Chapter-8

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Leaching is the process of a solute becoming detached and extracted from its carrier substance by way of a solvent. Various elements and metals are extracted by leaching methods and it is most widely used till now (Seferinoglu 2003). Recovery of REEs from coal is possible to meet the requirement. However, these REEs are entrained in the predominant aluminosilicate phase, hampering their solubilization and requiring strong acidic conditions (Pan et al. 2020). The acid is selected based on the subsequent separation process. Sulphuric acid and nitric acid were used for the experimental works as per coal mineralogy and elements present in coal (Li et al. 2006; Peelman et al. 2016) in samples. Sodium hydroxide (base) is also used in another leaching experiment. Solid to liquid ratio (S/L ratio) was constant (1:10) in both the experiments. This process leaches some concentration of thorium and uranium together (co-extraction) with the REEs. The leaching process is also important because it recovers the elements without destroying the mineral's crystal structure (Todorovsky et al. 2016). Hence, leaching experiments were conducted on the coal samples to recover valuable elements, which were recovered by two different methods and chemical solutions. The detailed of each leaching experiment is discussed in subsequent paragraph.

8.1 Experiment No. 1: Leaching on coal by water and acidic solution (Slow method)

8.2 Introduction

Coal and its by-product are considered as a promising resource for critical and rare earth elements as revealed by detailed analysis of coal and coal by-products in previous chapter (chapter seven). Many research methods have tried to recover these valuable REEs (Honaker et al. 2017; Vass et al. 2019; Wang et al. 2019; Zhang et al. 2015; Zhang et al. 2018; Zhang et al. 2019; Vass et al. 2019; Huang et al. 2018; Lin et al. 2017; Laudal et al. 2018; Taggart et al. 2018). However, these methods have complications to apply on an industrial scale. The experiment one is given an encouraging result as far as release of REEs from coal by acidic and water is concerned. This leaching method has recovered more than 50% of TREEs and for some metals (REEs), the recovery value goes up to 90%. Leachate also shows the mobility of trace elements from coal to leachate samples. These trace elements may be harmful to the environment, and its recovery leads to the parallel beneficiation of coal. Trace elements must be removed after coal combustion in thermal power plants. So, this experiment method simultaneously recover REEs and trace elements from coal samples of the study area.

Coal combustion products (fly ash) generated by power plants contains many heavy metals as waste (Beddu et al. 2020). Many metals with higher concentrations are accessible for percolation and mobilization into the environment (Ribeiro and Flores 2021). These heavy metals may harm the environment if they percolate and contaminate any water resources nearby. So it needs to be removed from coal for utilization and environmental protection.

REEs include the elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), and samarium (Sm). europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Yttrium (Y) and scandium (Sc) are also included in this group due to their similarity with Lanthanide series elements (Binningham and Horovitz 1999). REEs are usually divided into two broad categories. Those broad categories are light rare earth elements (LREE) and heavy rare earth elements (HREE). Critical rare earth elements (Y, Nd, Eu, Tb, and Dy) are also part of those two categories.

REEs are identified as critical commodities due to their crucial roles in clean energy, high tech, and national defense industries (Chu, S. 2011; Blengini et al. 2017; Trump, D. 2018). Demand for REEs has increased many folds, but its limited supply by only few countries (China and USA) makes the pace of expanding requirement slow. Trade and permitting restrictions have increased concern over the mining availability of REEs along with economic and environmental issues. These factors also cause of a considerable increase in the interest for the recovery of REEs from coal, and its by-products (Dong et al. 2016; USGS 2020; Hassas et al. 2020; Zhang et al. 2015). Commonly, REEs are found in bastnaesite, monazite, and xenotime-like minerals on a commercial scale. These are called rare earth deposits (RED).

Coal also contains silicate minerals, so water leaching effectively removes silicate minerals. It dissolves the silicate minerals, removes the majority of silica and changes it from a glassy phase to a porous structure. The siliceous skeletons (frustules) of diatoms, and also possibly siliceous sponge spicules, are reported as mineral-matter components in a number of modern-day peat deposits (Andrejko et al. 1983b; Davis et al. 1984). Separate accumulations of diatomite may also occur in lacustrine deposits intimately associated with coal seams (Koukouzas 2007). Such biogenic particles are composed essentially of amorphous silica rather than crystalline quartz and are thus slightly more soluble in water. The water leaching process reduces mass transfer limitations, so the acid can easily diffuse into the particles. In this study, acid leaching tests were performed on coal by increasing the proportions of acidic content (molarity) (Ji and Zhang 2020). The acidic leaching can dissolve the majority of remaining residues and extract REEs and other elements such as aluminium (Pan et al. 2021). As a result, extraction of REEs along with other elements can occur because acid could easily diffuse into the particles (Pan et al. 2021).

Sulfur content in coal leads to acid mine drainage through dissolution and oxidation in water bodies (Sahoo et al. 2014; Zhu et al. 2017a, 2017b). It could be one of the possible ways for metal to get free into the water, thereby leading to high concentrations of metals such as cadmium (Cd), lead (Pd), copper (Cu), etc., into it (Cravotta 2001, 2015a; Cravotta and Brady 2015b, Johnson 2003; Zhao et al. 2014; Yue and Zhao 2008). Apart from it, heavy metals such as zinc (Zn), nickel (Ni), cobalt (Co) and cadmium (Cd) were released during the dissolution and oxidation of pyrite. However, the release of many elements such as chromium (Cr), lead (Pb), aluminium (Al) and arsenic (As) were affected by the pH of the leachate and absorption/co-precipitation (Yue and Zhao 2008). REEs can be recovered by many techniques such as the alkali fusion acid leaching method (Tang 2019). Acid leaching is a promising method to recover the REEs from coal and its by-products (Wen 2020). So, the main objective of this research is to identify the trace elements movement and recovery of REEs in coal samples of the study area by leaching of water and acidic solutions.

8.3 Trace elements in coal and solution

There is a significant concentration of various trace elements (chromium, manganese, cobalt, nickel, copper, zinc, arsenic, molybdenum, cadmium, hafnium and lead) in coal which is given in table 8.1.

Analysis by ICP-MS were done to know the concentrations of trace elements in the leachate samples collected after the experiment. A brief is discussed below.

8.4 Water leaching

Trace elements in coal mine water may pollute natural water bodies. These elements in coal may migrate from solid matrix to water by oxidation, ion exchange, adsorption-desorption, dissolution, and other ways (Shan et al. 2019). The large metal ions were much more resistant to leaching. The solubility of metal ions also depends upon the pH of the solution (Huggins et al. 2012).

However, migration of trace elements from coal to water was not much as given in table 8.2. It may be observed from this table that the concentration of elements such as manganese varies from 48 to 251 ppb. Concentration of manganese is shown with the help of graphical representation in collected water leachate samples (Fig. 8.1). Manganese is an alkaline earth metal ion which removes (mobility) very easily (Sracek et al. 2021). Manganese removal reaches a peak and then makes a plateau value. Furthermore, quality of de-ionized water (pH 7.05 at 22°C) was the same during the experiment, making a declining graph after the plateau. The average concentration of manganese in water

Elements	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Cd	Hf	Pb
Concentration (In ppb)	78910	55320	14420	19420	7820	26020	8000	11960	70	1060	16920

Table 8.1 : Trace elements average concentration in coal samples

S.N.	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Cd	Hf	Pb	pH
1	0.95	154.43	15.38	9.04	2.68	62.74	0.09	0.09	0.19	0.02	0.74	6.80
2	0.71	202.71	21.45	13.08	2.97	54.98	0.07	0.15	0.21	0.02	0.54	6.8
3	0.46	251.83	25.04	11.50	3.01	44.13	0.05	0.22	0.23	0.02	0.23	6.70
4	0.55	231.99	18.59	9.14	3.15	39.61	0.07	0.17	0.19	0.02	0.11	6.7
5	0.69	219.15	12.90	7.16	3.17	33.01	0.09	0.13	0.16	0.02	<0.00	6.70
6	0.51	187.91	10.17	6.11	2.13	29.93	0.06	0.14	0.12	0.01	0.02	6.6
7	0.40	153.87	8.41	5.29	<0.000	25.31	0.10	0.11	0.10	0.01	0.02	6.60
8	0.31	165.29	13.54	6	2.1	28.96	0.08	0.39	0.15	0.01	0.02	6.6
9	0.26	171.93	18.04	6.96	2.42	30.25	0.06	0.57	0.24	0.01	0.03	6.50
10	0.31	131.09	13.92	5.59	1.42	33.31	0.07	1.07	0.13	0.02	0.4	6.5
11	0.36	88.07	11.12	4.13	0.93	36.34	0.09	1.40	0.08	0.02	0.59	6.50
12	0.28	69.45	8.89	3.84	0.99	28.39	0.08	1.35	0.06	0.01	0.49	6.4
13	0.22	54.43	6.32	2.5	1.59	21.37	0.07	1.21	0.05	0.01	0.43	6.4
14	0.19	48.89	4.49	1.91	2.32	16.06	0.06	1.07	0.04	0.00	0.38	6.40
FWA	0.44	152.22	13.45	6.59	2.22	34.60	0.07	0.58	0.14	0.01	0.31	6.6
A11	0.49	57.10	5.54	1.91	1.46	20.69	0.37	1.04	0.20	0.11	1.78	6.10
A12	28.91	1719.91	279.53	140.76	170.01	650.82	0.82	0.54	2.12	0.11	89.92	5.8
A13	59.11	3176.85	535.71	325.66	331.86	1029.35	1.69	0.15	3.93	0.10	164.62	5.50
A14	156.67	7194.03	899.92	553.75	532.92	1249.67	2.52	0.09	7.45	0.09	331.27	5.1
A15	580.55	12412.48	1529.79	958.35	817.62	2962.55	5.38	0.04	10.59	0.08	531.82	4.80
A16	934.82	18352.37	1800.28	1250.38	1000	2538.01	6.99	0.02	15.93	0.09	701.24	4.5
A17	1198.20	21899.0	2136.84	1503.35	1209.40	5055.48	9.48	0.00	18.94	0.13	792.97	4.20
A18	1599.35	22384.38	2037.11	1661.30	1839.58	5349.72	13.31	0.39	20.11	0.32	1349	3.5
A19	2109.33	24113.23	2011.96	1699.28	2340.93	5862.35	18.20	0.83	22.30	0.59	1543.77	3.1
A20	2609.50	25918.28	1984.10	1724.91	2759.94	6247.28	23.76	1.10	23.83	0.75	1918.84	2.50
FAWA	927.69	13722.76	1322.08	981.96	1100.37	3096.59	8.25	0.42	12.54	0.24	742.52	4.5

