

## Partitioning of rare earth elements and yttrium (REY) in five coal-fired power plants in Guizhou, Southwest China<sup>☆</sup>

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### ABSTRACT

As indispensable strategic materials for high-tech industries, rare earth elements and yttrium (REY) have become particularly important in recent years, raising the demand of developing new approaches for reclamation of REY from REY-rich materials such as coal combustion products (CCPs). In this study, five coal-fired power plants (CFPPs) in Guizhou of southwest China were selected for investigating REY concentrations of solid samples, atmospheric emissions, and recovery potentials. REY concentrations of feed fuels are higher in this study (147.2–468.6 mg/kg) than what have been reported previously for coals in China and the world. REY atmospheric emissions are extremely low (38.70–180.11 mg REY/t coal). REY are enriched in bottom ash and fly ash, with average of  $658 \pm 296$  mg/kg and maximum of 1257 mg/kg from the five CFPPs. Relative enrichment factors (REF) of REY in bottom ash and fly ash compared with the feed fuel are 0.86–1.02 and 0.91–1.04, respectively. REY concentrations in desulfurized gypsum are very low (6–17 mg/kg), and that is mostly inherited from limestone. Critical REY (Nd, Eu, Tb, Dy, Y, and Er) in bottom/fly ash account for 34%–39% of the total REY and the outlook coefficients ( $C_{out}$ ) are in the range of 0.89–1.11. This study indicates a promising prospect to reclaim REY from REY-rich CCPs (bottom and fly ash) in CFPPs in Guizhou, especially in the central-north Guizhou, although such practices require further technology advancement.

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### 1. Introduction

Rare earth elements and yttrium (REY) have been widely used in a broad range of commercial and non-commercial applications

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because of their special physicochemical properties.<sup>1</sup> REY mainly come from natural minerals, such as bastnaesite, monazite, yttrium phosphorus ore, and weathered crustal deposits, and are mainly distributed in China (44 Mt), Brazil (22 Mt), Vietnam (22 Mt), and Russia (18 Mt).<sup>2</sup> The overall shortage and geographically unbalanced distributions of REY determine their crucial strategic position. Recycling of REY from batteries, permanent magnets, and fluorescent lamps has been widely implemented worldwide, but such practices can only generate very limited amounts of REY.<sup>2</sup> Since at the end of the 20th century, coal seams enriched with REY have been identified and coal combustion products (CCPs) with high REY concentrations have attracted wide attention.<sup>1,3–10</sup> Studies on REY contents in whole coal from different areas in the world showed an average value of 68.47 mg/kg for the world coal,<sup>11</sup> 65.5 mg/kg for the U.S. coal,<sup>12</sup> and 135.89 mg/kg for Chinese coal.<sup>13</sup> Specifically, the average REY content in coal from Guizhou province in southwest

China is 165.9 mg/kg,<sup>14</sup> suggesting a potential advantage of REY recycling in Guizhou province coals.

Coal is an important energy source for generating electricity and coal-fired power plants (CFPPs) currently produce 37% of global electricity.<sup>15</sup> In China, coal-fired power accounted for 72% of total power generation in 2016 (6129 TW·h) from the 1826 Mt of coal (48% of total consumption) consumed by CFPPs during the same year.<sup>16</sup> Guizhou has the fifth largest coal reserve in China and the largest in south China with an annual output of 163 Mt in 2017.<sup>17</sup> As an important energy base for a west-to-east power transmission project, Guizhou consumed 66 Mt of coal for electricity generation in 2017.<sup>17</sup> The ash yield (avg. 38% on air-dried basis) of the feed coal for Guizhou's CFPPs (the number of samples  $N = 14$ , in this research and unpublished internal data) was more than twice the national average (16.85%), and large quantities of fly ash and bottom ash are produced each year (25 Mt/y) by Guizhou's CFPPs. The reuse ratio of ash materials is much lower (38%) in Guizhou province compared with the national average (69%),<sup>18,19</sup> with the majority of fly or bottom ash being discarded, a practice that may pollute the environment.<sup>20</sup>

In the present study, concentrations of REY in solid materials, including coal, bottom ash, fly ash, limestone, and gypsum, from five CFPPs in Guizhou were investigated using inductively coupled plasma mass spectrometry (ICP-MS). The behaviors of REY inside these CFPPs were then explored and their atmospheric emissions were estimated. In addition, the prospects of recovering REY from coal combustion products from Guizhou's CFPPs were discussed. Knowledge gained from this study would provide important scientific evidences for guiding future practices of reclamation of REYs from potential CFPPs in Guizhou.

## 2. Methodology

### 2.1. Sampling power plants

Situated in southwest China, Guizhou province has large coal reserves (more than 50 Gt) of Late Permian age (Fig. 1(a)).<sup>21</sup> The locations of the five CFPPs selected for the present study are illustrated in Fig. 1(b). CFPPs #1, #2, and #3 are located in the western part of the province, #4 is in the centre, and #5 is in the east. All of the CFPPs use the local fuel (coal, gangue, and coal slime), except for #5, which uses coal produced in western

Guizhou. The information about the boiler type, capacity (MW), air pollution control devices (APCDs), and the sampling locations are shown in Table 1 and Fig. 2. Briefly, CFPP #1 is equipped with a circulating fluidized bed boiler (CFB, Fig. 2(a)) and CFPPs #2–#5 are pulverized coal boilers (PC, Fig. 2(b)). APCDs for the CFB boiler in CFPP #1 consist of in-furnace desulfurization (IFD), selective non-catalytic reduction (SNCR), a cold-side electrostatic precipitator combined with a fabric filter (C-ESP + FF), and limestone slurry wet flue gas desulfurization (WFGD), APCDs at the four PC CFPPs (CFPP #2–#5) consist of selective catalytic reduction (SCR), C-ESP or C-ESP + FF, and limestone slurry WFGD.

