A review on mineralogical speciation, global occurrence and distribution of rare earths and Yttrium (REY) in coal ash

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Rare earths and Yttrium (REY) are a group of critical metals essential for this electronic and digital era. China is the leading producer of REY with more than 90% of global export. Mines of REY are limited and the need for green and efficient energies have augmented the demand of REY and it is putting enormous pressure on global production. REY market is predicted to grow from USD 5.3 billion in 2021 to 9.6 billion by 2026, at a CAGR (Compound Annual Growth Rate) of 12.3%. The need for permanent magnets is propelling the demand of the critical group REY and is expected to rise gradually in the coming years. In the present review, we have summarized the minable REY resources and their applications. The requirement for alternative resource is pivotal to meet our future needs. We have extensively reviewed the studies of REY in coal fly ash (CFA). A comprehensive analysis has been done for the REY resources worldwide for the last several decades in coal ash (CFA and bottom ash) and divulged into the application, speciation and distribution for major coal-consuming countries like China, India, USA, Russia, UK, Poland, etc., individually. We have also made a comparative global study and inferred potential extractable coal ash resources using various parameters such as global average, critical percentage ($C_{p}$), outlook coefficient ($C_{out}$), etc., for a better understanding of economic exploitation.

Keywords. Rare earths and Yttrium (REY); coal ash (CA); thermal power plant (TPP); waste utilization; hazardous materials.

1. Introduction

Coal is the most abundant fossil fuel in the world and a vital raw material in the energy and industrial sectors. Most of these coals are used in coal-fired thermal power plants (TPP) for electricity generation and steel making. In 2019, coal accounted for more than 36% of world electricity-generating fuel (Coal-Fired Power – Analysis - IEA, n.d.). A prediction shows that in 2040, coal will still contribute around 22% to global electricity generation, retaining its position as the single largest source for electricity.

In India, ~83% of power is generated by coal-fired thermal power stations (CEA annual report 2019–20 2021). One of the by-products of burning pulverized coal is fly ash, which is a global pollutant because of its hazardous nature and production in extensive amounts. Due to the increase in
energy demand, coal fly ash (CFA) production is expected to grow, making research into the use of CFA a necessity. CFA can be a valuable solid waste residue produced after the combustion of coal in the TPPs. It is believed that most of the rare earth elements and Yttrium (REY) are carried in CFA (Huang et al. 2020). India produces ~ 217.04 million tonnes of CFA per year, of which only 77.59% is utilized (CEA annual report 2019–20 2021). Hence, this unused CFA is being disposed as landfills, which contaminates land, water, and air. Researchers are focusing on several ways to further utilize the CFA by extracting REY and other valuable elements which have a variety of applications and are of strategic and economic importance. CFAs having adequate quantity of REEs will be a good secondary resource for these elements.

Rare earths are relatively abundant in the Earth’s crust but discovered minable concentrations are less common than most other mineral commodities (Mineral Commodity Summaries 2021). In India, entire landmass around the Indian Ocean contains REY in the surrounding rocks and almost the entire coastline of the Indian Ocean is enriched in ‘mineral sands’ (Maity et al. 2021). Global resources of REY are mainly concentrated in bastnasite and monazite. China and USA account for majority of the world’s bastnasite deposits, whereas monazite deposits in Australia, China, India, Malaysia, Brazil, South Africa, Sri Lanka, Thailand, and USA constitute the second largest portion. Apatite, eudialyte, loparite, cer- alite, phosphorites, rare-earth-bearing ion adsorption clays, secondary monazite, spent uranium solutions, and xenotime make up most of the remaining resources. The undiscovered resources of REY are assumed to be very high relative to the expected demand (Mineral Commodity Summaries 2014).

REY+Sc is a group of 17 elements – 15 from Lanthanide group and two transition metal elements (Scandium and Yttrium), which are considered as the essential raw materials, vital for many clean and green technologies. As the gap between the global demand and supply has increased, the search for alternative resources has become more important, especially for the countries, which depend heavily on their import. The unutilized CFA is considered as a waste and could be a potential source of many elements, including the REY.

In this review, we have discussed about REY application, mineralogical speciation and trends in REY distribution in ash. This article presents thoroughly proven data on widespread accumulation of REY in CFA and BA derived from TPPs and other sources across the world.

Many studies such as Seredin and Dai (2012), Bliss et al. (2014), Kolker et al. (2017), and Taggart (2017) have shown that CFA can be an attractive alternative source of REY and should be

![Figure 1. Global mined production and reserves of REY (tons) during the year 2019–2020. Data source: Mineral Commodity Summaries (2021).](image)
explored extensively. In the following subsections, global production, reserves and environmental impact for mining are briefly summarized.

1.1 Global production and reserves

REY minable resources are found in four geological environments: carbonatites, alkaline igneous systems, ion-adsorption clay deposits, and monazite–xenotime-bearing placer deposits. Carbonatites and placer deposits are the leading sources of production of LREY. Ion-adsorption clays are the leading source of production of HREY (Mineral Commodity Summaries 2021). In 2020, China produced nearly 58.3% (140,000 tons) of global mined production, which was earlier 60% (132,000 tons) in 2019. The decrease in production during the year 2020 can be attributed to the COVID-19 pandemic. Other major REY mining nations are United States of America (12.7% in 2019 and 15.8% in 2020), Burma (11.4% in 2019 and 12.5% in 2020) and Australia (9.1% in 2019 and 7.1% in 2020). The majority of REY reserves are located in China with 36.6% (44 million tons) of global REY reserves, with other large reserves are held by Vietnam with 18.3% (22 million tons) and Brazil with 17.5% (21 million tons) (figure 1). Other countries like United States, Australia, and Greenland have less than 5% share in the global REY reserves (Mineral Commodity Summaries 2021).

1.2 Environmental impact of mining, processing and recycling

Most of the REY are produced from traditional methods (Mineral Commodity Summaries 2021); however, due to the surge of REY demand, many dormant rare earth processing projects are being revived or relaunched globally. Mining and

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| Activity                        | Emission source(s)                  | Primary pollutants of concern                                                  |
|---------------------------------|-------------------------------------|--------------------------------------------------------------------------------|
| Mining (aboveground and         | Overburden                          | Radiological; metals; mine influenced; waters/acid mine drainage/alkaline       |
| underground methods)            | Waste rock                           |                                                                                  |
|                                 | Sub-ore stockpile                    |                                                                                  |
|                                 | Ore stockpile                        |                                                                                  |
| Processing                      | Grinding/crushing                    | Dust                                                                            |
|                                 | Tailings                             | Radiological; metals; turbidity; Organics, dust and associated pollutants       |
|                                 | Tailings impoundment                 |                                                                                  |
|                                 | Liquid waste from processing         |                                                                                  |
| Recycling                       | Collection                            | Transportation pollutants                                                       |
|                                 | Dismantling and separation           | Dust and associated pollutants;                                               |
|                                 | Scrap waste                          | VOCs; metals; organics                                                         |
|                                 | Landfill                             |                                                                                  |
|                                 | Processing                           | Dust and associated pollutants;                                               |
|                                 |                                      | VOCs; dioxins; metals; organics                                                |

Table 1. Emission source and pollutants of concern from mining, processing and recycling of REY (EPA 2012).

Figure 2. Pictorial representation of classification scheme of REY.
Table 2. Applications of REY and Sc.

| Element symbol | Classification | Applications |
|----------------|----------------|--------------|
| Sc             | Not included   | • Metal alloys for the aerospace industry. |
| Y              | MREY and critical | • Ceramics, metal alloys, lasers, fuel efficiency, microwave communication for satellite industries. Used in colour televisions, computer monitors, and temperature sensors.  
• For targeting and weapon systems and communication devices in Defence sector.  
• Required for developing clean energy technologies. |
| La             | LREY and uncritical | • Used as catalysts for petroleum refining.  
• Required in electric car batteries, high-tech digital cameras, video cameras, laptop batteries, X-ray films, and lasers.  
• Used by Defence sector in communication devices.  
• Required for clean energy technologies. |
| Ce             | LREY and excessive | • Used as catalysts.  
• Required for polishing, metal alloys, and lens polishing (for glass, television faceplates, mirrors, optical glass, silicon microprocessors, and disk drives).  
• Required for clean energy technologies. |
| Pr             | LREY and uncritical | • Required for improving magnet resistance to corrosion.  
• Used as pigments, searchlights, airport signal lenses, and photographic filters.  
• Used by Defence sector in guidance and control systems and electric motors. |
| Nd             | LREY and critical | • High-power magnets for laptops, lasers.  
• Used as fluid-cracking catalysts.  
• Used by Defence sector in guidance and control systems, electric motors, and communication devices.  
• Required for clean energy technologies. |
| Pm             | Radioactive. Not included | • Beta radiation source.  
• Fluid-cracking catalysts. |
| Sm             | LREY and uncritical | • High-temperature magnets, reactor control rods.  
• Used by Defence sector in guidance and control systems and electric motors. |
| Eu             | MREY and critical | • Used in Liquid crystal displays (LCDs), fluorescent lighting and glass additives.  
• Used by Defence sector in targeting and weapon systems and communication devices.  
• Required for clean energy technologies. |
| Gd             | MREY and uncritical | • Required for magnetic resonance imaging contrast agent.  
• Glass additives. |
| Tb             | MREY and critical | • Phosphors for lighting and display.  
• Used by Defence sector in guidance and control systems, targeting and weapon systems, and electric motors.  
• Required for clean energy technologies. |
| Dy             | MREY and critical | • Used as high-power magnets, and lasers.  
• Used by Defence sector in guidance and control systems and electric motors.  
• Required for clean energy technologies. |
| Ho             | HREY and excessive | • Highest power magnets are known. |
| Er             | HREY critical    | • Used as lasers and glass colourant. |
| Tm             | HREY and excessive | • High-power magnets. |
| Yb             | HREY and excessive | • Fiber-optic technology, solar panels, alloys (stainless steel), lasers.  
• Used as a radiation source for portable X-ray units. |
| Lu             | HREY and excessive | • Used as X-ray phosphors. |

Data source: Zaghlol (2016).
processing of REY can create a number of environmental risks to both human health and environment. The problem with rare earth mining is that the REY ores contain different metals in their structure including aluminium, arsenic, barium, cadmium, radioactive materials, like uranium and thorium, etc. and thus, depending on the REY-bearing ore, there is variation in pollutants being generated EPA (2012). Separating REY from the REY-mineral ore requires large amount of carcinogenic toxins such as hydrochloric acid, ammonia, sulphates, etc. The unregulated and unsustainable mining of rare earths could produce wastewater and tailing ponds that can leak heavy metals, acids and radioactive elements into the groundwater (Hassas et al. 2020). The international tension regarding supply chain of rare earths could lead to some countries or projects ignore these environmental restrictions to reduce the price. One example is Bayan-Obo, the largest rare earth project in China, which has been operational for more than four decades, has an 11 km² area of waste pond, which contains toxic sludge having elevated concentrations of Thorium (Boom in Mining Rare Earths Poses Mounting Toxic Risks - Yale E360, n.d.).

