Partitioning of Rare Earth Elements (REEs) from Coal to Coal Fly Ash in Different Thermal Power Stations (TPSs) of India

Sudip Maity1,2*, Akshay K Singh Choudhary1,2, Santosh Kumar1,2 and Pavan K. Gupta1

1CSIR-Central Institute of Mining and Fuel Research (Digwadih), PO: FRI, Dhanbad – 828 108, India
2Academy of Scientific and Innovative Research (AcSIR), Ghaziabad - 201 002, India
E-mail: sudip_maity@yahoo.com*, sudipmaity@cimfr.nic.in; dynamicakshay007@gmail.com; kumarsantoshzb1993@gmail.com; pkchehit@gmail.com

Received: 31 March 2021 / Revised form Accepted: 6 August 2021
© 2022 Geological Society of India, Bengaluru, India

ABSTRACT

Rare earth elements (REEs) have been a topic of profound interest for several decades especially in the present age of electronic and digital revolution. India has the world’s richest beach sands with REEs, yet it imports some strategic REEs to fulfill its demand. It’s high time to explore alternative sources to meet its demand. And coal ash from Thermal Power Stations (TPS) can be a very good alternative resource. In the present study, coal and coal fly ash (CFA) from seven Indian TPSs have been evaluated for estimation of REEs and variations in minerals compositions. Mineralogy of the samples is estimated using X-Ray diffraction (XRD) technique. Coal samples mostly consist of quartz and kaolinite however phase transformations of minerals occurred due to high temperature treatment during combustion. CFA mostly contains quartz and mullite. REEs have been determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and considerable occurrence of any specific REE is not observed. Among the studied TPSs, Pr has the highest concentration among REEs in ash, reaching up to 63 ppm. The Outlook Coefficient (Cout) of REEs is in the range of 0.3 - 4.5 and 0.1 - 1.2 for coal and CFA respectively. In this research paper, Enrichment Coefficient (∆) has been introduced to see the enrichment of REE in CFA with respect to the mother coal and a graph of ∆ vs glassy phase has been plotted to observe the partitioning of REEs. Occurrence of Light REEs is more prominent than Heavy REEs.

INTRODUCTION

Coal is at the core of energy supply chain worldwide and as a result of which large amount of coal fly ash (CFA) is generated across the globe. CFA is one of the most complex industrial anthropogenic waste materials and its inappropriate dumping has become a hazard for environment because of its physical and chemical properties which resulted in wastage of recoverable resources (Wang et al. 2020). Because in the past few years, wide range of possible applications of these elements have emerged such as use of REEs in medical equipments like MRI, CT-Scan, PET Imaging etc., as chips in satellites for guidance and control, surge in trend of using electric motors which uses permanent magnets made from REE and emphasis on green energy and emerging technologies. Now virtual has become real and for this reality to exist, we need REE, since it is a major component in various important industries like computers and IT, green energy, healthcare, defense, advanced transportation services and many other specialized fields (Krishnamurthy et al. 2020). Scandium and Yttrium are considered REEs since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. The annual turnover of the Indian rare earth industry is estimated to be around Rs 90,000 crore (approx. 13.5 billion USD) which is still underused as per the industry outlook. Indian Rare Earths Ltd (IREL) is the sole authority for production and distribution of REEs in India. Indian REE reserves are only 1.3 million metric tons and stands at 5th position globally as strategically USA and Russia do not produce any REE at present though they have huge reserves of 14.0 and 21.0 million metric tons of proven REE reserves respectively. At present, China is the largest producer of REEs as well as it has the highest reserve. Global REE production has increased from 190,000 MT in 2018 to 210,000 MT in 2019. Major countries and their production of REE in 2018 and 2019 are given in Table 1 (Statista 2019).