Table 8.2: Trace elements in water collected from experiment one
FWA= Final water Average, FAWA= Final acidic water average
Result in ppb (Parts per billion)
pH=Potential of hydrogen

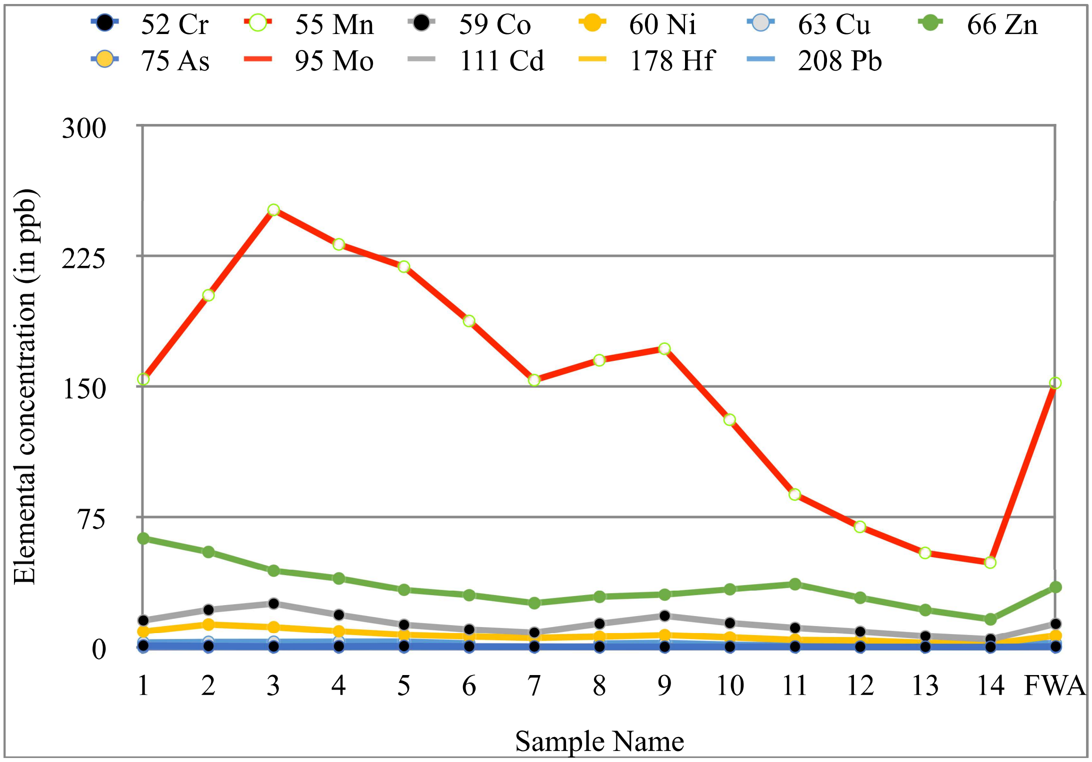


Fig. 8.1: Elemental concentration in water leaching

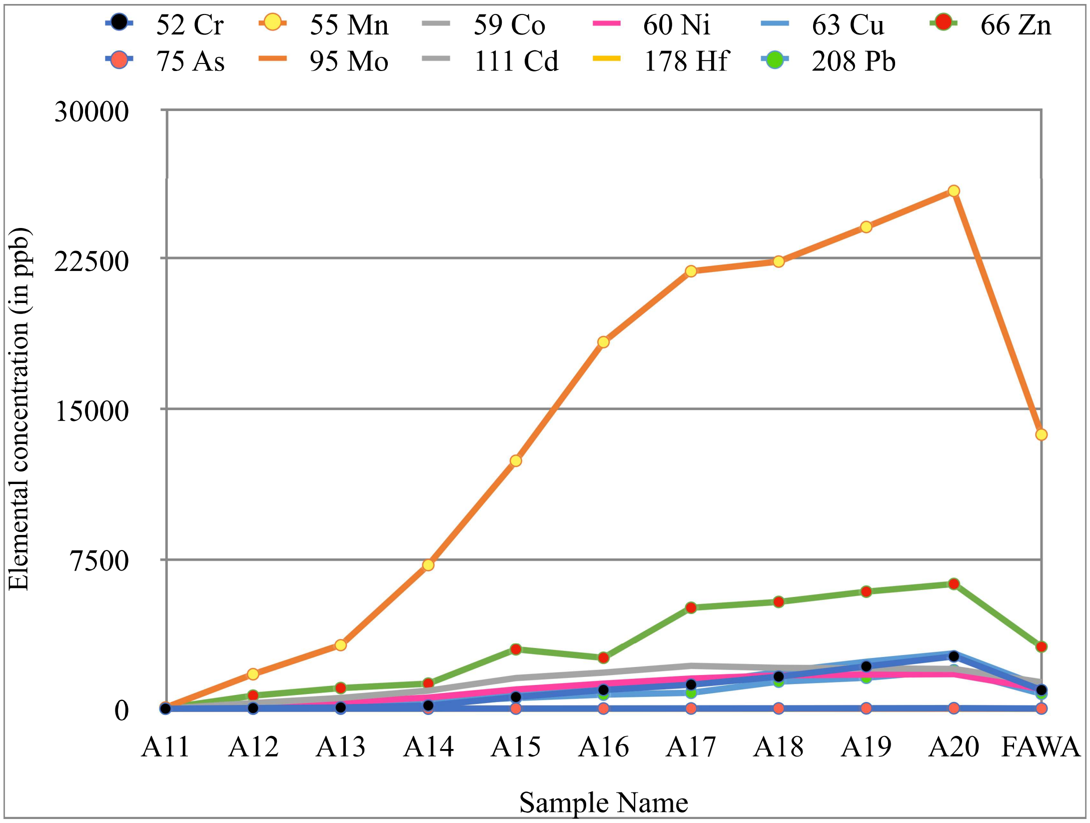


Fig. 8.2: Elemental concentration in acid leaching

samples was 152 ppb. Concentration of zinc varies from 16 to 62 ppb, and the average concentration is 34 ppb. Cobalt varies from 4 to 25 ppb, and the average concentration is 13 ppb. Nickel varies from 2.5 to 13 ppb, and the average concentration is 6.59 ppb. Copper varies from 0 to 3.17 ppb, and the average concentration is 2.22 ppb. Molybdenum varies from 0.11 to 1.40 ppb, and the average concentration is 0.58 ppb. Chromium varies from 0 .19 to 0.95 ppb and average concentration is 0.44 ppb. The average concentrations of lead, cadmium, arsenic and hafnium are 0.31 ppb, 0.14 ppb, 0.07 ppb, and 0.01 ppb (Fig. 8.1). Standard deviation and mean for final water average (FWA) are 45.34 and 19.14 ppb.

Several metals were identified in leachates, but it is unclear whether the remaining metals were present in a non-leachable form (insoluble to water). The potential of hydrogen (pH) of the solution was also measured in leachate samples. The pH of the leachate (sample 1 to 14) is decreasing, it may be probably due to reaction of water (pH 7.05) with pyrite in coal which leads to increase of acidic condition (pH) in leachate samples. This experiment shows that the rainfall or running water in the coal seam might not result in considerable contamination in the surrounding habitat due to the leaching effect.

8.5 Acidic leaching

Trace elements

The leaching of coal sample was done and the leachate samples were analyzed for 11 important trace elements by ICP-MS instrument. The values are plotted in figure 8.2. It may be observed from this figure that during acid leaching, the concentration of various elements were relatively more. This might be attributed due to their more significant mobilization in acid than that in water. It may be observed that the leaching of manganese was highest by acidic solution. It was directly proportional to the acidic concentration (molarity). Manganese concentration varies from 57 to 25,918 ppb, with an average value of 13,722 ppb in leachate. Zinc concentration varies from 20 to 6247 ppb, having an average value of 3096 ppb. The concentration of copper varies from 1.46 to 2759 ppb, having an average concentration of 1100 ppb, followed by nickel, having contracts from 1.91 to 1724 ppb with an average concentration of 981 ppb. The concentration of chromium varies from 0.49 to 2609 ppb, and an average concentration of 981 ppb.