All REY mining countries are putting emphasis on sustainable mining for the production of these metals. Due to the continuous growth of REY production, identifying and reducing the environmental impacts of this industry becomes an important step. Life cycle assessment (LCA) is the most widely accepted methodology for assessing the environmental impact of a product or service (Reisman et al. 2013). It is used by companies and governments globally (Ness et al. 2007; Evans et al. 2009). A summary of emission source of pollutants of concern from mining, processing and recycling of REY is given in table 1.

2. Classification and applications

REY have similar physical and chemical properties, and hence it is difficult to separate them from each other. Promethium is not included in either of the two classifications as it does not occur in nature and can only be artificially synthesized. REY are classified in two ways (Seredin and Dai 2012; Maity et al. 2021).

(a) On the basis of atomic number/atomic mass: If Yttrium is included in Lanthanides, it is abbreviated as REY (Lanthanides and Yttrium) and hence, the following three subgroups are formed: Elements from atomic number 57–62 except for Promethium (Pm), which is extremely rare and radioactive, are included in light elements (LREY: La, Ce, Pr, Nd, Sm), elements from atomic numbers 63–66 and 39 are included in medium elements (MREY: Eu, Gd, Tb, Dy, Y), and elements from atomic numbers 67–71 are included in heavy elements (HREY: Ho, Er, Tm, Yb, Lu).

(b) On the basis of global supply and demand: On the basis of supply and demand, REY are classified as critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu). If the demand for REY is very high and supply is low, it is classified as critical, whereas if there is a relative balance between supply and demand, it is termed as uncritical and if there is an overproduction or the supply exceeds demand, it is called excessive (Maity et al. 2021) (figure 2).

REY are used in everyday devices that people use, such as memory and storage devices, rechargeable batteries, magnet, fluorescent lightings, smart phones, etc. Besides, these are also utilized as catalysts, phosphors, polishing compounds and also for air pollution control, electronic displays, and the polishing of optical quality glass. REY are also widely used in high-technology and ‘green’ products because of their luminescent and catalytic properties. A brief application of REY is given in table 2 and figure 3.
While the demand for green technologies has garnered attention, there is also a huge demand for rare earth metals for energy production. Thus, ensuring the supply of REY is critical to the development of green and clean energy technologies (Zhou et al. 2016). One solution is exploring REY in secondary resources.

Figure 4. Fly ash production and utilization in million tons (MT) in 2018. Data source: Alterary and Marei (2020), Bhawan and Puram (n.d.), Luo et al. (2021), Annual Production and Utilisation Survey Report (2018).

Table 3. *Global average of REY in coal and CA.*

| Elements | Coals | Coal ashes |
|----------|-------|------------|
|          | Brown | Hard | Avg. | Brown | Hard | Avg. |
| La       | 10±0.5 | 11±1 | 11   | 61±3  | 76±3 | 69   |
| Ce       | 22±1   | 23±1 | 23   | 120±10| 140±10| 130  |
| Pr       | 3.5±0.3| 3.4±0.2| 3.5  | 13±2  | 26±3 | 20   |
| Nd       | 11±1   | 12±1 | 12   | 58±5  | 75±4 | 67   |
| Sm       | 1.9±0.1| 2.2±0.1| 2    | 11±1  | 14±1 | 13   |
| Eu       | 0.50±0.02| 0.43±0.02| 0.47 | 2.3±0.2| 2.6±0.1| 2.5  |
| Gd       | 2.6±0.2| 2.7±0.2| 2.7  | 16±1  | 16±1 | 16   |
| Tb       | 0.32±0.03| 0.31±0.02| 0.32 | 2.0±0.1| 2.1±0.1| 2.1  |
| Dy       | 2.0±0.1| 2.1±0.1| 2.1  | 12±1  | 15±1 | 14   |
| Y        | 8.6±0.4| 8.2±0.5| 8.4  | 44±3  | 57±2 | 51   |
| Ho       | 0.50±0.05| 0.57±0.04| 0.54 | 3.1±0.3| 4.8±0.2| 4    |
| Er       | 0.85±0.08| 1.00±0.07| 0.93 | 4.6±0.2| 6.4±0.3| 5.5  |
| Tm       | 0.31±0.02| 0.30±0.02| 0.31 | 1.8±0.3| 2.2±0.1| 2    |
| Yb       | 1.0±0.05| 1.0±0.06| 1    | 5.5±0.2| 6.9±0.3| 6.2  |
| Lu       | 0.19±0.02| 0.20±0.01| 0.2  | 1.10±0.10| 1.3±0.1| 1.2  |
| \(\sum{\text{REY}}\) (Ketris and Yudovich 2009) | 68.47 | 403.5 |
| LREY (%) | 75.22 | 74.1  |
| MREY (%) | 20.43 | 21.21 |
| HREY (%) | 4.35  | 4.68  |
| Critical (ppm) | 24.22 | 142.1 |
| Uncritical (ppm) | 19.2 | 118 |
| Excessive (ppm) | 25.05 | 143.4 |
| \(C_{out}\) | 0.97 | 0.99 |
| \(C_p\) | 35.37 | 35.22 |
| \(U_p\) | 28.04 | 29.24 |
| \(E_p\) | 36.59 | 35.54 |

Data source: Ketris and Yudovich (2009).
3. Need for an alternative resource for REY

Most of the end-use applications require at least one or two REY in separated form to perform their intended function. The rare-earth metals’ market is projected to grow from USD 5.3 billion in 2021 to 9.6 billion by 2026, at a CAGR of 12.3% during the forecast period. The increasing use of these elements in the permanent magnet applications is expected to boost the rare-earth market (Rare Earth Metals Market Global Forecast to 2026 Markets and Markets n.d.). Among these 17 REY; Nd, Dy and Pr are in high demand due to their wide application in permanent magnets.
China produced nearly 60% of the global rare earths in 2020. Global demand for REO (Rare Earth Oxide) was estimated at roughly 208,250 metric tons in 2019 and is forecasted to be 304,678 metric tons by 2025 (Rare Earth Oxide Demand Worldwide 2025 Statista n.d.). The total worldwide reserves of rare earths are *120 million metric tons*, out of which *44 million metric tons* are located in China (Rare Earth Reserves by Country 2020 Statista, n.d.). CFA can be utilized as an alternative source of REY to strategically protect the conventional mineral resources of REY (Maity 2019).

4. Why fly ash?

In modern thermal power stations, majority of the mineral matter in coal is excreted in the form of CFA (~90%) and the rest is the bottom ash (BA) (Fay and Golomb 2002). Fly ash production and utilization of four of the most intensive fossil fuel users of the world in 2018 are given in figure 4. In an ideal case, the countries using fossil fuels for electricity generation should aim for 100% ash utilization. However, these countries are unable to achieve this target (figure 4). For the past decade, researchers are trying to utilize this environmentally hazardous industrial waste as a resource for the extraction of REY. Although many researchers were successful in the extraction of the REY from CFA using different methods such as solvent extraction, ionic extraction, flash joule heating (Deng et al. 2022), not enough options are available for economical industrial-scale extraction of these elements. The extraction potentiality and application of modern analytical approaches to study the REY in coal ash have also been reviewed by Fu et al. (2022).

5. Global average of REY in coal ash (CA)

Ketris and Yudovich (2009) calculated the coal Clarke values, i.e., average trace element concentration in world coal and ash. They methodically
Table 4. Distribution of REY in CA from China.

