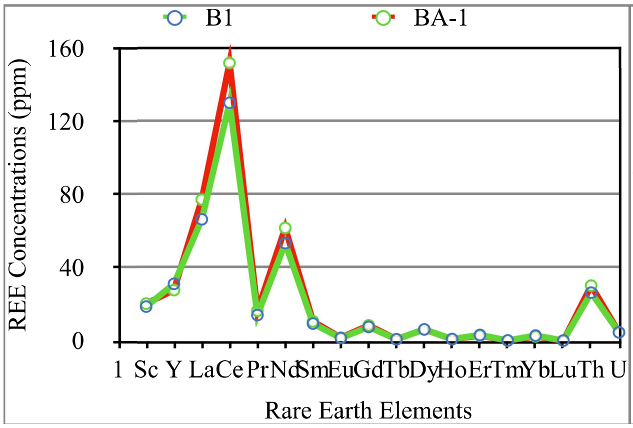


Fig. 7.3: Linear graphical representation for sample no. A1 and AA-1

Fig. 7.4: Logarithmic graphical representation for sample no. A1 and AA-1



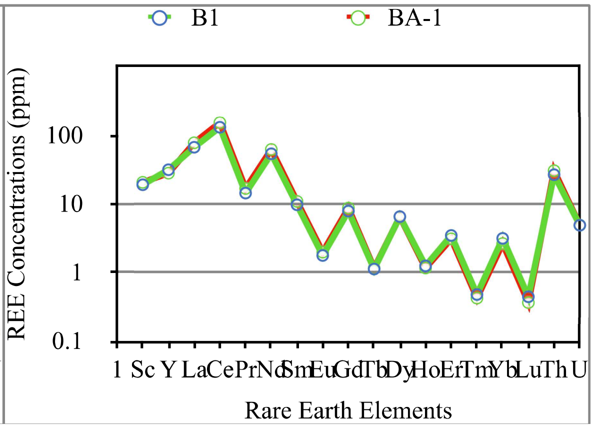
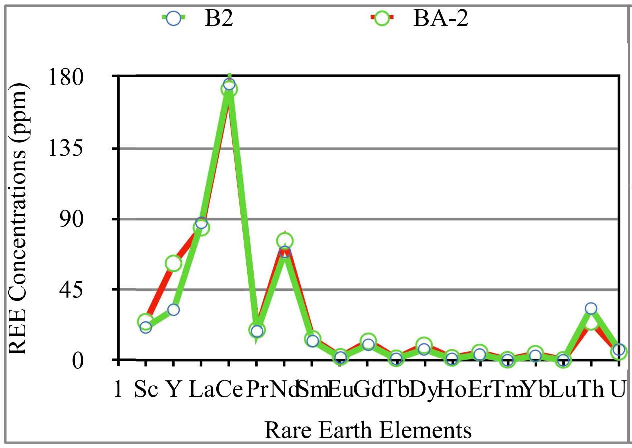


Fig. 7.5: Linear graphical representation for sample no B1 and BA-1

Fig. 7.6: Logarithmic graphical representation for sample no. B1 and BA-1



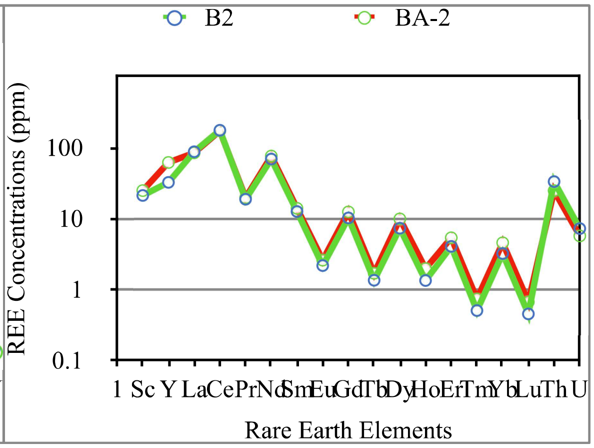


Fig. 7.7: Linear graphical representation for sample no B2 and BA-2

Fig. 7.8: Logarithmic graphical representation for sample no. B2 and BA-2

When REEs concentration in coal samples is compared for significance with US coal, Chinese coal and World coal (Table 7.3), then these values (Table 7.2) shows a significant variation in result. REEs concentrations in coal samples are higher than the US coal for all elements. REEs concentration in coal samples is higher for Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb than in Chinese coal, while it is lesser than for Dy, Ho, Er, Tm, Yb, Lu elements. When it compared with the REEs concentration in the world coal, every element falls within its range. The concentration of CREE in the Sohagpur coalfield is also higher than in the US coal. The critical REEs Y, Nd, and Eu of Sohagpur Coalfield are higher than Chinese coal except for Tb and Dy.