Concentration of lead varies from 1.87 to 1918 ppb with an average concentration of 742 ppb, while the concentration of cadmium varies from 0.20 to 23.83 ppb with an average concentration of 12 ppb. Apart from this, other metals have been also analyzed and the concentration of arsenic, molybdenum and hafnium are 8.27 ppb, 0.42 ppb, and 0.24 ppb which are very low concentration in leachate samples. The concentration of elements is given in table 8.2. The standard deviation and mean for final acidic water average (FAWA) are 3994 and 1992 ppb. It can be inferred from the concentration of various elements through the leaching experiment that almost all the trace elements follow the same trend of having an initial low concentration in acidic solution in sample no. A11 (leachate sample), and it gradually increased in samples no. A20 except for cobalt. It is due to change in molarity of acidic solution in leaching experiment from sample no. A11 to A20. In the acidic solution, the concentration of cobalt increased and attained its peak in sample no. A17, after which it gradually starts to decrease in leachate.

Elements	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Average concentration (in ppb)	300	2780	3330	5130	173	600	150	35	193	270	1640	330	120	15	160	30	100	32

Table 8.4: Rare earth elements average concentration in coal samples

S.N.	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.01	0.03	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
14	0.00	0.02	0.06	0.00	0.01	0.04	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
FWA	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
A12	0.03	40.19	53.92	90.34	9.01	33.92	8.21	1.89	11.49	1.99	13.59	2.37	6.73	0.88	4.79	0.65	0.02	0.63
A13	0.04	79.34	107.47	181.05	17.92	67.35	14.82	3.71	22.09	3.85	23.71	4.70	12.29	1.54	8.52	1.20	0.03	1.37
A14	0.20	150.20	173.23	330.55	31.83	130.46	24.64	6.69	40.21	5.38	43.92	9.13	21.99	3.01	14.93	1.99	0.19	2.06
A15	0.81	250.38	329.95	541.76	54.03	205.84	46.54	11.96	71.02	12.76	80.35	16.15	43.31	5.47	30.53	4.34	0.67	3.64
A16	1.10	301.95	471.32	770.98	75.01	275.82	63.11	15.06	90.95	18.94	100.67	21.88	63.56	7.16	41.43	5.76	0.93	4.18
A17	2.10	402.34	567.57	936.04	93.89	358.40	80.08	20.71	122.70	21.81	138.41	27.95	75.60	9.57	53.94	7.63	1.58	4.89
A18	15.91	458.37	615.00	1109.84	125.46	400.37	106.43	24.79	143.44	24.93	163.75	32.42	85.67	11.48	61.84	8.82	10.39	9.90
A19	30.95	532.26	778.63	1300.79	140.62	465.70	120.37	29.83	177.32	30.28	190.39	37.32	101.21	13.01	73.29	10.21	24.43	19.39
A20	31.92	604.38	881.63	1512.46	154.65	584.81	127.48	31.45	183.72	32.01	199.18	39.87	106.79	13.57	77.23	10.88	27.40	23.06
FAWA	8.31	281.94	397.87	677.38	70.24	252.27	59.17	14.61	86.30	15.20	95.40	19.18	51.72	6.57	36.65	5.15	6.57	6.91

Table 8.5: Rare earth elements in water and acidic solution collected from experiment (in ppb)
FWA= Final water average, FAWA= Final acid water average

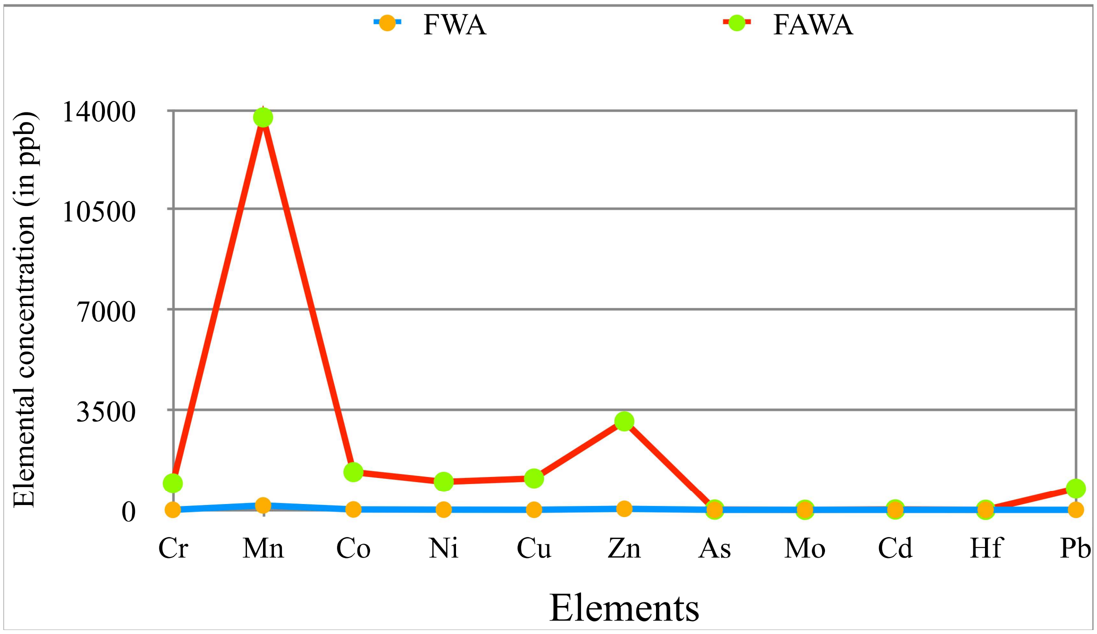


Fig. 8.3: Elemental concentration in Final water average (FWA) and Final acid water average (FAWA)

It can be inferred that the concentration of various elements in water leaching experiment is lesser than the concentration of various elements in acidic leaching experiment. This is also shown in fig. 8.3. The FAWA is the average concentration of toxic elements in acidic leachate (FWA<FAWA). It might be attributed to increased mobility of elements in acidic conditions than in de-ionized water. Toxic elements are more sensitive and soluble to the acidic solution than de-ionized water which can be seen from FWA and FAWA. The pH value of leachate samples were also determined and it has been observed that the pH of leachate samples show a gradual decrease in value of pH sample at the beginning and after leaching. It has been observed that pH value of leachate is fluctuating. However, the general trend of pH value is decreasing and ultimately reached to 2.5 from 6.10 pH value in acidic leaching.

8.6 Mobilization of REEs (Occurrence of REEs and leaching behaviour)

The table 8.4 revealed the concentration of REEs in coal. This table shows the concentration of REEs from scandium to lutetium along with thorium and uranium elements (total of 18 elements). This coal sample was used for leaching experiments. Figure 8.4 shows that LREE is higher than HREE quantitatively.

In the case of REEs, leachate samples show that recovery is possible with the help of acid leaching (Fig. 8.4 and table 8.5). As said in previous chapters, REEs are divided into LREE (light rare earth elements) and HREE (heavy rare earth elements). The light rare earth elements (LREE) include La through Sm, and the heavy rare earth elements (HREEs) include Eu to Lu (Seredin 1996; Hower et al. 1999; Mardon and Hower 2004; Dai et al. 2016b). With the help of graphical representation (Fig. 8.4), it can be said that LREE is higher than HREE quantitatively in leachate samples (LREE > HREE). The highest recovery of Sc is 31.92 ppb, Y is 604.38 ppb, La is 881.63 ppb, Ce is 1512.46 ppb, Pr is 154.65 ppb, Nd is 584.81 ppb, Sm is 127.48 ppb, Eu is 31.45 ppb, Gd is 183.72 ppb, Tb is 32.01 ppb, Dy is 199.18 ppb, Ho is 39.87 ppb, Er is 106.79 ppb, Tm is 13.57 ppb, Yb is 77.23 ppb, Lu is 10.88 ppb, Th is 27.40 ppb, and U is 23.06 ppb.

Mobilization of REEs concentration depends upon the mineral contents in coal. REEs are entrapped and associated with particular minerals. Xenotime is a major mineral of HREEs which is not found in these raw samples. While monazite which is major mineral for LREEs, can lead to higher concentration of LREEs in raw samples (coal) and leachates. It is also supported by XRD peaks (in chapter five).

The ratio of LREEs by HREEs was 6.04 in raw coal before leaching experiment. However, this ratio in FAWA was 7.92 which depicts that, recovery (mobility) of LREEs were little higher in leachates. It is difficult to say that REEs comes from organic or