| Element | C1  | C2  | C3  | C4  | C5  | C6  | C7  | C8  | C9  | C10 | C11 | C12 | C13 | C14 | C15 |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| La      | 230 | 127 | 301 | 300 | 288 | 161 | 385 | 168 | 322 | 243 | 168 | 172 | 186 | 158 |
| Ce      | 422 | 237 | 515 | 522 | 607 | 328 | 744 | 348 | 554 | 454 | 516 | 315 | 322 | 350 |
| Pr      | 50  | 30  | 66  | 74  | 85  | 38  | 91  | 37  | 70  | 52  | 64  | 38  | 36  | 41  |
| Nd      | 196 | 114 | 256 | 303 | 359 | 142 | 333 | 133 | 247 | 191 | 247 | 146 | 129 | 151 |
| Sm      | 39  | 24  | 46  | 58  | 73  | 27  | 58  | 24  | 44  | 38  | 47  | 30  | 25  | 28  |
| Eu      | 5   | 3   | 7   | 9   | 10  | 4   | 6   | 3   | 5   | 7   | 7   | 4   | 4   | 5   |
| Gd      | 44  | 25  | 44  | 59  | 61  | 23  | 43  | 20  | 38  | 35  | 40  | 23  | 23  | 26  |
| Tb      | 8   | 4   | 6   | 9   | 9   | 4   | 6   | 3   | 6   | 5   | 6   | 3   | 4   | 4   |
| Dy      | 50  | 26  | 39  | 62  | 48  | 21  | 32  | 18  | 36  | 31  | 38  | 21  | 24  | 27  |
| Y       | 284 | 166 | 295 | 462 | 267 | 104 | 182 | 97  | 192 | 169 | 203 | 104 | 122 | 143 |
| Ho      | 10  | 6   | 8   | 14  | 10  | 4   | 6   | 4   | 7   | 7   | 8   | 4   | 5   | 6   |
| Er      | 29  | 18  | 26  | 45  | 30  | 13  | 20  | 12  | 23  | 20  | 25  | 13  | 14  | 17  |
| Tm      | 4   | 3   | 3   | 6   | 4   | 2   | 3   | 2   | 3   | 3   | 3   | 2   | 2   | 2   |
| Yb      | 24  | 18  | 21  | 38  | 26  | 11  | 19  | 11  | 21  | 19  | 23  | 11  | 12  | 15  |
| Lu      | 4   | 3   | 3   | 6   | 4   | 2   | 3   | 3   | 3   | 3   | 3   | 3   | 2   | 2   |
| ∑REY    | 1399| 804 | 1636| 1967| 1881| 884 | 1931| 882 | 1571| 1277| 1479| 887 | 896 | 1002|
| LREY (%)| 67  | 66.2| 72.4| 63.9| 75.1| 78.7| 83.4| 80.5| 78.7| 76.6| 75.9| 78.6| 76.3| 75.5|
| MREY (%)| 28  | 27.9| 23.9| 30.6| 21  | 17.7| 13.9| 16  | 17.6| 19.3| 19.9| 17.8| 19.8| 20.4|
| HREY (%)| 5.1 | 6   | 3.7 | 5.5 | 3.9 | 3.6 | 2.6 | 3.5 | 3.6 | 4.1 | 4.2 | 3.6 | 3.9 | 4.2 |
| Critical (ppm)| 572 | 331 | 629 | 890 | 723 | 288 | 579 | 266 | 509 | 423 | 526 | 294 | 297 | 346 |
| Uncritical (ppm)| 363 | 206 | 457 | 491 | 507 | 249 | 577 | 249 | 474 | 368 | 400 | 259 | 256 | 281 |
| Excessive (ppm)| 464 | 267 | 550 | 586 | 651 | 347 | 775 | 367 | 588 | 486 | 553 | 334 | 343 | 375 |
| Cout    | 1.2 | 1.2 | 1.1 | 1.5 | 1.1 | 0.8 | 0.8 | 0.7 | 0.9 | 0.9 | 1   | 0.9 | 0.9 | 0.9 |
| Cp      | 40.9| 41.2| 38.5| 45.3| 38.4| 32.6| 30  | 30.2| 32.4| 33.1| 35.6| 33.2| 33.2| 34.5|
| Up      | 26  | 25.6| 27.9| 25  | 27  | 28.2| 29.9| 28.2| 30.2| 28.8| 27.1| 29.2| 28.6| 28  |
| Ep      | 33.2| 33.2| 33.6| 29.8| 34.6| 39.3| 40.1| 41.6| 37.4| 38.1| 37.4| 37.7| 38.3| 37.4|
| Element | C16 | C17 | C18 | C19 | C20 | C21 | C22 | C23 | C24 | C25 | C26 | C27 | C28 | C29 | C30 | Avg. |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| La      | 161 | 144 | 133 | 339 | 217 | 441 | 208 | 217 | 280 | 174 | 187 | 156 | 140 | 147 | 128 | 217.7 |
| Ce      | 309 | 329 | 265 | 502 | 389 | 955 | 425 | 443 | 656 | 360 | 381 | 294 | 274 | 297 | 304 | 423.8 |
| Pr      | 37  | 43  | 30  | 53  | 47  | 117 | 52  | 54  | 58  | 42  | 46  | 40  | 32  | 34  | 38  | 51  |
| Nd      | 134 | 178 | 106 | 185 | 169 | 436 | 202 | 205 | 199 | 161 | 196 | 162 | 139 | 125 | 153 | 194.2 |
| Sm      | 25  | 37  | 19  | 38  | 32  | 79  | 34  | 35  | 32  | 32  | 35  | 28  | 29  | 29  | 33  | 37.1 |
| Eu      | 4   | 5   | 4   | 6   | 5   | 8   | 7   | 8   | 3   | 7   | 8   | 6   | 4   | 4   | 5   | 5.7 |
| Gd      | 23  | 33  | 18  | 36  | 25  | 73  | 32  | 35  | 26  | 32  | 28  | 42  | 32  | 28  | 31  | 34.1 |
| Tb      | 4   | 5   | 3   | 6   | 4   | 11  | 5   | 5   | 5   | 6   | 5   | 8   | 6   | 5   | 5   | 5.5 |
| Dy      | 22  | 27  | 18  | 28  | 20  | 55  | 32  | 29  | 24  | 27  | 23  | 49  | 40  | 36  | 30  | 31.9 |
| Y       | 117 | 172 | 97  | 117 | 94  | 233 | 189 | 170 | 95  | 142 | 121 | 296 | 245 | 189 | 175 | 178.7 |
| Ho      | 4   | 5   | 3   | 6   | 4   | 11  | 5   | 5   | 5   | 6   | 4   | 5   | 4   | 10  | 8   | 7   | 6   |
| Er      | 14  | 16  | 10  | 15  | 11  | 31  | 19  | 16  | 11  | 15  | 13  | 33  | 25  | 21  | 18  | 19.6 |
| Tm      | 2   | 2   | 2   | 2   | 2   | 5   | 3   | 2   | 1   | 2   | 2   | 5   | 4   | 3   | 3   | 2.8 |
| Yb      | 12  | 16  | 10  | 13  | 11  | 30  | 17  | 14  | 9   | 11  | 10  | 35  | 26  | 22  | 18  | 17.8 |
| Lu      | 2   | 2   | 2   | 2   | 2   | 5   | 2   | 2   | 1   | 2   | 2   | 5   | 4   | 3   | 3   | 2.8 |
| ΣREY    | 870 | 1014| 720 | 1348| 1032| 2490| 1233| 1240| 1404| 1018| 1061| 1179| 1008| 950 | 950 | 128.9 |
| LREY (%)| 76.6| 72.1| 76.8| 82.9| 82.8| 81.5| 74.7| 76.9| 87.3| 75.5| 79.6| 58.5| 60.9| 66.5| 69.1 | 74.9 |
| MREY (%)| 19.5| 23.9| 19.4| 14.3| 14.3| 15.3| 21.5| 19.9| 10.9| 21  | 17.4| 34  | 32.4| 27.6| 25.9 | 21.1 |
| HREY (%)| 3.9 | 4   | 3.8 | 2.8 | 2.9 | 3   | 3.8 | 3.2 | 1.9 | 3.4 | 2.9 | 7.5 | 6.7 | 5.9 | 5.1 | 4.1 |
| Critical (ppm)| 295| 403| 238| 357| 303| 774| 454| 433| 337| 358| 366| 554| 459| 380| 386| 455.5 |
| Uncritical (ppm)| 246| 257| 200| 466| 321| 710| 326| 341| 396| 296| 276| 233| 238| 230| 339.9 |
| Excessive (ppm)| 329| 354| 282| 525| 408| 1006| 453| 466| 671| 380| 399| 349| 316| 332| 334| 453.6 |
| C_out  | 0.9 | 1.1 | 0.8 | 0.7 | 0.7 | 0.8 | 1   | 0.9 | 0.5 | 0.9 | 0.9 | 1.6 | 1.5 | 1.1 | 1.2 | 1   |
| C_p    | 33.9| 39.7| 33.1| 26.5| 29.4| 31.1| 36.8| 34.9| 24  | 35.2| 34.5| 47  | 45.5| 40  | 40.6| 35.5 |
| U_p    | 28.3| 25.4| 27.8| 34.6| 31.1| 28.5| 26.4| 27.5| 28.2| 27.5| 27.9| 23.4| 23.1| 25.1| 24.2| 27.6 |
| E_p    | 37.8| 34.9| 39.2| 39  | 39.5| 40.4| 36.7| 37.6| 47.8| 37.3| 37.6| 29.6| 31.4| 35  | 35.2| 36.9 |

Data source: Seredin and Dai (2012).
and thoroughly collected analytical data of coal for the last 50 years and conducted thousands of analyses to give an average. This study is considered as a benchmark for global average of trace elements or coal Clarke value in coal and ash. The authors analysed the average concentration of trace elements in both brown (lignite and sub-bituminous C) coal and their ashes and hard coal (anthracite, bituminous and sub-bituminous A, B) and their ashes. For this study, we require only average values of individual REY and average total REY in coal and ash, which are given in table 3. The global average of REY in ashes from coals is 403.5 ppm, which is about three times higher than that in upper continental crust – 168.4 ppm (Yardley 1986). The critical percentage is 35.2% and outlook coefficient ($C_{out}$) is 1 (described in section 7).

6. Speciation of REY bearing phases in CFA

Speciation and distribution of REY in CFA are necessary for further leaching and extraction processes. Speciation of REY in ash helps in determining the type of chemicals and processes that can be employed for effective and efficient extraction of these critical elements. Various studies have been conducted to understand the speciation and distribution behaviour of REY.

Maity et al. (2021) have done a study on the enrichment of REY in CFA by calculating the enrichment coefficient ($A_e$) and plotting it against the glassy phase present in CFA (figure 5). The author observed the partitioning and simultaneous dilution of REY from coal to the glassy phase in CFA during combustion. The formula used is given in equation (1):

Table 5. Distribution of REY in BA samples from China.

| Element | BA Wang et al. (2019) | BA1 Ma et al. (2019) | BA2 Ma et al. (2019) | BA3 Ma et al. (2019) | BA4 Ma et al. (2019) | Avg. |
|---------|----------------------|----------------------|----------------------|----------------------|----------------------|------|
| La      | 131.4                | 5.6                  | 6                    | 6.7                  | 5                    | 30.9 |
| Ce      | 268                  | 19.8                 | 23.6                 | 22.9                 | 21.2                 | 71.1 |
| Pr      | 29.8                 | 12.4                 | 13.1                 | 11.1                 | 15.5                 | 16.4 |
| Nd      | 117.5                | 111                  | 121                  | 124                  | 122                  | 119.1|
| Sm      | 22.8                 | 5.1                  | 5                    | 4.9                  | 5                    | 8.6  |
| Eu      | 4.2                  | 3.4                  | 2.8                  | 2.3                  | 2.3                  | 3    |
| Gd      | 23.1                 | 2.5                  | 2.1                  | 3.3                  | 1.7                  | 6.5  |
| Tb      | 3.2                  | 3.3                  | 3                    | 3.5                  | 3                    | 3.2  |
| Dy      | 18                   | 2.4                  | 2.2                  | 3.2                  | 2.1                  | 5.6  |
| Y       | 93                   | 28.8                 | 31                   | 28.5                 | 27.2                 | 41.7 |
| Ho      | 3.4                  | 0.4                  | 0.4                  | 0.5                  | 0.4                  | 1    |
| Er      | 9.8                  | 11.5                 | 11.7                 | 16                   | 13.1                 | 12.4 |
| Tm      | 1.3                  | 1.5                  | 1.9                  | 2.2                  | 2.3                  | 1.8  |
| Yb      | 8.8                  | 1.3                  | 1.1                  | 1.4                  | 1.3                  | 2.8  |
| Lu      | 1.2                  | 1.5                  | 1.5                  | 2.1                  | 2.2                  | 1.7  |
| $\Sigma$REY | 735.3               | 210.5                | 226.6                | 232.5                | 224.1                | 325.8|
| LREY (%) | 77.5                | 73.1                 | 74.5                 | 72.9                 | 75.2                 | 74.6 |
| MREY (%) | 19.2                | 19.2                 | 18.2                 | 17.6                 | 16.2                 | 18.1 |
| HREY (%) | 3.3                 | 7.7                  | 7.3                  | 9.5                  | 8.6                  | 7.3  |
| Critical (ppm) | 245.6          | 160.5                | 171.7                | 177.5                | 169.6                | 185  |
| Uncritical (ppm) | 207.1          | 25.6                 | 26.3                 | 26                   | 27.1                 | 62.4 |
| Excessive (ppm) | 282.7         | 24.4                 | 28.6                 | 29                   | 27.4                 | 78.4 |
| $C_{out}$ | 0.9                 | 6.6                  | 6                    | 6.1                  | 6.2                  | 5.2  |
| $U_y$    | 33.4                 | 76.3                 | 75.8                 | 76.4                 | 75.7                 | 67.5 |
| $E_y$    | 28.2                 | 12.1                 | 11.6                 | 12.1                 | 12.1                 | 15   |
| Avg.     | 38.4                 | 11.6                 | 12.6                 | 12.5                 | 12.2                 | 17.5 |