In the last few decades, especially in this Covid-19 era, REEs have become an indispensable part of the global economy mostly because in the past few years, wide range of possible applications of these elements have emerged such as use of REE in medical equipments like MRI, CT-Scan, PET Imaging etc., as chips in satellites for guidance and control, surge in trend of using electric motors which uses permanent magnets made from REE and emphasis on green energy and emerging technologies. Now virtual has become real and for this reality to exist, we need REE, since it is a major component in various

**Table 1.** Top 11 countries in rare earth mine production (in metric tonnes Rare Earth Oxides (REO))

| Sl. No. | Country | Production in 2018 | Production in 2019 |
|--------|---------|--------------------|--------------------|
| 1       | China   | 120,000            | 132,000            |
| 2       | USA     | 26,000             | 18,000             |
| 3       | Myanmar | 22,000             | 19,000             |
| 4       | Australia | 21,000             | 21,000             |
| 5       | India   | 2900               | 3000               |
| 6       | Russia  | 2700               | 2700               |
| 7       | Madagascar | 2000              | 2000               |
| 8       | Thailand | 1000               | 1800               |
| 9       | Brazil  | 1100               | 1000               |
| 10      | Vietnam | 920                | 900                |
| 11      | Burundi | 630                | 600                |

*0016-7622/2022-98-4-460/$ 1.00 © GEOL. SOC. INDIA*
devices like oxymeters, smartphone, cameras, electronic displays, LEDs which is essential for this digital age.

The entire landmass around the Indian Ocean contains REEs in the surrounding rocks and almost the whole coastline of the Indian Ocean is enriched in “mineral sands”. Major sources of REEs in “mineral sands” are ilmenite, sillimanite, garnet, zircon, monazite and rutile collectively known as Beach Sand Minerals (BSM) available in Kerala, India. Monazite is the major source of radioactive elements such as thorium and uranium but it also contains prominent REEs (Balaram, 2019). Due to environmental and economic issues as well as legislation and trade restrictions, conventional mining of REEs is constrained (U.S. EPA, 2015). However, as the demand of REEs is constantly increasing, there is a search of alternative resource which includes coal and coal combustion by-products like CFA (U.S. Geological Survey, 2020; Zhang et al. 2015; Vaziri et al. 2020; Dong et al. 2016; Maity S 2019; Pan et al. 2020). Strategically, India should find out alternative resources for production of REEs and should not use its conventional mineral resources. Yuan et al. (1993) has reported that worldwide CFA contains substantial concentrations of REEs such as NIST SRM 1633b and IRANT EOP, which are the standard reference materials for CFA containing 420 mg·kg$^{-1}$ and 806 mg·kg$^{-1}$ of REEs, respectively. Presently, India produces ~85% of power by coal-fired TPSs and it has a major issue of ash disposal. Potentiality of REEs in the Indian CFA is almost unexplored and it may be utilized as an alternative source of REEs to strategically protect the conventional mineral resources of REEs. REEs have been recognized as critical raw materials, crucial for many clean technologies. As the gap between the global demand and supply increases, the search for alternative resources becomes more and more important, especially for those countries that depend highly on import. Most countries are heavily dependent on China for their REEs supply.

CFA is a byproduct derived from non-combustible inorganic mineral matter originally present in the coal (Wang 2020). Consequently, REEs are fully preserved in CFA produced after the combustion of coal in the TPS (Kolker et al. 2017). These TPSs can be considered as REE concentrators because during combustion of coal, removal of moisture, volatile matter and carbon takes place. These ashes can be considered as low-grade ore for REEs (Stuckman et al. 2018). Few studies are available on partitioning of these critical elements (REEs) from coal to CFA. In this study, we have focused on CFA rather than bottom ash as the concentration of REE is more prominent in CFA in comparison to bottom ash of the same coal source. The reason behind this is during combustion of coal in the TPS, some REEs will volatilize due to the high temperatures of the boilers, and then they condense and mix with the CFA and consequently will be picked up by the electrostatic precipitator (Firman et al. 2021 and Lin et al. 2017). The other reason for focusing on fly ash, that it is the most voluminous byproduct of coal accounting for more than half of the coal waste and it occupies more than 65000 acres of land (Kambekar et al. 2013). Therefore, the possibility of occurrence of substantial concentration of REEs in CFA could increase the utilization of environmentally hazardous CFA as a source of these critical elements and decrease the stress put on natural resources like land and water. This could tackle the problem of contamination of air and water to a large extent especially in an emerging and developing country like India.