Coal sample, A1 showed an adequate amount of REEs concentration, but when we analyzed its ash (prepared in the laboratory), we found a considerable change of REEs concentration up to 30 folds (Figs. 7.3 and 7.4). The coal ash sample of AA-1 was very much higher for Ce (237 in ppm), La (122 in ppm), and Nd (100 in ppm) than any other coal sample and its ash. Shaly coal samples, B1 and B2, along with its ash sample, BA-1 and BA-2, were also higher and show here adequate amount of REE concentration in samples, and its ash.

Mineral content in coals already unveiled that it has several minerals in coal samples. 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) The major minerals were identified such as kaolinite (clay mineral), quartz (silicates), illite (clay and aluminosilicate) and monazite (phosphate mineral) in samples of the study area which was discussed in the previous chapter. Monazite is a major source of cerium elements in coal samples.

Elements	Chinese coal[1]		US coal[2]		World coal		
	Av.	No.	Av.	No.	Ra.[3]	Av.[4]	No.[4]
La	18	110	12	6235	1-40	11	10
Ce	35	110	21	5525	2-70	23	11.5
Pr	3.8	110	2.4	1533	1-10	3.5	ND
Nd	15	110	9.5	4749	3-30	12	4.7
Sm	3	110	1.7	5151	0.5-6	2	1.6
Eu	0.65	110	0.4	5268	0.1-2	0.47	0.7
Gd	3.4	110	1.8	2376	0.4-4	2.7	ND
Tb	0.52	110	0.3	5024	0.1-1	0.32	0.3
Dy	3.1	110	1.9	1510	0.5-4	2.1	ND
Ho	0.73	110	0.35	1130	0.1-2	0.54	ND
Er	2.1	110	1.0	1792	0.5-3	0.93	ND
Tm	0.34	110	0.15	365	ND	0.31	ND
Yb	2	110	0.95	7522	0.3-3	1	0.5
Y	9	110	8.5	7897	2-50	8.4	15
Sc	4	110	4.2	7808	1-10	3.9	5
Lu	0.32	110	0.14	5008	ND	0.20	0.07
LREE	78.85	—	48.8	—		54.67	34.70
HREE	22.11	—	17.49	—		17.7	24.75
Total	100.96		66.29			72.37	59.45

Table 7.3: Comparison of REEs concentration in Chinese coal, US coal, and World coal

Note. Values are in parts per million; Av = the average concentration; ND = number of samples; Ra = the range of concentration.

[1]From Tang and Huang (2004). [2]From Finkelman (1994). [3]From Reg et.al. [4]From Ketris and Yudovich (2009).

The standard deviation and standard error of the mean are 2.7 and 0.68 for sample A1. The standard deviation and standard error of the mean are 3.9 and 0.98 for sample A2. The standard deviation and standard error of the mean are 34.9 and 8.7 for sample B1. The standard deviation and standard error of the mean are 46.8 and 11 for sample B2. The standard deviation and standard error of the mean are 2.2 and 0.56 for sample B3. The standard deviation and standard error of the mean are 9.8 and 2.45 for sample D1. The standard deviation and standard error of the mean are 9.7 and 2.44 for sample C1. The standard deviation and standard error of the mean are 64.1 and 16.1 for sample AA1. The standard deviation and standard error of the mean are 40.8 and 10.2 for sample BA1. The standard deviation and standard error of the mean are 46.7 and 11.6 for sample BA2. Variance is very much high in ash samples and shaly coal having a high concentration of REEs.

7.3 Characteristic of coal ash

Mineralogical studies of coal ash showed the presence of mullite, feldspar, clay and to some extent quartz, hematite and magnetite from previous research works (Ketris and Yudovich, 2009). The coal ash was prepared in the laboratory of coal samples and shaly coal. It is also analyzed by ICP-MS. The analysis is given in table 7.2. The graph was plotted between the coal samples and ash. Here the graphs were plotted between REEs and their concentration among coal samples, shaly coal and its ash. The concentration of LREE is higher than HREE in samples. The graphs were plotted on an axis scale of linear and logarithmically to see the variations of REEs concentration as said earlier. The highlighted font in sky-blue of table 7.2 shows the critical rare elements (Y, Nd, Eu, Tb, Dy).