Data source: Wang et al. (2019), Ma et al. (2019).
### Table 6. Distribution of REY in CFA from India.

| Element | MTPS/F | RTPS/F | DSTPS/F | MPL/F | FSSTPS/F | RSTPS/F | CSTPS/F | Blusawal | Durgapur | Kaperkheda | Kota | Panipat | Avg. |
|---------|--------|--------|---------|-------|----------|---------|---------|----------|---------|------------|------|---------|------|
| La      | b.d.l  | 1      | 0.5     | 0.5   | 1.1      | 1.4     | 1.5     | 60       | 63      | 50         | 88.7 | 50.2    | 26.5|
| Ce      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 140      | 127     | 120        | 200  | 100     | 57.3|
| Pr      | 53.5   | 56.7   | 56.1    | 51.5  | 62.9     | 47.6    | 49.7    | 48       | 14.3    | 0          | 27   | 11.9    | 39.9|
| Nd      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 53       | 48      | 30         | 60   | 38.4    | 19.1|
| Sm      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 3.5      | 9.8     | 0          | 7.7  | 8.5     | 2.5 |
| Eu      | 0.1    | 0.1    | 0.1    | 0.1   | 0.2      | 0.2     | 1.8     | 3.5      | 0       | 3          | 3.2  | 1       | 1    |
| Gd      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 5.1      | 10.8    | 0          | 3.1  | 9.6     | 2.4 |
| Tb      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 0.7      | 2.5     | 0          | 0.6  | 2.3     | 0.5 |
| Dy      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 5.4      | 7.3     | 0          | 5.3  | 6.5     | 2   |
| Y       | b.d.l  | 0.2    | b.d.l  | 0.1   | 0.8      | 1.4     | 1.4     | 40       | 31.4    | 30         | 40   | 31      | 14.7|
| Ho      | 0.5    | 0.5    | 0.5    | 0.6   | 0.5      | 0.5     | 0       | 2.3      | 0       | 0          | 0    | 2.1     | 0.7 |
| Er      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 0        | 4.6     | 120        | 0    | 4       | 10.7|
| Tm      | b.d.l  | b.d.l  | b.d.l  | b.d.l | b.d.l    | b.d.l   | b.d.l   | 0        | 1.6     | 0          | 0    | 1.5     | 0.3 |
| Yb      | b.d.l  | 0.1    | b.d.l  | 0.1   | 0.3      | 0.2     | 4.3     | 4.2      | 2       | 5          | 3.7  | 1.7     |      |
| Lu      | 0.6    | 0.6    | 0.8    | 0.6   | 0.7      | 0.5     | 0.6     | 1.8      | 1.6     | 0          | 2    | 1.5     | 0.9 |
| ∑REY    | 54.7   | 59.3   | 58.1   | 53.4  | 66.4     | 51.8    | 54      | 363.6    | 331.9   | 352        | 442.4| 274.4   | 180.2|
| LREY (%)| 97.8   | 97.3   | 97.4   | 97.6  | 96.4     | 94.4    | 94.7    | 83.8     | 79      | 56.8       | 86.7 | 76.2    | 88.2|
| MREY (%)| 0.1    | 0.6    | 0.2    | 0.4   | 1.4      | 3.1     | 2.9     | 14.6     | 16.7    | 8.5        | 11.8 | 19.2    | 6.6 |
| HREY (%)| 2.1    | 2.1    | 2.3    | 2     | 2.2      | 2.5     | 2.4     | 1.7      | 4.3     | 34.7       | 1.6  | 4.7     | 5.2 |
| Critical (ppm) | 0.1 | 0.4 | 0.1 | 0.2 | 1 | 1.6 | 1.5 | 100.9 | 97.3 | 180 | 108.9 | 85.4 | 48.1 |
| Uncritical (ppm) | 53.5 | 57.7 | 56.7 | 52.1 | 64 | 48.9 | 51.2 | 116.6 | 97.9 | 50 | 126.5 | 80.2 | 71.3 |
| Excessive (ppm) | 1.1 | 1.2 | 1.4 | 1.1 | 1.4 | 1.3 | 1.3 | 146.1 | 135.1 | 122 | 207 | 107.3 | 60.5 |
| C<sub>out</sub> | 0.1 | 0.3 | 0.1 | 0.2 | 0.7 | 1.2 | 1.2 | 0.7 | 0.7 | 1.5 | 0.5 | 0.8 | 0.7 |
| C<sub>p</sub> | 0.1 | 0.6 | 0.2 | 0.4 | 1.4 | 3.1 | 2.9 | 27.8 | 29.3 | 51.1 | 24.6 | 31.1 | 14.4 |
| U<sub>p</sub> | 97.8 | 97.3 | 97.4 | 97.6 | 96.4 | 94.4 | 94.7 | 32.1 | 29.5 | 14.2 | 28.6 | 29.2 | 67.4 |
| E<sub>p</sub> | 2.1 | 2.1 | 2.3 | 2 | 2.2 | 2.5 | 2.4 | 40.2 | 41.2 | 34.7 | 46.8 | 39.7 | 18.2 |

Data source: Mondal et al. (2019), Maity et al. (2021).

* b.d.l: below detection limit.
DREE is classified as Class F and Class C (ASTM C618-19). Class F contains at least 70% pozzolanic compounds (silica oxide, alumina oxide, and iron oxide), while Class C contains 50–70% pozzolanic compounds. Class C has higher calcium oxide content (>20%) than Class F and both have some cementitious properties (ASTM C618, 2019). Kolker et al. (2017) confirmed the occurrence of REY in aluminosilicate glassy phase and correlated REY with Al and Si containing aluminosilicate glass only and with Ca and Fe rich aluminosilicate glass. CFA samples were Class C and Class F. They found that the samples containing Ca and/or Fe rich aluminosilicate glass had similar or more REY-enrichment than in the bulk sample. Liu et al. (2019), using SEM-EDX, observed two types of REY occurrences in CFA. One is pure REY phosphates and the other is minor REY in lime and zircon (figure 6). It is interpreted that one REY phosphate particle is enriched in LREY (figure 6a), while the other is enriched in HREY with close association to aluminosilicate glass (figure 6b). The authors have predicted that the two REY phosphate minerals might be the monazite/rhabdophane, which is the LREY-enriched phosphate and xenotime/churchite, which is the HREY-enriched phosphate. They found lime (figure 6c) and zircon (figure 6d) particles containing minor REY. Using µXRF and µXANES analyses, they identified potential REY bearing phases such as REY phosphates, apatite, REY oxides and REY-bearing glassy phase. They also conducted leaching tests at various pH and found that REY were associated with oxides and carbonates, apatite, REY phosphate and hematite and the rest in zircon and glassy phase. These samples were also Class C and Class F. Pan et al. (2020) suggested that most of the REY (~70%) in CFA of Class F are associated with the aluminosilicate glassy phase followed by the acid-soluble form and the organic form (figure 7).

Table 7. The REY analysis of CFA from the USA.

| Element | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Y | REY | LREY (%) | MREY (%) | HREY (%) | Critical (ppm) | Uncritical (ppm) | Excessive (ppm) |
|---------|----|----|----|----|----|----|----|----|----|----|-----|-----------|-----------|-----------|-----------------|-----------------|-----------------|
| 93488   | 34.3 | 72.4 | 8.4 | 31.4 | 6.3 | 1.4 | 5.9 | 0.9 | 5.3 | 30.1 | 204.3 | 74.8 | 21.3 | 4.0 | 17.4 | 26.8 | 37.9 |
| 93882   | 44.5 | 96.4 | 10.6 | 39.8 | 8.1 | 1.9 | 8.3 | 1.3 | 7.8 | 46.9 | 276.0 | 72.2 | 23.3 | 4.5 | 36.6 | 26.7 | 37.7 |
| 93647   | 50  | 100.5 | 28.9 | 41.2 | 23.4 | 4.2 | 27.1 | 1.3 | 8.1 | 22.4 | 763.6 | 72.7 | 23.8 | 4.4 | 36.7 | 25.8 | 37.3 |
| 92277   | 117.9 | 266.3 | 28.2 | 113.2 | 3.9 | 2.1 | 11.8 | 1.8 | 22.4 | 149.4 | 723.4 | 74.4 | 23.8 | 4.3 | 35.1 | 26.7 | 37.4 |
| 93953   | 117 | 260.7 | 29 | 109.9 | 12.9 | 1.6 | 24.9 | 1.6 | 19.4 | 227.6 | 718.7 | 75 | 19.3 | 3.9 | 34.6 | 26.6 | 38.4 |
| 93954   | 116.8 | 261.1 | 27.7 | 113.4 | 10.7 | 1.6 | 24.8 | 1.6 | 11.4 | 277.4 | 717.1 | 75 | 19.2 | 3.9 | 37.2 | 26.8 | 38.6 |
| 93955   | 119 | 264.7 | 27.8 | 108.8 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 740.2 | 70.9 | 19.2 | 3.9 | 37.6 | 26.8 | 38.5 |
| 93956   | 113.6 | 252.3 | 28.3 | 113.4 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 745.7 | 70.5 | 19.0 | 3.9 | 37.9 | 26.8 | 38.5 |
| 93957   | 113.2 | 252.3 | 27.1 | 109.1 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 760.6 | 70.4 | 18.9 | 3.9 | 37.9 | 26.8 | 38.5 |
| 93958   | 115.7 | 256.7 | 26.5 | 111.3 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 765.6 | 70.4 | 18.9 | 3.9 | 37.9 | 26.8 | 38.5 |
| 93960   | 110.2 | 246.4 | 26.5 | 106.4 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 765.6 | 70.4 | 18.9 | 3.9 | 37.9 | 26.8 | 38.5 |
| 93963   | 95.1 | 201.1 | 23.9 | 95.6 | 10.7 | 1.6 | 24.8 | 1.6 | 9.5 | 285.5 | 765.6 | 70.4 | 18.9 | 3.9 | 37.9 | 26.8 | 38.5 |
| Avg.*   | 68.8 | 145.5 | 16.4 | 63.1 | 13.3 | 4.5 | 4.2 | 3.9 | 18.3 | 103.8 | 70.7 | 10.6 | 1.5 | 4.6 | 13.6 | 7.0 | 6.3 |

Data source: Taggart et al. (2016).