Recovering valuable elements such as REEs from coal ash would be inclined towards the idea of “Waste to Value” and would be a sustainable route for REEs extraction as well as disposal practices and it would be more attractive than traditional mining. In the present article, coal and coal ash from seven TPSs from various parts of India have been studied for estimation of REEs, its enrichment to CFA and variations in minerals compositions. REEs have been determined by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and mineralogical variations by XRD technique. Outlook Coefficient ($C_{out}$) has been determined and relative abundance of Light REEs and Heavy REEs is also estimated to understand the possible utilization of CFA as REE resource (Seredin 2010).

Fig. 1. Map of seven TPSs visited for sample collection
EXPERIMENTAL

Sampling

Seven samples of coal, both station and CFA, are collected by visiting seven different TPSs. Five of these TPSs are located in the state of West Bengal, one in Telangana and the other in the state of Maharashtra (Fig 1). Names of the TPSs and their operating capacity (MW) are given in Table 2. Coal samples are collected by visiting the coal bunker and taking approximately 1 kg of raw station coal. Similarly, approximately 1 kg of CFA samples are collected from CFA silos, ponds or storage units. The collected samples (both coal and CFA) are dried at 140°C for 8 hours to remove moisture and then crushed in pestle and mortar to get fine powder (72 mesh).

Proximate Analysis

Proximate analyses of all the coal samples are determined using ASTM (D 3172 – 13) method to understand the nature and quality of the coal (Table 3). The gross calorific value (GCV) in kcal/kg is calculated using the formula given by (Dey et al., 2012).

\[
GCV = 8496.4 \text{ – } 155.8M \text{ – } 96.1A \tag{1}
\]

where ‘A’ is ash yield; and ‘M’ is moisture content. Both A and M are measured at 60 % relative humidity and 40 °C. Equation 1 is chosen among various other equations, as the R² value (coefficient of determination) is highest (Kumari et al., 2019).

XRD

XRD analysis was performed using an automated high-resolution \(\theta - \theta\) multipurpose X-ray Diffractometer with expert system Guidance software (Model: SmartLab X-ray Diffractometer; Make: Rigaku, Japan) using CuK\(\alpha\) radiation (\(\lambda\): 1.5406 Å). The X-ray intensities of the coals and CFAs are collected in the 2\(\theta\) range of 10 – 80° with 3 kW sealed X-ray tube, CBO optics, D/teX Ultra 250 silicon strip detector. An X-ray amorphous sample holder was used for coal sample loading and the scan is made in continuous mode having scan speed of 10.40182/min and step size of 0.01°. Analysis is done by using PDFX2 software and ICDD data bank for mineral identification. The X-ray diffractograms of coals and CFAs are given in Fig. 2 and Fig. 3 respectively. The quantitative analysis is performed employing PDFX2 software using Rietveld method and applying RIR (Relative Intensity Ratio) technique to calculate the percentage of each mineral and glassy phase.

ICP-AES

Analyses for REEs are conducted using ICP – AES (Model: ARCOS, Simultaneous ICP Spectrophotometer, Make: SPECTRO Analytical Instruments GmbH, Germany). Samples are digested in Microwave Digestion System (Model: MICROWAVE PRO 3000 SYSTEM, Make: ANTON PAAR) using mineral acids. The coal sample (0.5 g) is digested in a mixture of 4 mL HNO\(_3\) +2 mL HF + 2 mL of H\(_2\)O\(_2\) and CFA (0.5 g) is digested in a mixture of 4 mL HNO\(_3\) + 2 mL HF + 2 mL H\(_2\)SO\(_4\) + 1 mL of HCl in the microwave digestion system. Final solution after digestion is made up to 30 mL by adding double distilled water.