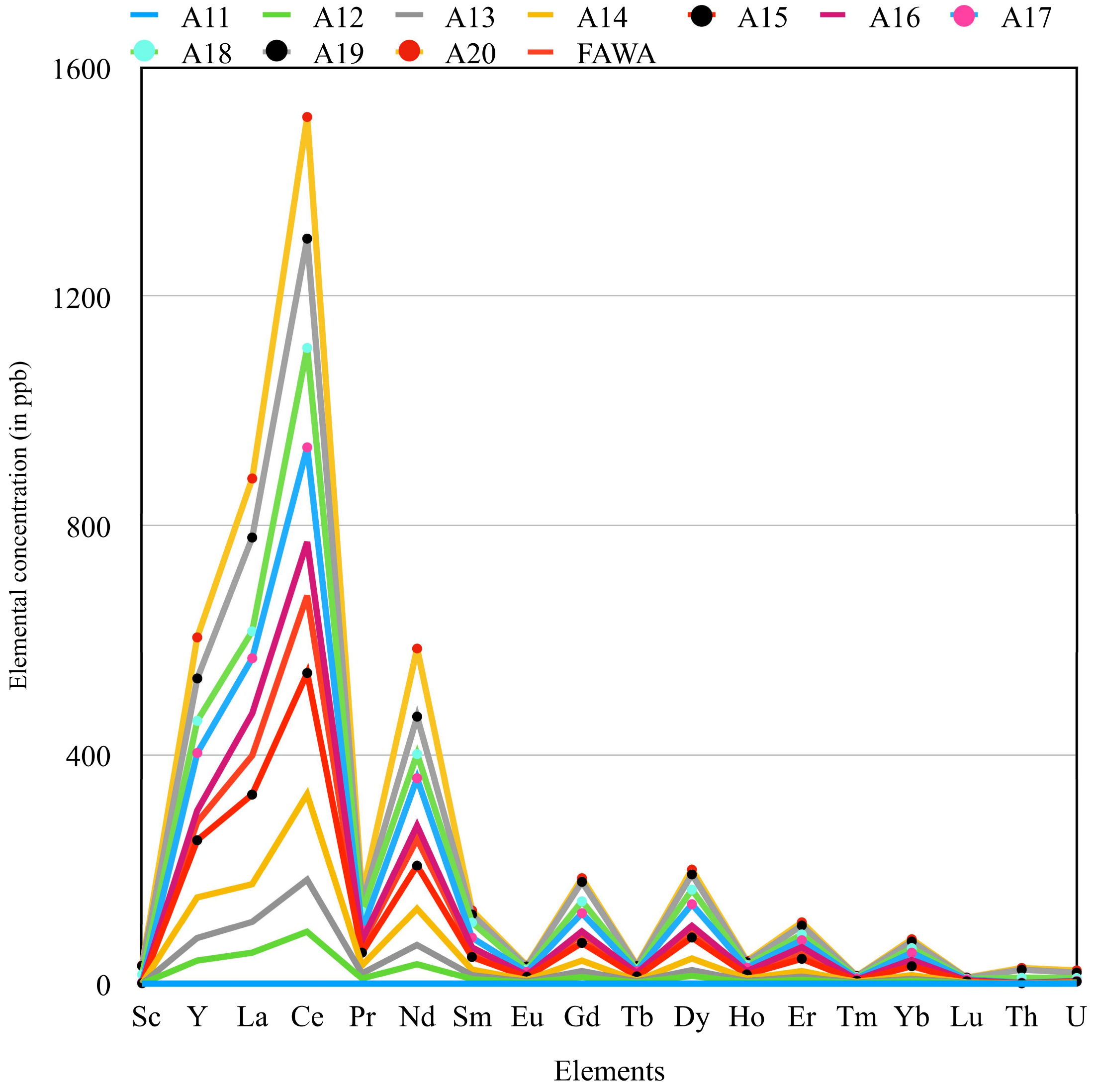


Fig. 8.4: Rare earth elements concentration in acidic samples

inorganic content of coal due to this ratio. It is furthermore discussed in chapter nine of discussion chapter.

8.7 Recovery of REEs

Recovery of REEs in acidic leaching is high in leachate samples from coal. Figure 8.5 shows the recovery percentage of REEs in leachates determined by the ICP-MS analysis. Concentration of REEs shows that the recovery of REEs in leachate is more than 50% such as praseodymium (89%), neodymium (97%), samarium (85%), europium (90%), gadolinium (95%), erbium (89%), thulium (90%) and uranium (72%) element. The recovery percentage (Table 8.6) was made by comparison of average REEs in coal samples (Table 8.4) and the highest REEs concentration in acid water samples (Table 8.5). The table 8.6 shows the recovery percentage of REEs from coal as a result of leaching. It may be observed from this table that there are a few REEs, which is recovered less than 15% such as scandium (10%), terbium (12%), dysprosium (12%) and holmium (13%) element. The standard deviation and mean for recovery percentage are 34.68 and 52.4 for the leachate samples. Furthermore, recovery is also supported by surface morphology change in coal and residue samples.

Elements	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Recovery (%)	10.4	21.7	26.4	29.4	89.3	97.4	84.9	89.8	95.1	11.8	12.1	13.2	88.9	90.4	48.2	36.2	27.4	72.1

Table 8.6: Recovery of REEs in acid samples

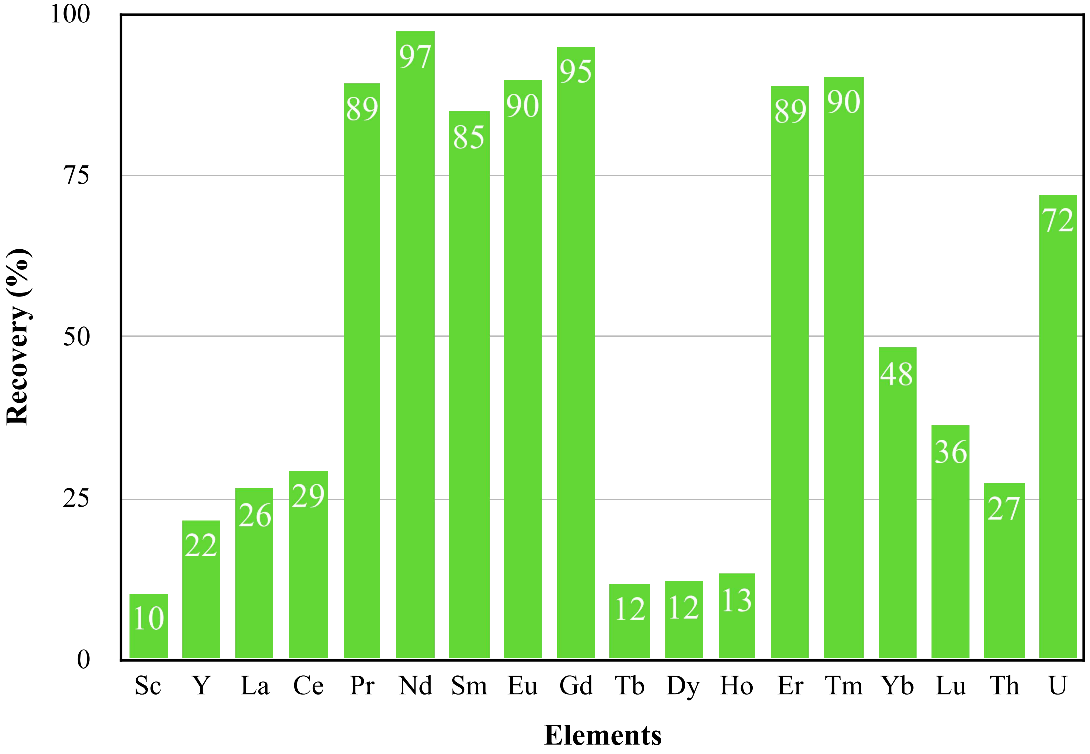


Fig. 8.5: Graphical representation of recovered REEs in acid leaching

8.8 Changes in surface morphology

The coal samples were analyzed by scanning electron microscopy (SEM) to see the morphological changes in coal samples before and after the leaching experiments with water and acid solution.

With the help of microscopic images produced by SEM, it can be said that the coal samples were angular to sub-angular in shape with rough surface before leaching. However, after the leaching, when SEM again analyzed residue sample, the same coal samples became cloudy in appearance, smooth, semi-spherical in shape and bumpy in structure. Here, two µm and 20 µm images unveil the effect of water and acid leaching on coal samples. It can also be seen in figs. 8.6 and 8.7.

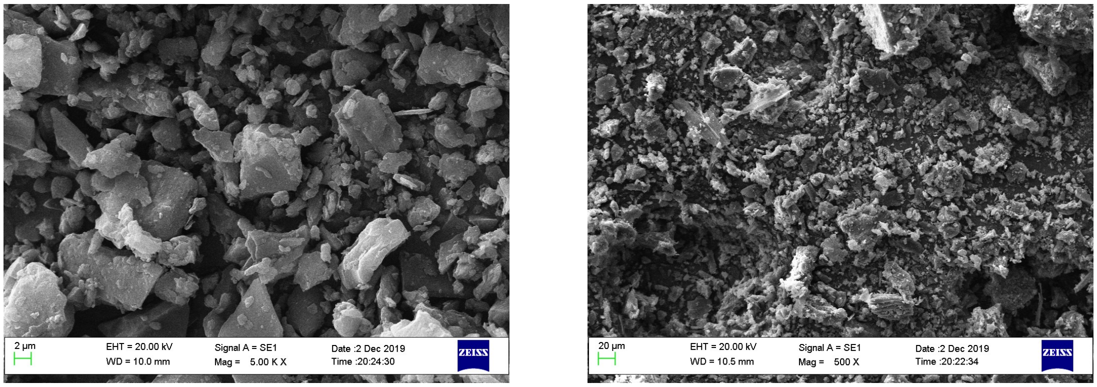


Fig. 8.6: Microscopic images of coal sample on 2 µm and 20 µm scale, before the experiment

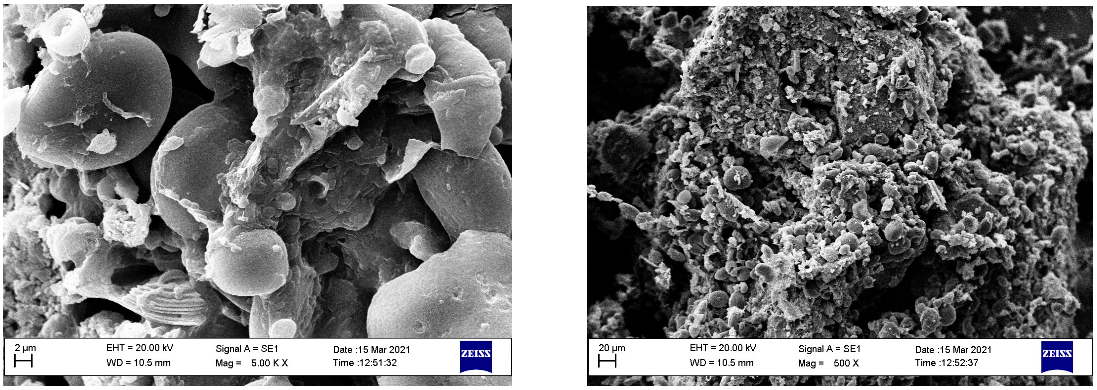


Fig. 8.7: Microscopic images of coal sample on 2 µm and 20 µm scale, after the experiment

8.9 Experiment 2: Leaching on coal by acidic solution and basic solution (Fast method)

8.10 Introduction

Selective leaching is a subsidiary methodology to determine the mode of occurrence of an element and this is the most effective way to remove the inorganic matter up to 90% in conditional circumstances (Behera et al. 2018). With the help of strong acid and strong base, recovery of REEs can be possible, as these chemicals can dissolve the metals (REEs) in it (Middleton et al. 2020). Information on the modes of occurrence of REEs in coal can help to assess the potential extraction procedures from coal and coal combustion by-products (Finkelman 1993; Seredin and Dai 2012; Barik et al. 2012, Seredin et al. 2013; Sun et al. 2016; Dai and Finkelman 2018; Finkelman et al. 2018).