*Average of 157 samples.

\[
A_c = \frac{\sum \text{REE}_{\text{Ash}} - \sum \text{REE}_{\text{Coal}}}{\sum \text{REE}_{\text{Coal}}}. \tag{1}
\]

The CFA is classified as Class F and Class C (ASTM C618-19). Class F contains at least 70% pozzolanic compounds (silica oxide, alumina oxide, and iron oxide), while Class C contains 50–70% pozzolanic compounds. Class C has higher calcium oxide content (>20%) than Class F and both have some cementitious properties (ASTM C618, 2019). Kolker et al. (2017) confirmed the occurrence of REY in aluminosilicate glassy phase and correlated REY with Al and Si containing aluminosilicate glass only and with Ca and Fe rich aluminosilicate glass. CFA samples were Class C and Class F. They found that the samples containing Ca and/or Fe rich aluminosilicate glass had similar or more REY-enrichment than in the bulk sample. Liu et al. (2019), using SEM-EDX, observed two types of REY occurrences in CFA. One is pure REY phosphates and the other is minor REY in lime and zircon (figure 6). It is interpreted that one REY phosphate particle is enriched in LREY (figure 6a), while the other is enriched in HREY with close association to aluminosilicate glass (figure 6b). The authors have predicted that the two REY phosphate minerals might be the monazite/rhabdophane, which is the LREY-enriched phosphate and xenotime/churchite, which is the HREY-enriched phosphate. They found lime (figure 6c) and zircon (figure 6d) particles containing minor REY. Using µXRF and µXANES analyses, they identified potential REY bearing phases such as REY phosphates, apatite, REY oxides and REY-bearing glassy phase. They also conducted leaching tests at various pH and found that REY were associated with oxides and carbonates, apatite, REY phosphate and hematite and the rest in zircon and glassy phase. These samples were also Class C and Class F. Pan et al. (2020) suggested that most of the REY (~70%) in CFA of Class F are associated with the aluminosilicate glassy phase followed by the acid-soluble form and the organic form (figure 7).
7. Global occurrence of REY in CA

In this review, we have done extensive literature analysis and collected data published by different authors worldwide on the composition of REY from CFA and BA and compared them with each other using common parameters. The parameters (equations 2–5) are as described by Blissett et al. (2014) and Seredin (2010) such as outlook coefficient ($C_{\text{out}}$), $\sum$REY, critical percentage ($C_p$), uncritical percentage ($U_p$) and excessive percentage ($E_p$). The formulae used are given below (Seredin and Dai 2012; Blissett et al. 2014; Maity et al. 2021):

$$C_{\text{out}} = \frac{\sum \text{Critical (ppm)}}{\sum \text{Excessive (ppm)}},$$

$$C_p = \frac{\sum \text{Critical (ppm)}}{\sum \text{REE (ppm)}} \times 100,$$

$$U_p = \frac{\sum \text{Uncritical (ppm)}}{\sum \text{REE (ppm)}} \times 100,$$

$$E_p = \frac{\sum \text{Excessive (ppm)}}{\sum \text{REE (ppm)}} \times 100.$$

As the name suggests, critical elements are in high demand, hence, $C_p$ and $C_{\text{out}}$ are very important parameters, which decide whether the given samples are economically viable to extract or not. As reported by Seredin and Dai (2012) and Framus et al. (2015), $C_p$ above 30% and $C_{\text{out}}$ above 1 are considered good, although as the formula suggests (equation 2), the value of $C_{\text{out}}$ is governed by both $C_p$ and $E_p$. A $C_{\text{out}} < 1$ does not necessarily mean that the sample cannot be a good secondary source for REY. Hence, all the four parameters as described above have to be analysed to decipher an economical source. In the following sub-sections, country-wise review of REY occurrences in CA has been analysed.
Table 10. Distribution of REY in CA from Russia.

| Element | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 | R9 | R10 | Avg. |
|---------|----|----|----|----|----|----|----|----|----|-----|------|
| La      | 411| 819| 780| 145| 67 | 178| 586| 196| 265| 167 | 312.5|
| Ce      | 519| 924| 706| 298| 152| 497|1021|383 |492 |316 | 546.6|
| Pr      |  91| 182| 99 | 31 | 24 | 48 | 117| 48 | 61 | 40 | 43.2|
| Nd      | 405| 823| 445|115 |109 |178 |484 |179 |242 |144 | 297.2|
| Sm      | 135| 244|146 | 25 | 33 | 41 | 110| 41 | 50 | 32 | 46.4|
| Eu      |   7|  15|  7 |  4 |  7 | 10 | 16 |  3 |  5 |  3 |  12|
| Gd      | 234| 463|242 | 28 | 49 | 45 |  88| 43 | 60 | 32 | 51.2|
| Tb      |  42|  80|  42|  4 |  9 |  7 |  16|  7 |  9 |  5 |  12|
| Dy      | 251| 527|239 | 26 |  6 | 55 |  95| 39 | 57 | 30 | 39.2|
| Y       | 1992|3540|1784|197 |339 |198 |570 |238 |332 |179 | 735.1|
| Ho      |  61| 116| 56 |  6 | 14 |  8 |  20|  8 | 12 |  6 |  8.4|
| Er      | 176| 337|154 | 16 | 46 |  21|  58| 23 | 37 | 16 | 34.9|
| Tm      |  25|  46| 21 |  2 |  7 |  3 |  8 |  3 |  5 |  2 |  5.9|
| Yb      | 177| 270|137 | 14 | 46 | 19 |  57| 21 | 35 | 14 | 26.7|
| Lu      |  25|  38| 20 |  2 |  8 |  3 |  9 |  3 |  6 |  2 |  6.4|

\[ \sum \text{REY} = 4551 \quad \text{LREY} (%) = 34.3 \quad \text{MREY} (%) = 55.5 \quad \text{HREY} (%) = 10.2 \]

\[ \text{Critical (ppm)} = 2873 \quad \text{Uncritical (ppm)} = 871 \quad \text{Excessive (ppm)} = 807 \]

Data source: Seredin and Dai (2012).
7.1 REY in CA from China

Thirty samples from Sichuan, SW China, Inner Mongolia, Guizhou, Yunnan, Guangxi region of China (Seredin and Dai 2012) are reported. All these sites are known for their REY-rich deposits. The CA samples are rich in REY with total REY concentration reaching a maximum of 2490 ppm with the lowest being 720 ppm, which is also very high in comparison to the global average. The average LREY content has the highest share with 74.86% followed by MREY (21.1%) and HREY (4.1%). The \( C_{\text{out}} \) reaches a value of maximum up to 1.6 and a minimum of 0.5 (table 4). The lower value of \( C_{\text{out}} \) is due to the higher content of Ce (656 ppm) and other excessive rare earths. The maximum value of \( C_{\text{out}} \) (1.6) is due to higher concentration of critical elements like Nd (162 ppm) and Y (296 ppm). These ashes can be suitable for the beneficial recovery of REY.

Five BA samples, four of which were investigated by Wang et al. (2019), were from the Pingshuo Coal Gangue Power Plant and one by Ma et al. (2019), which was from the Luzhou Power plant. The average total REY of all the five samples is 325.8 ppm. Nd is the major REY followed by Ce and Y. The samples contained largely LREY (\( \approx 74\% \)) trailed by MREY (18%) and HREY (\( \approx 8\% \)). Since, the critical percentage is around 67.5%, the \( C_{\text{out}} \) value is 5.1 (table 5) which is on the higher side.

7.2 REY in CA from India

A total of 12 CFA samples, seven by Maity et al. (2021) and five by Mondal et al. (2019) were collected from various thermal power stations (TPSs)
Table 12. The REY content in examined CFA samples from Poland.

| Element | L4 | L5 | L10 | L14 | L15 | L19 | P-1 | P-2 | P-3 | Avg. |
|---------|----|----|-----|-----|-----|-----|-----|-----|-----|------|
| La      | 41.7 | 37.9 | 42.7 | 21  | 41.1 | 61.4 | 52.6 | 60.7 | 42.7 |
| Ce      | 86.5 | 76.5 | 84.8 | 49.7 | 57.6 | 86.4 | 124.5 | 107.5 | 125.5 | 88.8 |
| Pr      | 9.5  | 8.9  | 9.6  | 5.9  | 6.8  | 10  | 13.9 | 12.2 | 13.7 | 10.1 |
| Nd      | 38   | 30.3 | 37.3 | 22.6 | 26.6 | 37.1 | 56.6 | 48.6 | 56.6 | 39.3 |
| Sm      | 7.6  | 6.6  | 7.1  | 4.9  | 5.3  | 7.3  | 11.6 | 10  | 10.1 | 7.8  |
| Eu      | 1.9  | 1.6  | 1.6  | 1.1  | 1.4  | 1.7  | 2.6  | 2.5  | 2.6  | 1.9  |
| Gd      | 6.5  | 6.1  | 5.5  | 5.3  | 4.8  | 7.6  | 11.3 | 9.1  | 10.4 | 7.4  |
| Tb      | 0.9  | 0.9  | 1    | 0.8  | 0.9  | 1.2  | 1.5  | 1.6  | 1.8  | 1.2  |
| Dy      | 5.6  | 5.1  | 5.3  | 4.6  | 5.1  | 7.4  | 9.7  | 8.1  | 9.5  | 6.7  |
| Y       | 30.1 | 28.3 | 29.5 | 24.2 | 24.4 | 39.2 | 51.4 | 44  | 53.8 | 36.1 |
| Ho      | 1    | 0.9  | 1    | 0.8  | 1    | 1.4  | 1.9  | 1.7  | 2    | 1.3  |
| Er      | 3.1  | 2.9  | 3    | 2.4  | 2.7  | 4.2  | 5.7  | 5    | 5.2  | 3.8  |
| Tm      | 0.5  | 0.3  | 0.4  | 0.4  | 0.4  | 0.7  | 0.7  | 0.7  | 0.7  | 0.5  |
| Yb      | 2.7  | 2.5  | 2.8  | 2.5  | 2.5  | 4    | 4.7  | 4.1  | 5.4  | 3.5  |
| Lu      | 0.4  | 0.4  | 0.3  | 0.4  | 0.4  | 0.6  | 0.7  | 0.7  | 0.7  | 0.5  |
| REY (%) | 236 | 209.2 | 231.9 | 146.6 | 165 | 249.9 | 358.2 | 308.4 | 358.7 | 251.5 |
| MREY (%) | 77.7 | 76.6 | 78.3 | 71  | 73.6 | 72.8 | 74.8 | 74.9 | 74.3 | 74.9 |
| Critical (ppm) | 79.6 | 69.1 | 77.7 | 55.7 | 61.1 | 90.8 | 127.5 | 109.8 | 129.5 | 89  |
| Uncritical (ppm) | 65.3 | 59.5 | 64.9 | 37.1 | 42  | 66  | 98.2 | 83.9 | 94.9 | 68  |
| Excessive (ppm) | 91.1 | 80.6 | 89.3 | 53.8 | 61.9 | 93.1 | 132.5 | 114.7 | 134.3 | 94.6 |
| C_{out} | 0.9  | 0.9  | 0.9  | 1    | 1    | 1    | 1    | 1    | 1    | 0.9  |
| C_{p}   | 33.7 | 33   | 33.5 | 38  | 37  | 36.3 | 35.6 | 35.6 | 36.1 | 35.4 |
| U_{p}   | 27.7 | 28.4 | 28  | 25.3 | 25.5 | 26.4 | 27.4 | 27.2 | 26.5 | 26.9 |
| E_{p}   | 38.6 | 38.5 | 38.5 | 36.7 | 37.5 | 37.3 | 37  | 37.2 | 37.4 | 37.6 |