RESULTS AND DISCUSSION

Proximate Analysis

Table 3 gives the result of proximate analysis of all coal samples. The moisture content of the samples ranges from 1.1% to 8.8%. The samples yield 16.4 – 24.2% volatile matter on air dried basis and ash percentage is in the range of 34.6 – 52.8%. The fixed carbon of all the samples tested ranged between 25.6 – 47.9%. The rank of the coals is sub-bituminous.

| Sl No | Name of the Power Plants | Sample Type | Sample Id | Capacity (MW) | Operated by |
|-------|--------------------------|-------------|-----------|--------------|------------|
| 1     | Mejia Thermal Power Station, West Bengal | Station Coal | MTPS/C | 2340 | D.V.C. |
| 2     | Raghunathpur Thermal Power Station, West Bengal | Station Coal | RTPS/C | 1200 | D.V.C. |
| 3     | Durgapur Steel Thermal Power Station, West Bengal | Station Coal | DSTPS/C | 1000 | D.V.C. |
| 4     | Maithon Private Limited, West Bengal | Station Coal | MPL/C | 1050 | Tata Power |
| 5     | Farakka Super Thermal Power Station, West Bengal | Station Coal | FSTPS/C | 2100 | N.T.P.C. |
| 6     | Ramagundam Super Thermal Power Station, Telangana | Station Coal | RSTPS/F | 2600 | N.T.P.C. |
| 7     | Chandrapur Super Thermal Power Station, Maharashtra | Station Coal | CSTPS/C | 2920 | MAHAGENCO |

| Sl No | Sample | Air Dried Basis (ASTM Method) | Moisture (%) | Ash (%) | Volatile Matter (%) | Fixed Carbon (%) | GCV kcal/kg* |
|-------|--------|-----------------------------|--------------|--------|-------------------|-----------------|--------------|
| 1     | MTPS/C | 2.9 | 2.9 | 2.9 | 2.9 | 2.9 | 2.9 |
| 2     | RTPS/C | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |
| 3     | DSTPS/C | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 | 4.3 |
| 4     | MPL/C | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| 5     | FSTPS/C | 8.8 | 8.8 | 8.8 | 8.8 | 8.8 | 8.8 |
| 6     | RSTPS/C | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 | 5.7 |
| 7     | CSTPS/C | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 |

* Dey et al., 2012
Coal Type and Characteristics

The coal samples collected from TPSs are composite coal which could be blend of Indian and imported coals or other high grade Indian coals. The coal type in the present study is in the sub-bituminous range which has ash percentage in the range of 34.6 – 52.8% (Table 3). The GCV values shown in Table 3 indicate that the coal is essentially non-coking with values ranging from 2752.38 - 4999.96 kcal/kg.

Results of XRD

The mineralogy of coal and CFA determined using XRD is shown in Tables 4 and 5 respectively. The station coal samples contained 45.5 – 57.7% non-crystalline matter. The coal samples mostly composed of quartz and kaolinite. The quartz content in coal samples ranges from 18.1 – 27.9% and kaolinite content varies between 20.3 – 30.7%. Some samples also have minerals like siderite, anatase, rutile and calcite in minor quantities. The glassy phase in CFA samples ranges between 46.1–56.6%. The mineralogy of CFA samples is dominated by quartz (22.8 – 31.2%) and mullite (17.7 – 27.6%) with some minor quantities of rutile found in few samples.

Results of ICP-AES

Two types of classification schemes (Table 6) have been proposed for REEs (Seredin 2010; Blissett et al. 2014). Type I refers to global concentration of REE and Type II refers to REE characteristics.
However, four different kinds of parameters are evaluated to understand the occurrence of the REEs in different sources. The parameters are outlook coefficient \( C_{ou} \), critical percentage \( C_p \), uncritical percentage \( U_p \) and excessive percentage \( E_p \) as given by Bliss et al. (2014). The equations are given below.

\[
C_{ou} = \frac{\Sigma \text{Critical (ppm)}}{\Sigma \text{Excessive (ppm)}} \tag{2}
\]

\[
C_p = \frac{\Sigma \text{Critical (ppm)}}{\Sigma \text{REE (ppm)}} \times 100 \tag{3}
\]

\[
U_p = \frac{\Sigma \text{Uncritical (ppm)}}{\Sigma \text{REE (ppm)}} \times 100 \tag{4}
\]

\[
E_p = \frac{\Sigma \text{Excessive (ppm)}}{\Sigma \text{REE (ppm)}} \times 100 \tag{5}
\]