In this study, acidic and basic leaching experiments were performed to recover the REEs. The recovery of REEs has been made in coal, shaly coal and calcined materials through leaching. In leaching, de-ionized water (pH=7.05 at 22°C), acidic solution and basic solution were used. The experimental work addresses a thorough understanding of the distribution and modes of occurrence of REEs in coal, shaly coal and calcined material and the potential recovery of REEs through the chemical extraction and treatments process.

It is seen that leachate collected after de-ionized water showed very minimal or negligible recovery of REEs, as seen in previous work (in experiment one). So, that is why this experimental work only focuses on leachate collected after acidic/basic solutions. The collected solution (leachate) showed encouraging results in acidic and basic leaching (Table 8.7 and 8.8). Hence, first there is discussion of recovery in A1 (I) coal samples (Table 8.9 and fig. 8.8), second in B2 (I) shaly coal samples (Table 8.10 and

ppb	A1 (I)	A1 (R)-B	A1(R)-A	A1(CR)-A	B2(I)	B2(R)-B	B2(CR)-B	C3(I)	C3(CR)-A	C3(CR)-B
Sc	2039.28	315.60	11156.24	14380.48	22385.01	138.86	2.58	4562.91	994.90	187.32
Y	5360.46	248.68	17892.66	19269.76	38533.79	159.66	1.96	13474.86	1966.18	442.46
La	6815.36	277.50	23230.64	37848.12	86092.17	372.28	5.02	19053.60	3101.56	588.92
Ce	11646.57	550.84	49554.98	73670.88	170694.46	739.90	10.34	17874.41	6116.82	1175.42
Pr	1533.24	64.58	5544.46	13976.24	18787.60	88.84	1.22	4363.59	764.84	144.16
Nd	5857.62	245.64	21753.44	36556.70	70145.28	342.44	3.74	16905.58	2858.18	547.30
Sm	1081.49	41.98	3346.02	6354.64	12747.82	57.44	0.80	3181.28	484.28	93.44
Eu	216.32	8.38	664.64	1800.38	2284.28	11.38	0.18	660.81	96.16	18.36
Gd	1025.16	40.86	3702.00	5912.00	10439.22	54.82	0.72	2877.50	432.88	85.54
Tb	145.02	4.96	443.26	1181.70	1424.05	6.46	0.12	394.47	53.18	10.32
Dy	872.44	24.32	2387.82	6003.96	8014.92	32.12	0.48	2386.22	263.10	51.78
Ho	173.56	4.40	473.88	1358.72	1521.71	6.10	0.14	486.45	47.40	9.48
Er	517.74	12.02	1345.18	2371.62	4417.67	15.62	0.06	1362.61	125.00	24.90
Tm	70.78	1.60	184.90	500.34	583.13	2.06	0.06	191.30	16.12	3.26
Yb	459.84	9.18	1201.98	1148.74	3748.91	12.06	0.32	1254.86	95.18	19.02
Lu	67.84	1.46	198.80	721.34	524.11	1.86	0.10	167.28	15.62	2.98
Th	2079.98	51.68	2660.72	3999.56	31357.25	71.70	1.74	3873.24	544.96	115.20
U	721.25	7.68	927.74	1759.12	6614.82	10.58	56.20	1338.72	82.24	17.04
Avg.	2260.21	106.18	8148.29	12711.90	27239.78	118.01	4.76	5244.98	1003.25	196.49

Table 8.7: Rare earth element concentration (in ppb) in initial sample and collected samples after leaching.
Note: I= Initial (in red font); R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

Initial sample	**Leached samples**
A1(I)	A1(R)-B, A1(R)-A, A1(CR)-A
B2(I)	B2(R)-B, B2(CR)-B
C3(I)	C3(CR)-A, C3(CR)-B

Table 8.8: Initial and it's leached samples names

fig. 8.9), and then in C3 (I) coal samples (Table 8.11 and fig. 8.10). After this, there is discussion on recovery shown by acidic solution (leachate) comparatively (Fig. 8.11) and then in basic solution (leachate) comparatively (Fig. 8.12) for all samples. In the end, figure 8.13 shows the recovery of REEs in all leachates for all samples. The process of calcination of samples is already discussed in chapter four.

8.11 Recovery from sample A1(I)

Sample number A1 (I) has an average concentration of 2260.21 ppb of REEs as initial concentrations in coal samples before leaching. When this sample, A1 (I), underwent in leaching experiment, as discussed in chapter four (methods of study), it showed a tremendous change in concentration of REEs in leachate samples, A1 (R)-B, A1 (R)-A and A1 (CR)-A. Sample number A1 (R)-B was collected from a basic leaching experiment (sodium hydroxide-NaOH). Sample numbers A1 (R)-A and A1 (CR)-A were collected from the acidic leaching experiment (sulphuric acid-H_2SO_4). Acidic leaching was performed using sulphuric acid on coal and calcined coal samples to determine the highest recovery possible. Base (sodium hydroxide) is also used to study the recovery of REEs from coal samples comparatively. In all samples, A1 (R)-B, A1 (R)-A and A1 (CR)-A collected from the leaching experiment, the recovery pattern follows the same as in the present initial sample (linear pattern). The highest recovery is from the cerium element for all samples. The rest of the recovered REEs are as follows in decreasing order of recovery:

In sample number A1 (R)-B:

Ce>Sc>La>Y>Nd>Pr>Th>Sm>Gd>Dy>Er>Yb>Eu>U>Tb>Ho>Tm>Lu

In sample number A1(R)-A:

Ce>La>Nd>Y>Sc>Pr>Gd>Sm>Th>Dy>Er>Yb>U>Eu>Ho>Tb>Lu>Tm

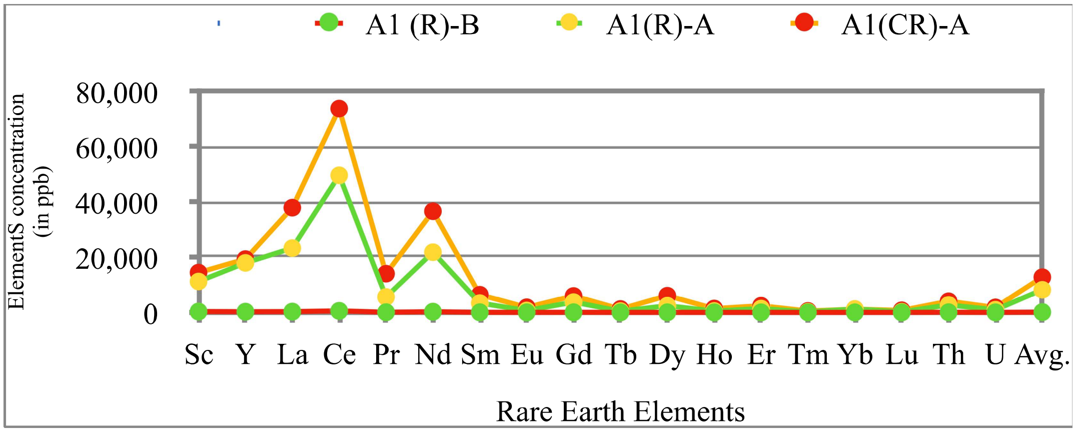


Fig. 8.8: Graphical representation of rare earth element concentration (in ppb) in initial sample and collected samples after leaching in A1(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

ppb	A1 (I)	A1 (R)-B	A1(R)-A	A1(CR)-A
Sc	2039.28	315.60	11156.24	14380.48
Y	5360.46	248.68	17892.66	19269.76
La	6815.36	277.50	23230.64	37848.12
Ce	11646.57	550.84	49554.98	73670.88
Pr	1533.24	64.58	5544.46	13976.24
Nd	5857.62	245.64	21753.44	36556.70
Sm	1081.49	41.98	3346.02	6354.64
Eu	216.32	8.38	664.64	1800.38
Gd	1025.16	40.86	3702.00	5912.00
Tb	145.02	4.96	443.26	1181.70
Dy	872.44	24.32	2387.82	6003.96
Ho	173.56	4.40	473.88	1358.72
Er	517.74	12.02	1345.18	2371.62
Tm	70.78	1.60	184.90	500.34
Yb	459.84	9.18	1201.98	1148.74
Lu	67.84	1.46	198.80	721.34
Th	2079.98	51.68	2660.72	3999.56
U	721.25	7.68	927.74	1759.12
Avg.	2260.21	106.18	8148.29	12711.90
pH	NA	9.50	4.90	4.50

Table 8.9: Rare earth element concentration (in ppb) in initial sample and collected samples after leaching in A1(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average; pH= Potential of hydrogen

In sample number A1 (CR)-A:

Ce>La>Nd>Y>Sc>Pr>Sm>Dy>Gd>Th>Er>Eu>U>Ho>Tb>Yb>Lu>Tm

For sample number A1 (CR)-A, the recovery ranges from 73,000 ppb for cerium to 500 ppb for thulium. At the same time, the average recovery is 12,711 ppb. For sample number A1(R)-A, the recovery ranges from 4900 ppb for cerium to 100 ppb for thulium. At the same time, the average recovery is 800 ppb. For sample number A1 (R)-B, the recovery ranges from 500 ppb for cerium to 1 ppb for lutetium. At the same time, the average recovery is 106 ppb. So, the highest recovery is possible in calcined coal samples using sulphuric acid in the leaching experiment. The standard deviation and mean are 151 and 106 ppb for leachate sample A1(R)-B. The standard deviation and mean are 12814 and 8148 ppb for leachate sample A1(R)-A. The standard deviation and mean are 19106 and 12711 ppb for A1 (CR)-A leachate sample.