Data source: Blissett et al. (2014), Adamczyk et al. (2018).
from different parts of India. The power plants studied by Maity et al. (2021) are: the Mejia Thermal Power Station, the Raghunathpur Thermal Power Station, the Durgapur Steel Thermal Power Station, the Maithon Private Limited, the Farakka Super Thermal Power Station, the Ramagundam Super Thermal Power Station, the Chandrapur Super Thermal Power Station. The other five TPSs studied by Mondal et al. (2019) are Bhusawal, Kaperkheda, Durgapur, Panipat and Kota.

The coal rank used by most of the TPSs is mostly bituminous. The average total REY of all the CFA samples is 180.2 ppm, which is almost 45% lower than the global average. Also, the Indian CFA has very high average LREY share (88.2%), followed by MREY (6.6%) and HREY (5.2%), with average \( C_{\text{out}} \) value 0.7 having a maximum of 1.5 (table 6). The lower \( C_{\text{out}} \) value is due to the presence of the excessive REY, Ce, in high concentration in comparison to the critical REY.

### 7.3 REY in CA from the United States of America (USA) and in CFA from Republic of South Africa (RSA)

A total of 157 samples of CFA are reviewed in this section as reported by Taggart (2017). Out of these 157 samples, 153 were collected from various TPPs located in USA, and 4 samples were collected from RSA. Since, no details were provided about the nature of coal used, we have assumed that the coal rank is bituminous, sub-bituminous or its blend (Coal explained – U.S. Energy Information Administration 2020). The results of 12 important samples have been tabulated (table 7), however, averaging has been carried out for 153 samples. The average total REY concentration in the CFAs from the USA is 426 ppm, which is slightly higher than the global average. The LREY (72.3%) has the largest average share among the REY, followed by the MREY (23.5) and HREY (4.1%). The average \( C_{\text{out}} \) is also 1, which can be considered good. Here a large number of CFA samples have

| Element | D3 | D11 | D13 | D25 | D26 | D27 | Avg. |
|---------|----|-----|-----|-----|-----|-----|------|
| La      | 32 | 28.9| 23.3| 18.7| 11  | 6.8 | 20.1 |
| Ce      | 63 | 56.3| 49.8| 44  | 21.8| 14.9| 41.6 |
| Pr      | 7.3| 6.2 | 5.4 | 4.2 | 2.5 | 1.6 | 4.5  |
| Nd      | 26.5| 22.1| 19.3| 15.9| 9   | 6.2 | 16.5 |
| Sm      | 4.9| 4.1 | 4.4 | 3.5 | 1.4 | 1.2 | 3.3  |
| Eu      | 1.2| 1   | 1   | 0.8 | 0.3 | 0.2 | 0.8  |
| Gd      | 4.5| 3.8 | 3.4 | 2.5 | 1.5 | 1   | 2.8  |
| Tb      | 0.6| 0.6 | 0.5 | 0.5 | 0.2 | 0.1 | 0.4  |
| Dy      | 3.6| 3.4 | 3.1 | 2.6 | 1.3 | 0.6 | 2.4  |
| Y       | 19.3| 18.2| 18.4| 15.9| 7.5 | 5.1 | 14.1 |
| Ho      | 0.7| 0.6 | 0.6 | 0.5 | 0.2 | 0.2 | 0.5  |
| Er      | 1.9| 1.7 | 1.5 | 1.4 | 0.8 | 0.5 | 1.3  |
| Tm      | 0.3| 0.3 | 0.3 | 0.2 | 0.1 | 0.1 | 0.2  |
| Yb      | 1.7| 1.7 | 1.6 | 1.3 | 0.7 | 0.5 | 1.3  |
| Lu      | 0.3| 0.3 | 0.3 | 0.2 | 0.1 | 0.1 | 0.2  |
| \( \Sigma \)REY | 167.8| 149.2| 132.9| 112.2| 58.4 | 39.1 | 109.9|
| LREY (%) | 79.7| 78.8| 76.9| 76.9| 78.2 | 78.5 | 78.2 |
| MREY (%) | 17.4| 18.1| 19.9| 19.9| 18.5 | 17.9 | 18.6 |
| HREY (%) | 2.9 | 3.1 | 3.2 | 3.2 | 3.3 | 3.6 | 3.2  |
| Critical (ppm) | 53.1| 47  | 43.8| 37.1| 19.1 | 12.7 | 35.5 |
| Uncritical (ppm) | 48.7| 43  | 36.5| 28.9| 16.4 | 10.6 | 30.7 |
| Excessive (ppm) | 66  | 59.2| 52.6| 46.2| 22.9 | 15.8 | 43.8 |
| \( C_{\text{out}} \) | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8  |
| \( C_p \) | 31.7| 31.5| 33  | 33.1| 32.7 | 32.5 | 32.4 |
| \( U_p \) | 29  | 28.8| 27.5| 25.8| 28.1 | 27.1 | 27.7 |
| \( E_p \) | 39.3| 39.7| 39.6| 41.2| 39.2 | 40.4 | 39.9 |

Data source: Adamczyk et al. (2018).
around two times more average total REY content than the global average with the highest being 775.5 ppm. Some of these CFA samples have almost two times the average concentration of Ce and Y than the global average and hence, show promising secondary resource for REY. A pilot-scale study of beneficiated CFA from two TPPs burning eastern Kentucky coal was carried out. The authors also studied the correlation between lanthanides and \( \text{P}_2\text{O}_5 \) in both the feed and spent CFAs (Hower et al. 2021). They showed that Gd, Nd and Dy are well differentiated between feed and spent ashes while HREY are disproportionately distributed in the final product (HNO\(_3\)-leachate) in comparison to the LREY.

The coal rank from RSA is also assumed to be bituminous (low-grade), since this rank of coal is produced in Witbank/Highveld coal fields in central South Africa (Jeffrey 2005). In contrast to the CFA samples obtained from USA, the CFA samples from RSA have more average REY content (531.5 ppm). It is around 1.3 times more than the global average of 403.5 ppm. The share of LREY, MREY and HREY followed the same trend as in the samples from USA, i.e., LREY >> MREY > HREY. The average \( C_{\text{out}} \) value of 0.7 (table 8) is due to more concentrations of excessive group elements.

The BA samples from the USA have average total REY of 396.7 ppm with LREY being the dominant type with 74%, followed by MREY (22%) and HREY (3.9%). The excessive percentage is highest, followed by critical percentage and uncritical percentage. This is the reason behind average \( C_{\text{out}} \) value of 0.9 (table 9).

### 7.4 REY in CA from Russia

The average total REY content of all the 20 ash samples analysed by Seredin and Dai (2012) is 2370.65 ppm which is almost 5.9 times more than the
global average. Sample number R2 has the highest REY content of 8424 ppm of all the samples in this review paper and has a $C_{out}$ of 3.8 (table 10). The minimum value of REY content in the Russian CA is 841 ppm. The maximum $C_{out}$ value is 3.9 amongst all the samples. The LREY value ranges from 31 to 77.9% and the MREY value is between 18.7 and 55.5%. These samples from Russia are the most promising as a secondary resource of REY.

7.5 REY in CA from the Republic of Korea (ROK)

One CFA sample from the Western Thermal Power Station (WTPS), ROK was analysed by Park et al. (2021) for REY content. The total REY in CFA sample is 115.3 ppm, which is low in comparison to the global average. The REY composition is dominated by LREY (62.1%) followed by MREY (31.5%) and HREY (6.4%). The $C_{out}$ is 1.2 and the critical percentage is 42.4% (table 11).

A total of five BA samples, one of them is from WTPS, ROK (Tuan et al. 2019) and the other four are from different coal-powered TPPs namely: Samcheok (Kospo), Yeosu (Hanwha), Shin Seocheon (Komipo), and Taean (Kepco) (Tuan et al. 2019). The average total REY of the five BA samples is 181.2 ppm, which is below the global average. The average LREY percentage is 68.3% followed by MREY (26.8%) and HREY (5%). The average value of critical percentage and $C_{out}$ are 40.9% and 2, respectively. The total REY from Taean TPP is maximum (346.3 ppm) among others, but the excessive percentage (36.1%) is very high in comparison to BA sample from the Shin Seocheon TPP, which is a meagre 8.5% (table 11). The $C_{out}$ of BA from the Seocheon TPP is 5.7, which is due to very high critical percentage (48%) and lower excessive percentage (8.5%). However, none of the samples could meet the required concentration of REY necessary for cost-effective extraction.

7.6 REY in CA from Poland

In Poland, electricity is mainly produced in coal-fired TPPs using hard coal and lignite as primary
source. The ashes resulting from these coal combustions have significant share in power generation waste (Uliasz-Bocheńczyk et al. 2015). A total of six CFA samples coded as L4, L5, L10, L14, L15, and L19 were collected by Adamczyk et al. (2018) from four different TPPs located in Poland. Out of these samples, L4 and L5 were collected from the Lagisza Power Plant, L10 from the Joworzno II TPP, L14 and L15 from the Siersza TPP and L19 from the Łączyska TPP. Similarly, out of the six BA samples collected by Adamczyk et al. (2018), D3 was obtained from the Lagisza TPP, D11 and D13 from the Joworzno II and the Siersza TPP, respectively, D25 from the Czechowice TPP and D26 and D27 from the Stalowa Wola TPP. Sample collected by Adamczyk et al. (2018), was from a fluidised bed gasifier. Samples P-1 to P-3 were obtained by Blissett et al. (2014), via CFA processing company, RockTron International Ltd. All the CFA samples were derived from bituminous coal and REY analysis were performed using ICP-MS (Inductively Coupled Plasma Mass Spectrometry).