ICP – AES analyses of coal and CFA are summarized in Tables 7 and 8. Lin et al., 2017 suggested that estimated cut-off grade for beneficial recovery of REE in coal is 115 – 130 ppm on the whole coal basis and 677 – 762 ppm on the ash basis. Based on the above literature review, the overall occurrence of REEs both in coal and CFA is not very prominent. The overall REE content in coal is 11.84 - 32.53 ppm and in ash it is 51.8 - 66.4 ppm which is below par for CFA is not very prominent. The overall REE content in coal is 11.84 ppm. Table 8 shows that the beneficial recovery of REE in coal is 115 – 130 ppm on the whole and 8. Lin et al., 2017 suggested that estimated cut-off grade for coal is in the range of 0.3 - 4.5 and for CFA it is 95 – 98% in CFA. In order to evaluate CFA as a source of REE (Seredin 2010), a graph is plotted \( C_p \) Vs \( C_{ou} \) (Table 7; Fig. 4). Though \( C_{ou} \) is greater than 0.7 for 3 TPSs (MTPS, DSTPS and RSTPS), but due to very low value of \( C_p \), none of the CFA is suitable as REE source.

It is evident from this study that among all REEs, LREEs are predominant especially praseodymium (Pr) which is above 90% of the total REEs (2REE) in all CFA samples. REE content of ash has increased considerably with respect to the parent coal for each of the power plant. It is opined by earlier workers that most of the REEs are associated with the aluminosilicate glassy phase of CFA (Pan et al. 2020). In order to understand the enrichment of REEs from coal to CFA, the enrichment coefficient (\( \Delta \)) has been determined (Table 8) using the formula (Equation 6, present study) as given below:

\[
\Delta = \frac{\Sigma \text{REE}_{\text{Ash}} - \Sigma \text{REE}_{\text{Coal}}}{\Sigma \text{REE}_{\text{Coal}}} \tag{6}
\]

A graph of glassy phase (%) vs \( \Delta \) is plotted (Fig.5) to understand degree of enrichment of REEs in glassy phase of CFA. Two different trend patterns are seen for the power plants. CFAs from MTPS, DSTPS and RSTPS are following one trend line while other four namely RTPS, MPL, FSTPS and CSTPS are following another trend line. Fig.5

### Table 4. Quantitative Rietveld analysis results of station coal from seven TPSs (results in %)

| Sl. No. | Sample Id | Non-Crystalline | Quartz | Kaolinite | Siderite | Anatase | Rutile | Calcite | Hematite | Gypsum |
|--------|-----------|-----------------|--------|-----------|----------|---------|--------|---------|----------|--------|
| 1.     | MTPS/C    | 51.3            | 22.6   | 20.3      | 1.3      | 2.9     | -      | -       | 1.6      | -      |
| 2.     | RTPS/C    | 47.4            | 27.9   | 23.5      | -        | 1.1     | 0.1    | -       | -        | -      |
| 3.     | DSTPS/C   | 49.1            | 20.5   | 25.2      | 2.7      | 1.7     | 0.8    | -       | -        | -      |
| 4.     | MPL/C     | 57.7            | 18.7   | 20.4      | -        | 1.5     | -      | -       | 1.7      | -      |
| 5.     | FSTPS/C   | 50.2            | 18.1   | 27.9      | 1.5      | 1.9     | 0.4    | -       | -        | -      |
| 6.     | RSTPS/C   | 49.3            | 23.5   | 25.5      | -        | -      | 1.7    | -       | -        | -      |
| 7.     | CSTPS/C   | 45.5            | 23.0   | 30.7      | -        | -      | 0.8    | -       | -        | -      |

### Table 5. Quantitative Rietveld analysis results of CFA from seven TPSs (results in %)

| Sl. No. | Sample Id/ TPS | Glassy Phase | Quartz | Mullite | Rutile | Coalite | Hematite | Gypsum |
|--------|---------------|--------------|--------|---------|--------|---------|----------|--------|
| 1.     | MTPS/F        | 49.1         | 24.6   | 22.9    | 3.4    | -       | -        | -      |
| 2.     | RTPS/F        | 56.6         | 24.9   | 18.5    | -      | -       | -        | -      |
| 3.     | DSTPS/F       | 49.6         | 26.5   | 21.2    | 2.7    | -       | -        | -      |
| 4.     | MPL/F         | 46.1         | 22.8   | 27.6    | 3.5    | -       | -        | -      |
| 5.     | FSTPS/F       | 54.3         | 27.9   | 17.8    | -      | -       | -        | -      |
| 6.     | RSTPS/F       | 53.9         | 28.4   | 17.7    | -      | -       | -        | -      |
| 7.     | CSTPS/F       | 49.3         | 31.2   | 19.5    | -      | -       | -        | -      |