The mean value of ash content (sample no AA-1, BA-1 and BA-2) is much higher than the mean value of coal samples (Table 6.2). The mean value of coal ash for Sohagpur Coalfield is higher than the Chinese and US coal samples as per data comparison of table 7.2 and table 7.3 for all REEs. When we compare these coal ash REEs concentrations with the world coal REEs data in table 7.3, it is also high for almost all elements except Ho. The highlighted yellow portion in table 7.2 is the ash of coal and shaly coal, prepared in the laboratory as follows:

1. A-1 (sample) = AA-1 (ash)
2. B-1 (sample) = BA-1 (ash)
3. B-2 (sample) = BA-2 (ash)

7.4 Enrichment of REEs in coal ash

Samples and its ash showed a considerable difference, which encourages exploring REEs in fly ash for future works. As already discussed, coal ash shows a higher concentration of REEs due to its mineral content. When coal combustion occurs in a thermal power plant, the operating temperature reaches up to 800°C to 1400°C, and it may affect the inorganic content in coal. The organic component of coal was burnt and used to produce energy in thermal power plants. So, in coal ash, most inorganic content may left, which is coal's mineral matter.

Furthermore, lanthanide series elements start to melt from 800°C (cerium) and go up to 1,663°C (lutetium), which means that REEs concentration in coal may hamper as such in fly ash (Hower et al. 2021). So, probably coal combustion may hamper REEs concentration in fly ash. That’s why recovery of REEs from coal should be done before combustion. However, coal combustion increases its concentration due to an increase in proportions (weight percentage) of inorganic contents (Lin et al. 2017a). Mineralogical studies of fly ash showed the presence of mullite, feldspar, clay and to some extent quartz, hematite and magnetite in previous research works (Ketris and Yudovich 2009). Mullite is alumino-silicate product, which forms on a very high temperate (above 1200°C). Various crystallographic studies (Hansen et al. 1981) have shown that the elements are predominantly embedded with glassy alumino-silicate minerals in coal ash. Clay, quartz, and hematite have already been seen in graphs of XRD peaks in chapter five. Hence, this can be the reason for REEs higher concentration in coal ash than coal samples of the study area.

Shaly coal samples (B1 and B2) were showing high concentrations in raw samples, and when its ash concentration was analyzed by ICP-MS, it didn't show any considerable change in ash. This is probably due to its mineral contents. Shaly coal samples have very high inorganic (ash) and low organic content from table 6.2 which leads to no considerable change in REEs concentration in its ash samples.

7.5 Significance of REEs concentration in coal and it's by products

The REEs concentrations in Sohagpur coalfield were also compared with the Chinese coal, US coal and World coal average from table 7.3 for its significance. The average content of critical rare earth elements for yttrium is 51.49 ppm, for neodymium is 79.34 ppm, for europium is 2.67 ppm, for terbium is 1.71 ppm, and for dysprosium is 9.76 ppm. The highest average value of REEs reported for cerium is 58.15 ppm in coal and 187 ppm in coal ash by-products. The coal by-products of the collected samples are a good resource for REEs than the Chinese coal, US coal and World coal average. REEs concentration will add value to coal and its by-products through its parallel extraction.

Furthermore, the statistical method also helps in correlation and its significance for REEs concentration.

7.6 Pearson coefficient correlation between rare earth elements

Pearson correlation coefficient (PCC) 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. Uranium is showing a moderate to low, positive correlation with every element. The highest correlations were shown by the holmium element with terbium, dysprosium, and thulium (Table 7.4). The lowest correlations were shown by the uranium element with neodymium, praseodymium and cerium elements. Linear correlations were higher in light rare earth elements (LREE) than heavy rare earth elements (HREE). This statistical analysis points toward that the correlations of elements on LREEs. This can be further helpful in future for cost cutting in the analysis of one or two elements rather than whole LREEs due to high correlations. Literature reports suggest that strong associations typically exist between La and other REEs (Ekmann 2012). This suggests that La may be used as a trace indicator of REEs enrichment for exploratory REE characterization work (Luttrell et al. 2016).