The REY content in the analysed samples of CFA varied between 146.6 and 249.9 ppm. The average total REY content in the ashes analysed is 206.4 ppm, which is two times lower than the world average for CA (Ketris and Yudovich 2009). LREY have the highest share of around 75% of the total rare earth elements content. HREYs have the lowest share (≤4% of the total REY content), with their average content being 43.3 ppm. The C_{out} of all the samples is in the range of 33–38%. The C_{out} has a maximum value of 1 and a minimum value of 0.9 (table 12).

Five BA samples were investigated by Adamczyk et al. (2018). The samples were taken from different TPPs (details mentioned above), from

### Table 16. Distribution of REY in CFA from Figueira Power Plant, Presidente Medici Power Plant (UTPM) and Jorge Lacerda TPP in Brazil.

| Element | FA-1 | FA-2 | FA-10 | FA-11 | FA-12 | FA-13 | FA-14 | FA-15 | FA-16 | Avg.  |
|---------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| La      | 118  | 52.7 | 67.1  | 63.6  | 73.6  | 73.9  | 70.8  | 69.6  | 75    | 73.8  |
| Ce      | 207  | 113.3| 177.2 | 168.1 | 194.5 | 197.7 | 188.2 | 181.5 | 194   | 180.2 |
| Pr      | 0    | 0    | 17.5  | 16.3  | 18.8  | 19.1  | 18.2  | 17.8  | 19    | 14.1  |
| Nd      | 123  | 55.2 | 74.7  | 68.3  | 79.3  | 80    | 77    | 74.7  | 79.5  | 79.1  |
| Sm      | 17.1 | 9    | 16.1  | 14.4  | 17    | 17    | 16.3  | 16    | 16.9  | 15.5  |
| Eu      | 4.3  | 0    | 2.1   | 1.9   | 2.3   | 2.2   | 2.2   | 2.2   | 2.2   | 2.2   |
| Gd      | 22.7 | 12.1 | 16.2  | 14.2  | 16.6  | 16.5  | 16.2  | 15.9  | 17.1  | 16.4  |
| Tb      | 4    | 1.8  | 2.2   | 1.8   | 2.2   | 2.2   | 2.2   | 2.2   | 2.4   | 2.3   |
| Dy      | 25.9 | 10.5 | 13    | 10.6  | 12.8  | 12.6  | 12.8  | 13.1  | 14.3  | 14    |
| Y       | 0    | 49   | 92.8  | 69    | 82.1  | 83.7  | 83.1  | 84.2  | 92.8  | 70.7  |
| Ho      | 0    | 1.7  | 2.7   | 2.2   | 2.6   | 2.6   | 2.6   | 2.7   | 3     | 2.2   |
| Er      | 0    | 5.7  | 7     | 5.6   | 6.7   | 6.7   | 6.8   | 6.9   | 7.7   | 5.9   |
| Tm      | 2.1  | 0.7  | 1.3   | 1.1   | 1.3   | 1.3   | 1.3   | 1.3   | 1.5   | 1.3   |
| Yb      | 12.2 | 6.3  | 7.6   | 6.4   | 7.6   | 7.5   | 7.6   | 7.8   | 8.7   | 8     |
| Lu      | 4.5  | 1.3  | 1.3   | 1.1   | 1.3   | 1.3   | 1.3   | 1.3   | 1.5   | 1.7   |
| ∑REY    | 540.8| 319.3| 498.8 | 444.6 | 518.7 | 524.3 | 506.6 | 497.2 | 535.7 | 487.3 |
| LREY (%)| 86   | 72.1 | 70.7  | 74.4  | 73.9  | 74    | 73.1  | 72.3  | 71.8  | 74.2  |
| MREY (%)| 10.5 | 23   | 25.3  | 21.9  | 22.4  | 22.4  | 23    | 23    | 24.1  | 21.8  |
| HREY (%)| 3.5  | 4.9  | 4     | 3.7   | 3.8   | 3.7   | 3.9   | 4     | 4.2   | 4     |
| Critical (ppm) | 157.2 | 122.2 | 191.8 | 157.2 | 185.4 | 187.4 | 184.1 | 183.3 | 199   | 174.2 |
| Uncritical (ppm) | 157.8 | 73.8 | 116.9 | 108.5 | 126   | 126.5 | 121.5 | 119.3 | 128   | 119.8 |
| Excessive (ppm) | 225.8 | 123.3 | 190.1 | 178.9 | 207.3 | 210.4 | 201   | 194.6 | 208.7 | 193.3 |
| C_{out} | 0.7  | 1    | 1     | 0.9   | 0.9   | 0.9   | 0.9   | 0.9   | 0.9   | 0.9   |
| C_{p}   | 29.1 | 38.3 | 38.5  | 35.4  | 35.7  | 35.7  | 36.3  | 36.9  | 37.2  | 35.9  |
| U_{p}   | 29.2 | 23.1 | 23.4  | 24.4  | 24.3  | 24.3  | 24    | 24    | 23.9  | 24.5  |
| E_{p}   | 41.8 | 38.6 | 38.1  | 40.2  | 40    | 40.1  | 39.7  | 39.1  | 39    | 39.6  |

Data source: Lange et al. (2017), Pires and Querol (2004), Silva et al. (2010).
fluidized bed boilers and the coal source was bituminous. The average total REY concentration is 109.9 ppm. The average $C_p$ and $C_{out}$ are 32.4% and 0.8, respectively (table 13). None of the samples have REY concentration higher than the global average.

7.7 REY in CA from Indonesia

The average total REY content of the CFA samples is 243.6 ppm, which is about 60% less than the global average. The LREY has the highest share with 67.6–71.3% of the total REY content followed by MREY (23.5–27.2%) and HREY (4.6–5.2%). No samples have more total REY content than the global average. The $C_{out}$ value is between 1.1 and 1.2 with an average value of 1.1 (table 14). Only one sample of BA was collected from the Banjarsari Power Plant by Firman and Haya (2021). The sample has very low concentration of total REY (45.7 ppm) with Ce (17.1 ppm) and Y (6.7 ppm) being the major rare earths (table 14).

7.8 REY in CA from the United Kingdom (UK)

Blissett et al. (2014) collected and examined six CFA samples from a CFA processing company RockTron International Ltd. The sample UK-1 was from a semi-anthracitic coal source while UK-2 and UK-3 were from a bituminous coal or biomass blend. The average total REY content was 340 ppm, which is 15% lower than the global average for REY in CA (Ketris and Yudovich 2009), but one sample coded as UK-1 has total REY content 15% more than the average global REY concentrations. The LREY has the highest share of around 75% followed by MREY ($21\%$) and then the HREY ($4\%$) (table 15). The critical percentage of all the CFA is in the range of
33.4–36.1% and the $C_{\text{out}}$ value is between 0.9 and 1.

### 7.9 REY in CA from Brazil

One CFA sample is from the Figueira TPP (FA-1) (Lange et al. 2017), one from the UTPM TPP (FA-2) (Pires and Querol 2004) and seven from Jorge Lacerda TPP (FA-10 to FA-16) (Silva et al. 2010). Although the coal rank was not mentioned for sample from the Figueira, the coal source is assumed to be bituminous (Graciano and Matos n.d.). The coal rank of samples FA-10 to FA-16 was high volatile C to high volatile A bituminous. The total REY content is maximum for the Figueira Thermal Power Plant (540.78 ppm) in comparison to other samples as reported by various authors like Pires and Querol (2004), Silva et al. (2010) among others. The average total REY from all the samples is 487.3 ppm. The average is 20% more than the global average and the average LREY percentage is 74.2% followed by MREY (21.8%) and HREY (4%). The average $C_{\text{out}}$ value is 0.9 (table 16), which is due to the higher content of excessive elements, especially Cerium (Ce), which is around 1.5 times more than the global average.

Except for BA-1, which is from the Presidente Medici Power Plant (UTPM), all the other samples (BA-10 to BA-16) are from the Jorge Lacerda TPP. The average total REY concentration is 465 ppm with the highest being 563 ppm. All the samples are rich in LREY (71.9–76.6%) followed by MREY (19.9–24.5%) and HREY (3.5–5%) with average $C_{\text{out}}$ of 0.9 (table 17).

### 7.10 REY in CA from Belorussia, Mongolia and Tajikistan

Seredin and Dai (2012) reported eight samples, one each from Belorussia and Mongolia and five from Tajikistan. All the CA samples are rich in total REY content, with samples from Belorussia and Mongolia having total REY content of 5035 and 2262 ppm, respectively (table 18). The ash from Belorussia has the higher LREY content (79.8%) followed by MREY (17.8%) and HREY (2.8%), whereas the ash sample from Mongolia has the maximum MREY content (36.8%). The $C_{\text{out}}$ of the Mongolian ash is 1.8, which is very high due to the high concentration of critical elements like Ce (523 ppm), Nd (315 ppm) and Y (617 ppm) and consequently, the $C_p$ is almost two times the excessive percentage. These ashes can be considered as a source of La, Ce, Gd and especially Y (~4.7 times the global average).

Six samples from Tajikistan reported by Seredin and Dai (2012) have been considered for this review. The average total REY of the six samples is 1535.3 ppm, which is 3.6 times more than the global REY average. The LREY ranges from 34.6–72.3%, while the MREY is between 24 and 54.9% and the HREY is between 3.4 and 14.2% (table 19). The $C_{\text{out}}$ values are very encouraging with a maximum of 2.5 and a minimum of 1.1. These samples are rich in Ce and Y, with one sample having Ce concentration almost four times the global average and another having Y content of 800 ppm (~16 times the global average).