### Table 6. Classification scheme of REEs

| Type     | Category | Elements                  |
|----------|----------|---------------------------|
| I        | Critical | Nd, Eu, Tb, Dy, Y and Er  |
|          | Uncritical | La, Pr, Sm and Gd       |
|          | Excessive | Ce, Ho, Tb, Yb and Lu   |
| II       | Light (LREE) | La, Ce, Pr, Nd, Sm | Medium (MREE) | Eu, Gd, Tb, Dy and Y |
|          | Heavy (HREE) | Ho, Er, Tb, Yb, Lu      |

(b.d.l - below detection limit)
shows, $\Delta_e$ is decreasing with increase of glassy phase in CFA. This is due to the fact that as the glassy phase is increasing, the REEs are partitioning into the glassy phase and simultaneously dilution of REEs is taking place which results in decrease of $\Delta_e$ with increasing glassy phase.

In order to determine the amount of unburnt carbon, LOI (Loss on Ignition) has been evaluated by heating each coal ash sample at 950°C for 3 h. LOI ranges between 0.2 - 2.7% (Table 8), signifying the higher efficiency of the boiler of the Power Plants.

| Element | MTPS/ RTPS/ DSTPS/ MPL/ FSTPS/ RSTPS/ CSTPS/ | F | F | F | F | F | F |
|---------|------------------------------------------|---|---|---|---|---|---|
| La      | b.d.l*                                   | 1.0| 0.5| 0.5| 1.1| 1.4| 1.5|
| Ce      | b.d.l                                   | 53.5| 56.7| 56.1| 51.5| 62.9| 47.6| 49.7|
| Pr      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Nd      | b.d.l                                   | 0.1| 0.5| 0.5| 0.6| 0.6| 0.5| 0.5|
| Sm      | b.d.l                                   | 0.3| 0.1| 0.2| 0.1| 0.2| 0.2| |
| Eu      | b.d.l                                   | 0.6| 0.6| 0.6| 0.7| 0.5| 0.6| |
| Gd      | b.d.l                                   | 0.1| 0.2| 0.1| 0.2| 1.4| 1.4| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Y       | b.d.l                                   | 0.1| 0.1| 0.1| 0.1| 0.8| 1.4| |
| Er      | b.d.l                                   | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Tb      | b.d.l                                   | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Dy      | b.d.l                                   | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Y       | b.d.l                                   | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Eu      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Tb      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Dy      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Y       |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Y       |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Eu      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Tb      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Dy      |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Y       |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Y       |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |
| Ho      |                                           | 0.5| 0.5| 0.5| 0.5| 0.5| 0.5| |
| Y       |                                           | 0.1| 0.1| 0.1| 0.1| 0.2| 0.2| |

Table 9. Comparison of the average total REE concentration of the present study with the global average of total REE concentration.

| Element | Coal (in ppm) | Ash (in ppm) |
|---------|---------------|--------------|
|         | Global Avg. $^a$ | Global Avg. $^b$ | Avg. $^a$ | Avg. $^b$ |
| La      | 11            | 2.43         | 69          | 1.00        |
| Ce      | 23            | 18.91        | 20          | 54.00       |
| Pr      | 5.01          | 67           | 0.00        |
| Nd      | 25.00         | 1.00         | 130         | 0.00        |
| Sm      | 4.00          | 1.00         | 20          | 54.00       |
| Eu      | 2.00          | 1.00         | 67          | 0.00        |
| Gd      | 2.00          | 1.00         | 13          | 0.00        |
| Ho      | 4.00          | 1.00         | 2.5         | 2.5         |
| Y       | 1.00          | 1.00         | 6.2         | 0.10        |
| Lu      | 0.2           | 1.00         | 1.2         | 0.63        |
| ΣREE   | 68.47         | 24.17        | 403.5       | 56.93       |