8.12 Recovery from sample B2 (I)

In sample number B2 (I), the basic solution is used for leaching in samples and calcined samples. The B2 (I) is a shaly coal sample with the REEs concentration (Table 8.10). However, it didn’t show much recovery as in the previous sample (Table 8.10 and fig. 8.9). The solution used in leaching was sodium hydroxide (NaOH) only. Calcined sample, B2 (CR)-B is also not responding very much relatively in basic leaching experiment. The highest recovery in B2(R)-B is for the cerium element, and the average recovery is 118 ppb. While in B2(CR)-B sample, the highest recovery is for the uranium element, and the average recovery is 4.76 ppb. The standard deviation and mean are 190 and 118 for leachate sample B2(R)-B. The standard deviation and mean are 13 and 4.7 for leachate sample B2 (CR)-B.

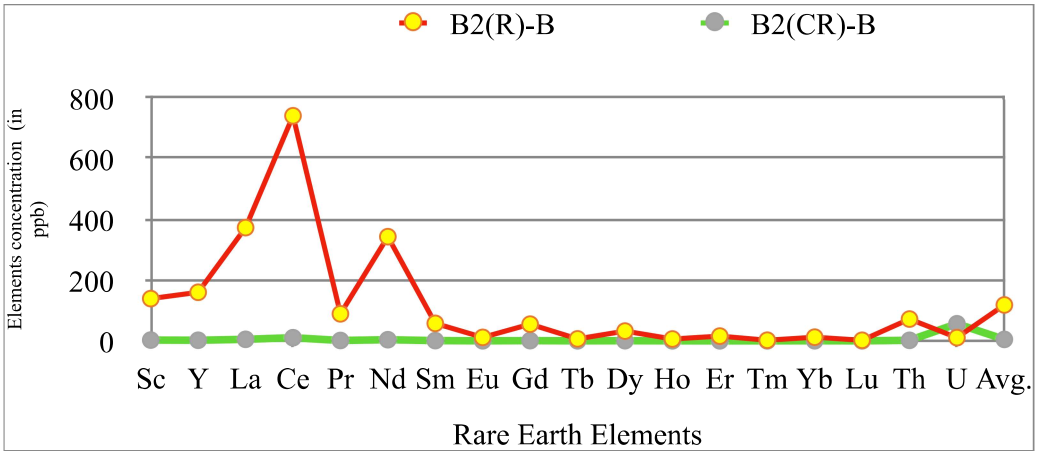


Fig. 8.9: Graphical representation of rare earth element concentration (in ppb) in initial sample and collected samples after leaching in B2(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

ppb	B2(I)	B2(R)-B	B2(CR)-B
Sc	22385.01	138.86	2.58
Y	38533.79	159.66	1.96
La	86092.17	372.28	5.02
Ce	170694.46	739.90	10.34
Pr	18787.60	88.84	1.22
Nd	70145.28	342.44	3.74
Sm	12747.82	57.44	0.80
Eu	2284.28	11.38	0.18
Gd	10439.22	54.82	0.72
Tb	1424.05	6.46	0.12
Dy	8014.92	32.12	0.48
Ho	1521.71	6.10	0.14
Er	4417.67	15.62	0.06
Tm	583.13	2.06	0.06
Yb	3748.91	12.06	0.32
Lu	524.11	1.86	0.10
Th	31357.25	71.70	1.74
U	6614.82	10.58	56.20
Avg.	27239.78	118.01	4.76
pH	NA	9.20	3.50

Table 8.10: Rare earth element concentration (in ppb) in initial sample and collected samples after leaching in B2(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

8.13 Recovery from sample C3 (I)

In sample number C3 (I), acidic and basic solution were used in the leaching experiment on calcined coal samples. The amount of recovery is shown in table 8.11. The highest recovery in C3 (CR)-A sample is cerium 6116 ppb, and the average recovery concentration of REEs is 1003 ppb. So, the recovery percentage for C3 (CR)-A with C3 (I) is 20%. C3 (CR)-B samples have less recovery than the C3 (CR)-A. The highest recovery in C3 (CR)-B sample is of cerium. The average concentration is just 196 ppb. The rest of the recovered REEs are as follows in decreasing order of recovery:

In sample number C3 (CR)-A,

Ce>La>Nd>Y>Sc>Pr>Th>Sm>Gd>Dy>Er>Eu>Yb>U>Tb>Ho>Tm>Lu

In sample number C3 (CR)-B

Ce>La>Nd>Y>Sc>Pr>Th>Sm>Gd>Dy>Er>Yb>Eu>U>Tb>Ho>Tm>Lu

Almost the same recovery pattern in both recovered samples except Yb and Eu have been observed. Standard deviation and mean are 1597 and 1003 for leachate sample C3 (CR)-A. Standard deviation and mean are 308 and 196 for leachate sample C3 (CR)-B.

8.14 Recovery of REEs by acidic solution and basic solution

The leachate samples collected by acidic and basic solutions showed the recovery of REEs. It can be seen that recovery is very high in acidic solutions as shown in figure 8.11. Probably due to the very tiny pores of bottles, acidic solution and basic solution were getting enough time to react with samples which are in very fine particles or can say in powder form. The highest recovery was shown by A1 (CR)-A, which is a calcined material (calcined sample). After this, leachate sample A1(R)-A is also showing the recovery of REEs, but it is less than the A1 (CR)-A sample. Leachate sample C3 (CR)-A

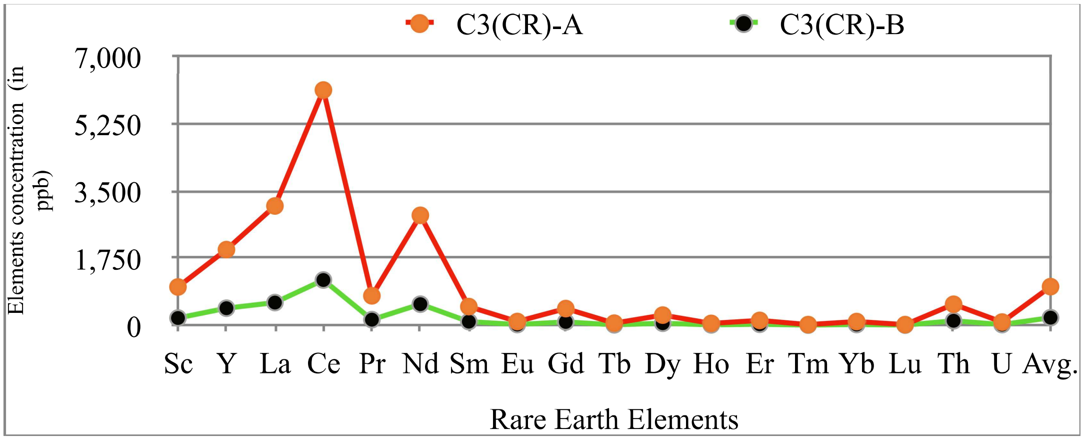


Fig. 8.10: Graphical representation of rare earth element concentration (in ppb) in initial sample and collected samples after leaching in C3(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

ppb	C3(I)	C3(CR)-A	C3(CR)-B
Sc	4562.91	994.90	187.32
Y	13474.86	1966.18	442.46
La	19053.60	3101.56	588.92
Ce	17874.41	6116.82	1175.42
Pr	4363.59	764.84	144.16
Nd	16905.58	2858.18	547.30
Sm	3181.28	484.28	93.44
Eu	660.81	96.16	18.36
Gd	2877.50	432.88	85.54
Tb	394.47	53.18	10.32
Dy	2386.22	263.10	51.78
Ho	486.45	47.40	9.48
Er	1362.61	125.00	24.90
Tm	191.30	16.12	3.26
Yb	1254.86	95.18	19.02
Lu	167.28	15.62	2.98
Th	3873.24	544.96	115.20
U	1338.72	82.24	17.04
Avg.	5244.98	1003.25	196.49
pH	NA	3.10	9.90

Table 8.11: Rare earth element concentration (in ppb) in initial sample and collected samples after leaching in C3(I) sample.
Note: I= Initial; R= Recovered; CR= Calcined recovery; A= Acidic; B= Basic; Avg.= Average

has the lowest recovery of REEs by acidic solution despite the calcined material sample. Calcination material leads to loss of organic matter in coal sample, which creates void space and increase in surface area, by which acidic solution get room (space) to interact within inter and intra space of particles (Zhang and Honaker 2019; 2020). LREE showed higher mobility than HREE in leachates from samples .