Table 18. Distribution of REY in CA from Belorussia and Mongolia.

| Element | B1   | M1   |
|---------|------|------|
| La      | 839  | 321  |
| Ce      | 1784 | 523  |
| Pr      | 239  | 64   |
| Nd      | 967  | 315  |
| Sm      | 170  | 62   |
| Eu      | 19   | 15   |
| Gd      | 154  | 106  |
| Tb      | 21   | 14   |
| Dy      | 111  | 80   |
| Y       | 590  | 617  |
| Ho      | 19   | 19   |
| Er      | 54   | 58   |
| Tm      | 8    | 8    |
| Yb      | 51   | 51   |
| Lu      | 9    | 9    |
| $\sum$REY | 5035 | 2262 |
| LREY (%) | 79.4 | 56.8 |
| MREY (%) | 17.8 | 36.8 |
| HREY (%) | 2.8  | 6.4  |
| Critical (ppm) | 1762 | 1099 |
| Uncritical (ppm) | 1402 | 553  |
| Excessive (ppm) | 1871 | 610  |
| $C_{\text{out}}$ | 0.9  | 1.8  |
| $C_p$ | 35   | 48.6 |
| $U_p$ | 27.9 | 24.5 |
| $E_p$ | 37.2 | 27   |

Data source: Seredin and Dai (2012).
Table 19. Distribution of REY in CA from Tajikistan.

| Element | T1  | T2  | T3  | T4  | T5  | T6  | Avg.  |
|---------|-----|-----|-----|-----|-----|-----|-------|
| La      | 70  | 60  | 131 | 195 | 414 | 261 | 188.5 |
| Ce      | 151 | 287 | 360 | 333 | 511 | 370 | 335.3 |
| Pr      | 17  | 35  | 30  | 50  | 70  | 40  | 40.3  |
| Nd      | 70  | 130 | 110 | 200 | 240 | 150 | 150   |
| Sm      | 24  | 29  | 14  | 42  | 44  | 17  | 28.3  |
| Eu      | 13  | 11  | 4   | 11  | 6   | 16  | 10.2  |
| Gd      | 25  | 80  | 25  | 30  | 35  | 100 | 49.2  |
| Tb      | 6   | 17  | 6   | 4   | 7   | 27  | 11.2  |
| Dy      | 40  | 100 | 37  | 30  | 43  | 140 | 65    |
| Y       | 400 | 650 | 250 | 200 | 350 | 800 | 441.7 |
| Ho      | 15  | 23  | 8   | 7   | 13  | 30  | 16    |
| Er      | 48  | 63  | 20  | 15  | 42  | 80  | 44.7  |
| Tm      | 8   | 9   | 2   | 2   | 7   | 10  | 6.3   |
| Yb      | 55  | 60  | 15  | 13  | 47  | 63  | 42.2  |
| Lu      | 9   | 9   | 2   | 2   | 8   | 9   | 6.5   |
| ∑REY    | 951 | 1563| 1014| 1134| 1837| 2113| 1435.3|
| LREY (%)| 34.9| 34.6| 63.6| 72.3| 69.6| 39.7| 52.5  |
| MREY (%)| 50.9| 54.9| 31.8| 24.3| 24  | 51.3| 39.5  |
| HREY (%)| 14.2| 10.5| 4.6 | 3.4 | 6.4 | 9.1 | 8     |
| Critical (ppm) | 577  | 971  | 427  | 460  | 688  | 1213  | 722.7 |
| Uncritical (ppm) | 136  | 204  | 200  | 317  | 563  | 418  | 306.3 |
| Excessive (ppm) | 238  | 388  | 387  | 357  | 586  | 482  | 406.3 |
| C_{out}   | 2.4   | 2.5   | 1.1   | 1.3   | 1.2   | 2.5   | 1.8   |
| C_{p}     | 60.7   | 62.1   | 42.1   | 40.6   | 37.5   | 57.4 | 50.1   |
| U_{p}     | 14.3   | 13.1   | 19.7   | 28   | 30.7   | 19.8   | 20.9   |
| E_{p}     | 25   | 24.8   | 38.2   | 31.5  | 31.9   | 22.8   | 29    |

Data source: Seredin and Dai (2012).

Figure 8. Global average REY concentration vs. average REY concentration of various countries (ppm). Data source: Pires and Querol (2004), Seredin and Dai (2012), Blissett et al. (2014), Taggart (2017), Lange et al. (2017), Adamczyk et al. (2018), Mondal et al. (2019), Rosita et al. (2020), Park et al. (2021). Note: Only countries with more than one sample of CFA were taken.
Table 20: List of countries with samples (CFA and BA) having total REY concentration greater than global average.

| Sl. no. | Countries               | Type       | Sample id | Coal source | Sample sites/source | Total REY (ppm) | Major elements (ppm) | Instrument used for analysis | Authors                          |
|---------|-------------------------|------------|-----------|-------------|---------------------|----------------|----------------------|-----------------------------|--------------------------------|
| 1       | China                   | CA         | CA C4     | NA          | Sanggao mine, SW China | 1967 Ce         | Ce > La > Nd > Y     | ICP-MS and INAA              | Seredin and Dai (2012)       |
| 2       | India                   | BA         | BA        | NA          | Dacara mine, Guizhou | 2490 Ce         | Ce > La > Nd > Y     | ICP-MS, INAA                 | Mondal et al. (2019)         |
| 3       | United States of America (USA) | BA        | BA        | NA          | Changhe mine, Sichuan | 804 Ce         | Ce > La > Nd > Y     | ICP-MS, INAA                 | Taggart et al. (2017)         |
| 4       | Poland                  | BA         | BA        | NA          | Adaohai mine, Inner Mongolia | 720 Ce       | Ce > La > Nd > Y     | ICP-MS, INAA                 | Mondal et al. (2019)         |
| 5       | United Kingdom          | CFA        | CFA      | UK-1        | No data available    | None of the samples have total REY more than global average | | ICP-MS, INAA                 | Mondal et al. (2019)         |
| 6       | Republic of South Africa (RSA) | BA        | BA        | NA          | No data available    | None of the samples have total REY more than global average | | ICP-MS, INAA                 | Mondal et al. (2019)         |
| Sl. no. | Countries    | Type  | Sample id | Coal source | Sample sites/source | Total REY (ppm) | Major elements (>100 ppm) | Outlook coefficient ($C_{out}$) | Instrument used for analysis | Authors          |
|--------|--------------|-------|-----------|-------------|---------------------|----------------|----------------------------|-------------------------------|--------------------------------|------------------|
| 7      | Indonesia    | CFA   | BA        | None        | None of the samples have total REY more than global average |
| 8      | Brazil       | CFA   | FA-1      | Bituminous  | Figueras TPP         | 540.8          | Ce>Nd>La>Gd                | 0.7                           | ICP-MS and ICP-OES         | Lange et al.      |
|        |              |       | FA-16     | High volatile C to high | Jorge Lacerda TPP | 535.7          | Ce>Y>Nd>La                | 1.0                           | ICP-MS, ICP-AES and HPLC | Silva et al. (2010) |
|        |              |       | FA-11     | Volatile A bituminous | Jorge Lacerda TPP | 444.6          | Ce>Y>Nd>La                | 0.9                           | ICP-MS, ICP-AES and HPLC |                |
|        |              |       | FA-15     |             |                     | 497.2          | Ce>Y>Nd>La                | 0.9                           | ICP-MS, ICP-AES and HPLC |                |
|        |              | BA    | BA-10     | High volatile C to high | Jorge Lacerda TPP | 563            | Ce>Y>Nd>La                | 1.0                           | ICP-MS, ICP-AES and HPLC |                |
|        |              |       | BA-11     | Volatile A bituminous | Jorge Lacerda TPP | 535.8          | Ce>Y>Nd>La                | 0.9                           | ICP-MS, ICP-AES and HPLC |                |
|        |              |       | BA-12     |             |                     | 484.2          | Ce>Nd>La>Y                | 0.9                           | ICP-MS and INAA           | Seredin and Dai (2012) |
| 9      | Belorussia   | CA    | B1        | NA          | Drill hole coal mine | 5035           | Ce>Nd>La>Y                | 0.9                           | ICP-MS and INAA           | Seredin and Dai (2012) |
|        |              | BA    | No data available |            |                      |                |                            |                               |                                |                  |
| 10     | Mongolia     | CA    | M1        | NA          | Aduunchuluun mine    | 2262           | Y>Ce>La>Nd                | 1.8                           | ICP-MS and INAA           | Seredin and Dai (2012) |
|        |              | BA    | No data available |            |                      |                |                            |                               |                                |                  |
| 11     | Tajikistan*  | CA    | T5        | NA          | Nazar–Ailok deposit, drill hole coal mine | 1837           | Ce>La>Y>Nd                | 1.2                           | ICP-MS and INAA           | Seredin and Dai (2012) |
|        |              |       | T6        |             | drill hole coal mine | 2113           | Y>Ce>La>Nd                | 2.5                           | ICP-MS and INAA           | Seredin and Dai (2012) |
|        |              |       | T1        |             |                     | 951            | Y>Ce>La=Nd                | 2.4                           |                                |                  |
|        |              |       | T3        |             |                     | 1014           | Ce>Y>La>Nd                | 1.1                           |                                |                  |
|        |              | BA    | No data available |            |                      |                |                            |                               |                                |                  |
| 12     | Russia*      | CA    | R2        | NA          | Pavlovka-2 mine, Russia Far East | 8421           | Y>Ce>Nd>La                | 3.8                           | ICP-MS and INAA           | Seredin and Dai (2012) |
|        |              |       | R3        |             | Russia Far East     | 4878           | Y>La>Ce>Nd                | 2.8                           | INAA                           | Dai (2012) |
|        |              |       | R4        |             |                     | 913            | Ce>Y>La>Nd                | 1.1                           |                                |                  |
|        |              |       | R20       | Shirokovsk mine, Ural |            | 841            | Y>Ce>Nd>La                | 2.4                           |                                |                  |
| 13     | Korea        | CFA   | BA        | No data available | None of the samples have total REY more than global average |

*Only two samples with the highest and two with the lowest total REY concentration are given for the sake of convenience.

# NA: not available.

Note: All the samples having total REY more than the global average are considered for this table.
8. Conclusion

In this review, we have collected data for REY in CFA and BA from 13 different countries and found that eleven of these countries have at least one sample with average REY concentration above the global average of ash. The results of CFA collected from the countries like China, Belorussia, Mongolia, Russia and Tajikistan are REY-rich samples and the $C_{out}$ value reached a maximum of 3.9 in one of the samples with $C_p$ of 68.8%. The highest total REY reported in this paper is 8424 ppm with $C_{out}$ of 3.8. The average concentrations of REY in CFA from the major coal-consuming countries have been compared with the global average concentration of REY in CA (figure 8) for comprehensive understanding of their variations and distribution.

There is an urgent need for finding new and efficient ways for extraction of rare earth elements from CA. So, in this review, we have concentrated on existing literatures available on the occurrence of rare earth elements from CA obtained from TPPs and other sources all over the globe and their rare earth concentrations. A summarized list of countries with samples having average total REY content greater than the global average is given in table 20.

All the samples analysed for this review have more LREY content, and in samples with average total REY more than the global average, it mostly follows the trend Ce > Y > Nd > La (table 20). Some of these samples could be a secondary resource of single REY element, like sample R2 from Russia can be a source of Y (3540 ppm). This paper could act as a data hub for REY from around the world for researchers to further study.

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Author statement

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