$^a$ Global total average from Ketris et al. (2009)

$^b$ Average total from seven Indian TPS samples

From the coal and coal ash samples analysed from seven TPS, pattern of occurrence of REEs in coal as well as CFA does not differ much and overall Pr is the most abundant REE with concentration reaching a maximum of 62.9 ppm. It is suggested that recovery of REEs is not economically feasible and further study of coal and CFA samples from more TPSs' are required to identify a source of coal and CFA which could have higher concentrations of these critical elements. CFA having $C_{out}$ higher than 30 % and $C_{out}$ more than 0.7 is promising (Group II) as a source of REEs (Seredin and Dai 2012, Blissett et al. 2014). In the present study, though $C_{out}$ for coal ash from three power plants is 0.7 or more but due to very low low $C_{out}$ (≤ 3.1), none of the coal ash is suitable as REE source.

A comparison of global average of REEs (Ketris et al. 2009) and that of the present work has been produced in Table 9. The global average of ΣREE concentrations in coal and ash are 68.5 and 403.5 ppm respectively while the average ΣREE concentrations for coal and ash in these seven TPS are 24.17 and 56.93 ppm respectively which is significantly lower. The comparison is also done for the average total of individual rare earth elements with the global average and it is worthy to observe that the average total of Praseodymium (Pr) in coal is 5.4 times the global average and for ash it is 2.7 times the global average.

CONCLUSION

The volatility in supply and demand of REE in the market has forced the researchers all over the globe to look for alternative and revolutionary sources of REE which are more favourable. Recovery of REE from CFA will potentially have huge value and a significant step forward in production of valuable metals by utilizing potentially hazardous material for the environment. As coal burning is essential for electricity production, utilization of CFA will find a new avenue in this way. Present study is an initiation for Indian coal and CFA for finding out the potential power plants from which REE could be resourced. It is evident that the REEs which are present in raw coal
initially is getting enriched from coal to CFA during the combustion process employed by these TPPs and in CFAs the REEs are partitioning to the glassy component which causes dilution of these elements and consequently resulting in decrease in $\Delta_e$ with increasing percentage of glassy phase. Of all the REEs, Praseodymium (Pr) has major stake at the overall concentration of REEs in all the samples (both coal and CFA). Understanding the partitioning of REE in CFA would give us better idea in determining which extraction technique or what chemical reagents can be used for their efficient extraction. Studies done by Rybak et al. 2021 and Kolker et al. 2017 have shown that most of REE are associated with aluminosilicate glass or the glassy phase in the context of this study. It can be very well understood that none of the fly ash is suitable for this purpose. More number of CFAs from different power plants will be studied. The present study clearly shows that, $\Delta_e$ has reached up to 3.51 and it may be assumed that considerable amount of partitioning is taking place from coal to CFA during combustion in the power plants.

Acknowledgements: SM likes to thank Science and Engineering Research Board, Govt. of India for Research Grant (No. EMR/2017/000856). We thankfully acknowledge all the Power Plants for allowing us to collect the samples. Authors thank SAIF, IIT, Bombay for providing us the ICP – AES analyses and RQA Research Group, CSIR – CIMFR, Dhanbad for providing the proximate analyses of coals. We also thankful to Director, CSIR- Central Institute of Mining and Fuel Research, Dhanbad for allowing publishing this manuscript.

References

Balaram, V. (2019) Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci. Front., v.10, pp.1285–1303. doi:10.1016/j.gsf.2018.12.005

Blissett, R.S., Smalley, N., Rowson, N.A. (2014) An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. Fuel, v.119, p.236-239. doi:10.1016/j.fuel.2013.11.053

Central Electricity Authority (2019) Annual Report on Fly Ash Generation and its utilization at coal/lignite based Thermal Power Stations in the country for the year 2018-19.

Dey, S., Saini, M.K., Narayan, J.P., Chaudhury, N. (2012) Prediction of gross calorific value of Indian non-caking coals on the basis of ash and moisture. Jour. Mines Met. Fuels, v.60(1 & 2), pp.31–38.