The leachate samples collected by the basic solution are A1 (R)-B, B2 (R)-B, B2 (CR)-B and C3 (CR)-B. The highest recovery was shown by the C3 (CR)-B leachate sample, which is calcined material (calcined sample). After this, B2 (R)-B and A1 (R)-B were almost have equal mobility of REEs from samples to leachates, but LREE showed higher mobility than HREE (Fig. 8.12). Leachate sample B2 (CR)-B showed the least mobility of REEs comparatively, probably due to the nature of shaly coal sample.

8.15 Calcined samples leaching results

Acidic and basic leaching experiments were performed on raw (coal and shale coal) and calcined samples (calcined coal and calcined shale coal). Recovery of REEs was notably

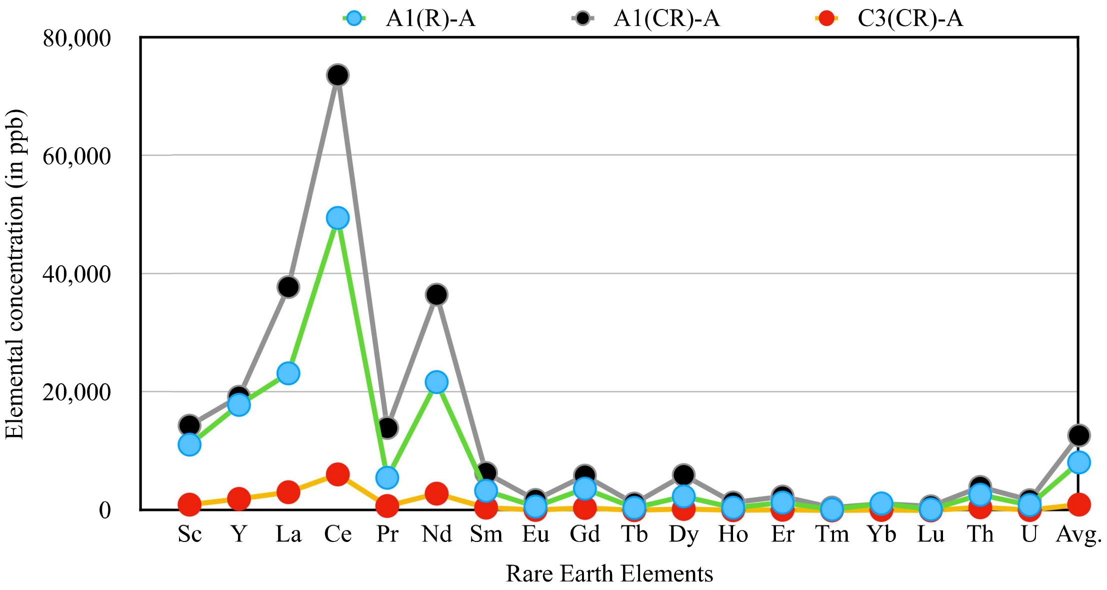


Fig. 8.11: Graphical representation of Rare Earth Elements concentration (in ppb) in acidic solution (acidic leachate)

improved in calcined samples. Further, recovery of REEs was relatively low without calcination. It may be observed that there is 33% less recovery in A1 (R)-A leachate sample in comparison with A1 (CR)-A samples (calcined sample). There is no impact on shaly coal samples due to calcination. When compared with an acidic or basic solution, recovery by acidic solution is more in sample C3 (CR)-A in comparison to basic solution in sample C3 (CR)-B of calcined sample.

REEs in coals can be classified into organic and inorganic associations (Wang et al. 2008 and Zhang et al. 2018). Two factors may provide to enhanced the recovery after calcination: (1) the organically and inorganically associated REEs were liberated after calcination, which might be more leachable (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. It may be concluded that the calcination of sample give relatively higher recovery of REEs in comparison to non-calcined sample.

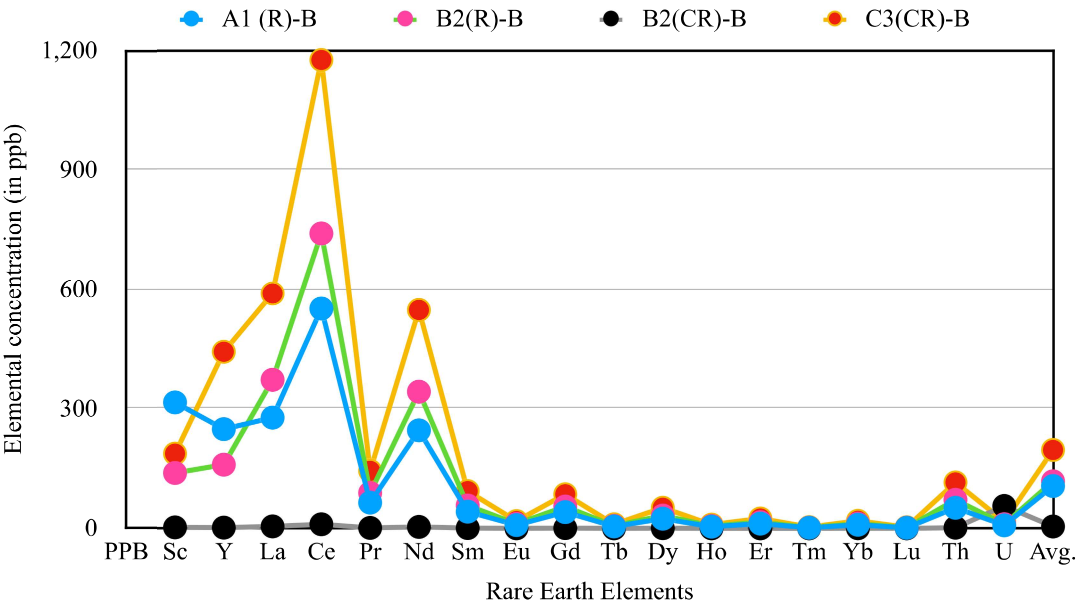


Fig. 8.12: Graphical representation of Rare Earth Elements concentration (in ppb) in basic solution (basic leachate)

8.16 Morphological features and elemental composition of coal and shaly coal samples

SEM-EDX results of all three samples are shown in figs. 8.14, 8.15 and 8.16. It may be observed from these figures that all particles in these samples are angular to sub-angular and irregular in shape. The surface of these particles are rough in appearance in normal condition before leaching. The elemental analysis by EDX is given tabular form also. It may be observed from this that the main elements in coal samples of A(I) and C3(I) include are carbon, oxygen, silicon and aluminium. The other minor elements including