7.7 Rare earth elements correlation with gross caloric value (GCV)

Rare earth elements (REEs) moderate correlate with the gross calorific value (GCV). Every element of REEs was showing a positive correlation with GCV, which means that with the increase of GCV, the concentration of REEs also increases (Fig. 7.9). It can be also said that, minerals of REEs associated with the organic content in these coal samples.

	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 7.4: Pearson coefficient relation between REEs of samples

REEs concentration varies from sample to sample. Some time it is associated with inorganic content, sometime it is associated with organic content and sometime with both (Lin et al. 2017b). So furthermore studies will clear more views on this context in future.

7.8 Ratio of LREEs with HREEs

The ratio of LREE by HREE for the A1 sample was 14, for the A2 sample was 13, for B1 was 18, for B2 was 21, for B3 was 12, for D1 was 16, and for C1 was 13. So, with this ratio, it can be depicted that the concentration of LREE was higher in coal samples.

This ratio of LREE by HREE in coal ash for the AA1 sample was 18, for BA1 was 18, and for BA2 was 17. This is not showing a very strong trend, however, this ratio is higher in coal ash, than in raw coal. It can also lead to that coal ash of the study area having higher LREEs than HREEs in samples. The reason for this is due to mineral content in coal, as already discussed that monazite (phosphate mineral) leads to a higher concentration of LREE than HREE in coal samples. Clays have low REEs concentration, however, relatively high heavy REE fractions make them a valuable REE resource (Kanazawa and Kamitani, 2006). Eskenazy (1987) found that coals, especially the low-ash coals, were relatively enriched in REEs with a lower light REE (LREE) to HREE ratio and concluded that the majority of the REEs might be strongly bound to the organic matter. Coal samples of the studied area show an average ratio of LREE/HREE as discussed earlier (Wang 2015). It means that REEs are associated with both, organic and inorganic contents in coal samples of the study area.

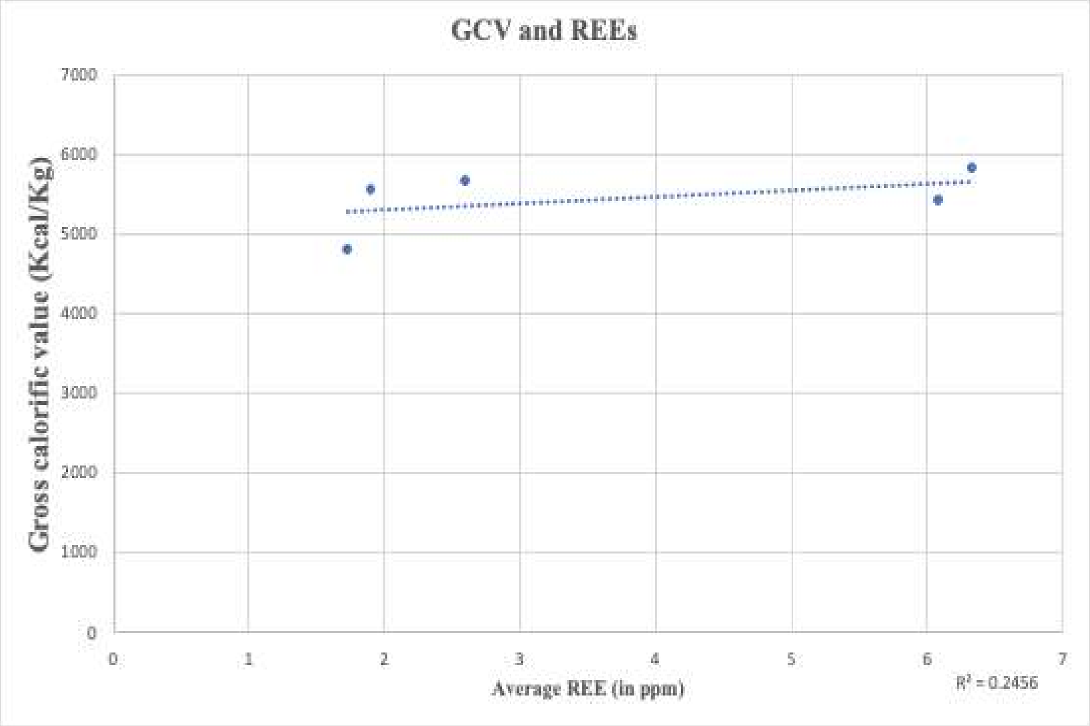


Fig. 7.9: Relation between GCV and average REEs content in coal samples