Dong, Y., Sun, X., Wang, Y., Huang, C., Zhao, Z. (2016) The sustainable and efficient ionic liquid-type saponification strategy for rare earth separation. Jour. Hazard. Mater., v.35, pp.295–330. doi:10.1080/19392699.2015.1033097

Kambekar, A., Haldive, S.A. (2013) Experimental Study on Combined Effect of Fly Ash and Pond Ash on Strength and Durability of Concrete. IJSER, v.4(5), pp.81-86.

Ketris, M.P., Yadovich, Y.E. (2009) Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. Internat. Jour. Coal Geol., v.78, pp.135-148. doi:10.1016/ j.coal.2009.01.002

Key World Energy Statistics (2019), International Energy Agency.

Kolker, A., Scott, C., Hower, J.C., Vazquez, J.A., Lopano, C.L., Dai, S. (2017) Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe. Internat. Jour. Coal Geol., v.184, pp.1-10. doi:10.1016/j.coal.2017.10.002

Krishnamurthy, P. (2020) Rare Metal (RM) and Rare Earth Element (REE) Resources: World Scenario with Special Reference to India. Jour. Geol. Soc. India, v.95, pp.465–474. doi:10.1007/s12594-020-1465-7

Kumuri, P., Singh, A.K., Wood, D.A, Hazra, B. (2019) Predictions of Gross Calorific Value of Indian Coals from their Moisture and Ash Content. Jour. Geol. Soc. India, v.93, pp.437–442. doi:10.1007/s12594-019-1198-5

Lin, R., Howard, B., Roth, E., Bank, T., Graniter, E., Soong, Y. (2017) Enrichment of Rare Earth Elements from Coal and Coal By-Products by Physical Separations. Fuel, v.200, pp.506-520. doi:10.1016/j.fuel.2017.03.096

Marty, S. (2019) Coal Fly Ash (CFA) as a source of Rare Earth Elements (REE): an alternative route of value addition utilized of Indian Coal Fly Ash. ENCO – 2019, 20 – 22 Feb, 2019, Vigyan Bhavan, New Delhi, v.1, pp.474- 479.

Pan, J., Hassas, B.V., Rezaee, M., Zhou, C., Pispupati, S.V. (2020) Recovery of rare earth elements from coal fly ash through sequential chemical roasting, water leaching, and acid leaching processes. Jour. Clean. Prod. v.284, 124725. doi:10.1016/j.jclepro.2020.124725

Rybak, A. and Rybak, A. (2021) Characteristics of Some Selected Methods of Rare Earth Elements Recovery from Coal Fly Ash. Metals, v.11(1), p.2-42. doi:10.3390/110110499

Seredin, V.V. (2010) A new method for primary evaluation of the outlook for rare earth element ores. Geol. Ore Depos. v.52 (5), p.428–433. doi:10.1134/S0775701510050077

Stuckman, M.Y., Lopano, C.L., Granite, E.J. (2018) Distribution and speciation of rare earth elements in coal combustion by-products via synchrotron microscopy and spectroscopy. Internat. Jour. Coal Geol., v.195, pp.125-138. doi:10.1016/j.coal.2018.06.001

U.S. Geological Survey (2020) Mineral Commodity Summaries 2020; U.S. Geol. Journal Surv. doi:10.3133/mcs2020

Wang, N., Sun, X., Zhao, Q., Yang, Y., Wang, P. (2020) Leachability and adverse effects of coal fly ash: A review. Jour. Hazard. Mater., v.396. 122725. doi:10.1016/j.jhazmat.2020.122725

Yuan, Z., Chengyi, W., Leiming, X., Yunxiang, N. (1993) The Distribution of Rare Earth Elements in Granitoids in the Nanling Region of China. Chin. Jour. Geochem., v.12(30), pp.193-205. doi:10.1007/BF02843359

Zhang, W., Rezaee, M., Bhagavatula, A., Li, Y., Groppo, J., Honaker, R. (2015) A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by products. Internat. Jour. Coal Prep. Util., v.35, pp.295–330. doi:10.1080/19392699.2015.1033097