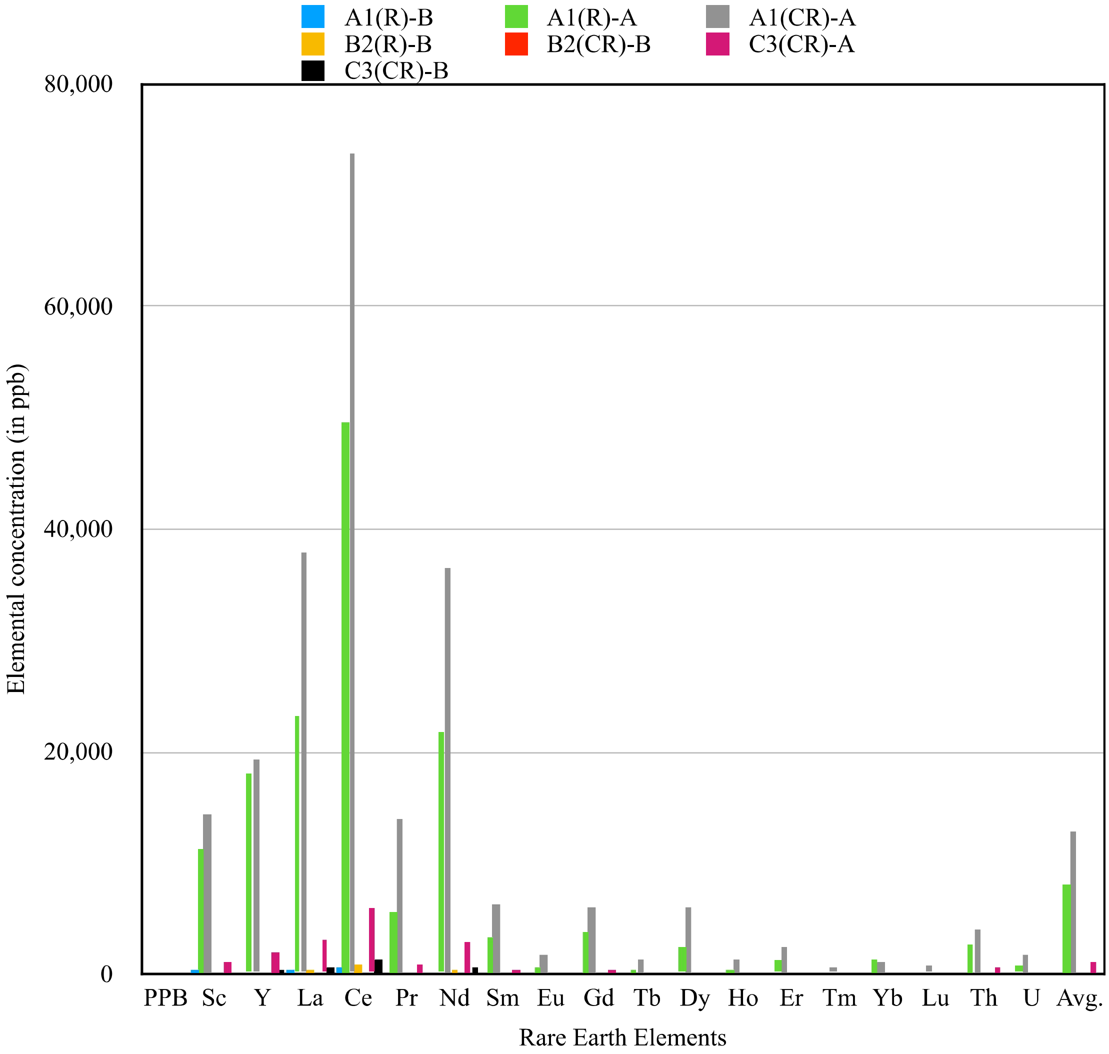


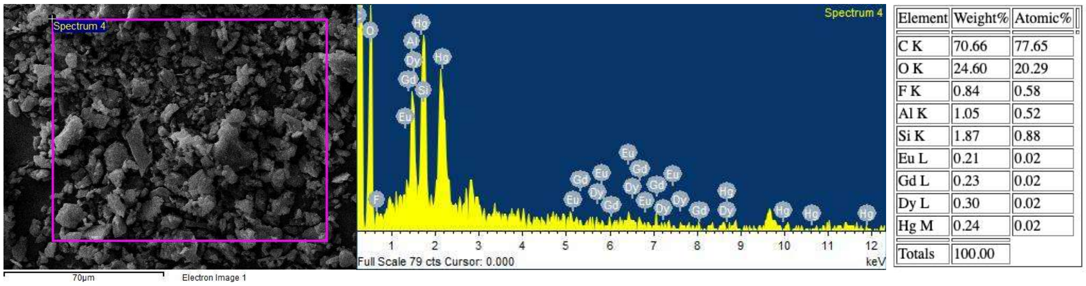
Fig. 8.13: Graphical representation of Rare Earth Elements concentration (in ppb) in leachate

REEs are less than one percent. The major elements in shaly coal are carbon, oxygen, silicon and aluminium. Silicon and aluminium are relatively higher in these samples due to shaly content.

Further, XRD study has also been conducted. The graphs are shown in figures 8.17, 8.18 and 8.19. It has been observed from XRD peaks that there is presence of kaolinite, quartz and albite minerals (Figs. 8.17 and 8.19). While shaly coal sample unveils the presence of kaolinite, birnessite, quartz, albite and graphite minerals (Fig. 8.18). There is no indentation of Pyrite mineral in XRD peaks of coal sample of the study area.

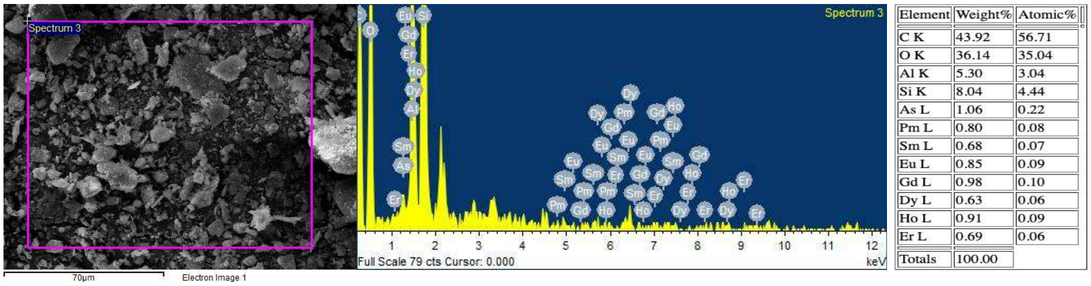
8.17 Co-extraction of uranium and thorium

During leaching experiment, the recovery of U and Th has also been found in significant concentration. The results are given in table 8.9, 8.10 and 8.11. It may be observed from leaching experiments that the recovery depends upon the type of sample and solution used for leaching. It is higher in calcined material and acidic leachate. Highest in A1 (CR)-A leachate sample for both elements. Uranium is mainly associated with non-matrix material (i.e., particle surfaces), while thorium is associated with the aluminosilicate matrix (Hansen and Fisher 1980; Tadmor 1986). These elements are hazardous and may have impact when coal is burned in power plant and coal along with fly ash are exposed to the atmosphere. These elements need to be removed from coal ash to have safer disposal of coal residuals.



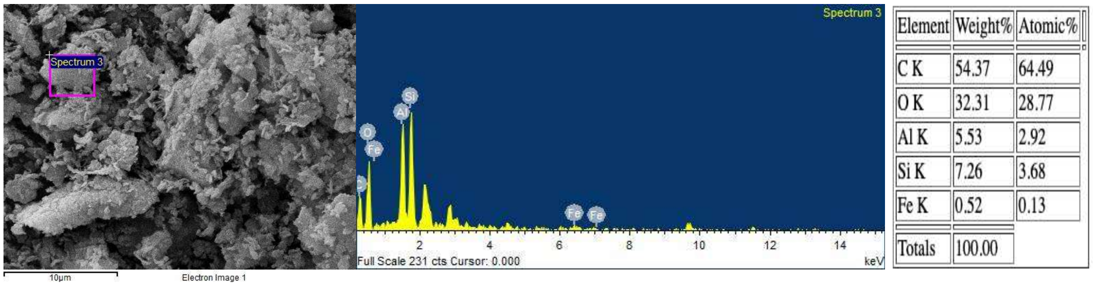
Element	Weight%	Atomic%
C K	70.66	77.65
O K	24.60	20.29
F K	0.84	0.58
Al K	1.05	0.52
Si K	1.87	0.88
Eu L	0.21	0.02
Gd L	0.23	0.02
Dy L	0.30	0.02
Hg M	0.24	0.02
Totals	100.00	

Fig. 8.14: SEM with EDX showing elemental distribution within coal sample A1 (I)



Element	Weight%	Atomic%
C K	43.92	56.71
O K	36.14	35.04
Al K	5.30	3.04
Si K	8.04	4.44
As L	1.06	0.22
Pm L	0.80	0.08
Sm L	0.68	0.07
Eu L	0.85	0.09
Gd L	0.98	0.10
Dy L	0.63	0.06
Ho L	0.91	0.09
Er L	0.69	0.06
Totals	100.00	

Fig. 8.15: SEM with EDX showing elemental distribution within shaly coal sample of B2 (I)



Element	Weight%	Atomic%
C K	54.37	64.49
O K	32.31	28.77
Al K	5.53	2.92
Si K	7.26	3.68
Fe K	0.52	0.13
Totals	100.00	

Fig. 8.16: SEM with EDX showing elemental distribution within coal sample of C3 (I)

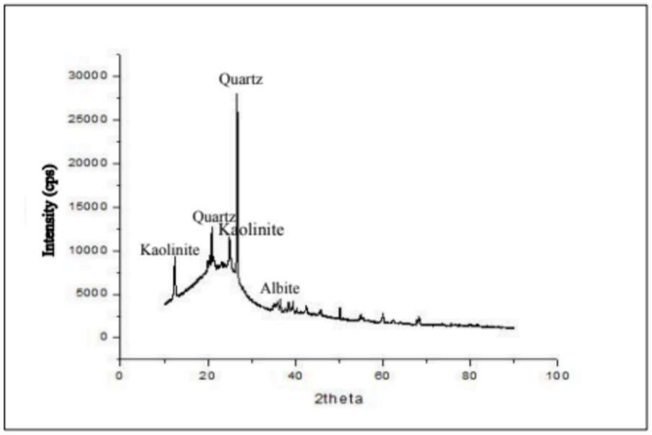


Fig. 8.17: XRD pattern for sample A1(I)

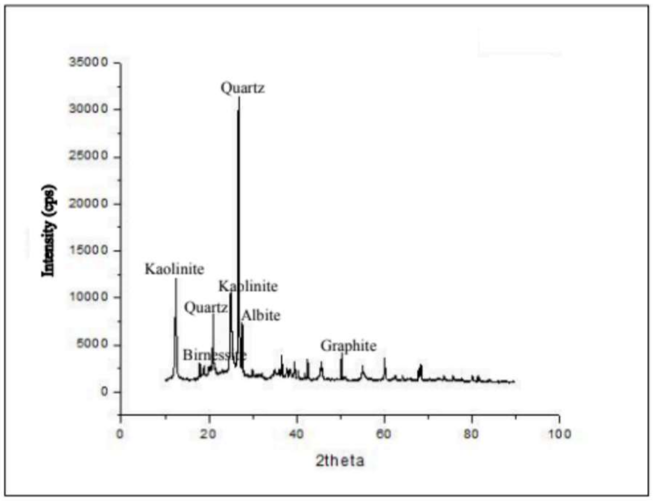


Fig. 8.18: XRD pattern for sample B2(I)

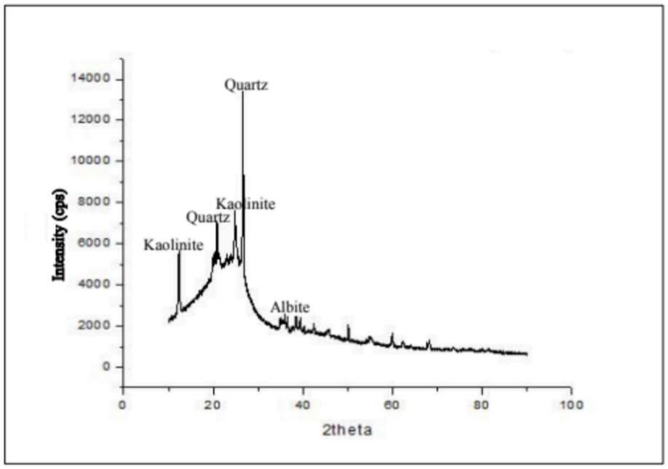


Fig. 8.19: XRD pattern for sample C3(I)