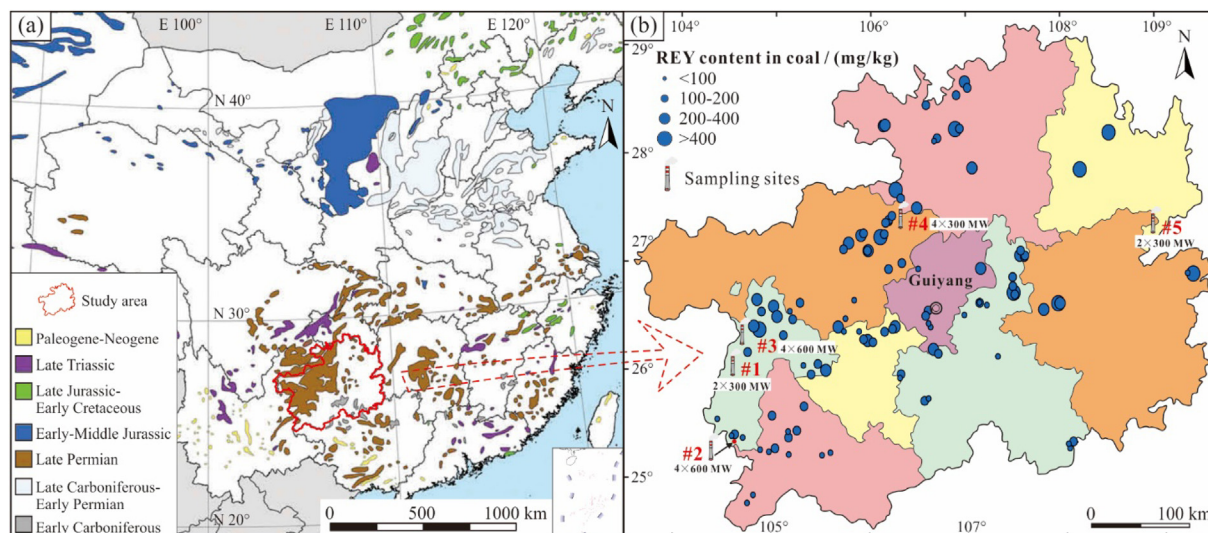
Solid samples and flue gas sampling sites in the two types of CFPP are illustrated in Fig. 2. Feed fuel (pulverized coal, gangue, and coal slime), CCPs (bottom ash and fly ash), limestone, and FGD gypsum were simultaneously collected (~1 kg for each sample) from a utility boiler system in each CFPP for 3–6 times during three days of sampling period. The fly ash was a mixture of different fly ash hoppers of ESP/ESP + FF. At the stack, particulate matter was withdrawn isokinetically from the flue gas and collected on a Teflon filter (Whatman, 0.45- $\mu\text{m}$  pore size) using an APEX Model XC-572 (APEX Instruments, USA, Fig. S1) according to USEPA method 5.<sup>22</sup> This method collected most PM in the flue gas as the PM size of fly ash was overwhelmingly larger than 1  $\mu\text{m}$ .<sup>23</sup> The flue gas sampling train was maintained at a temperature of  $120 \pm 20$  °C to avoid water condensation.<sup>22</sup> Each flue gas sample was collected for ~3 h, with three to six samples obtained along with other types of solid samples for a CFPP. REY concentration in the stack flue gas was determined by the total amount of REY on the filter relative to the volume of sampled flue gas. Since the flue gas temperature at the stack of five CFPPs ranged from 40 to 50 °C, much lower than the melting (798–1663 °C)

**Table 1**

Information of the five CFPPs surveyed in the present study.

| Power plants | Boiler type | Installed capacity (MW) | APCDs                  |
|--------------|-------------|-------------------------|------------------------|
| #1           | CFB         | 2 × 300                 | SNCR + C-ESP-FF + WFGD |
| #2           | PC          | 4 × 600                 | SCR + C-ESP + WFGD     |
| #3           | PC          | 4 × 600                 | SCR + C-ESP + WFGD     |
| #4           | PC          | 4 × 300                 | SCR + C-ESP-FF + WFGD  |
| #5           | PC          | 2 × 300                 | SCR + C-ESP + WFGD     |

Note: CFB, circulating fluidized bed boiler; PC, pulverized coal-fired boiler; SNCR, selective non-catalytic reduction; SCR, selective catalytic reduction; C-ESP + FF, cold side electrostatic precipitator and fabric filter; WFGD, wet flue gas desulfurization.



**Fig. 1.** Distribution and formation ages of coal in China ((a), modified from Dai and Finkelman),<sup>4</sup> and locations of five studied CFPPs in the present research and REY concentration in Guizhou's coal ((b), unpublished internal data).

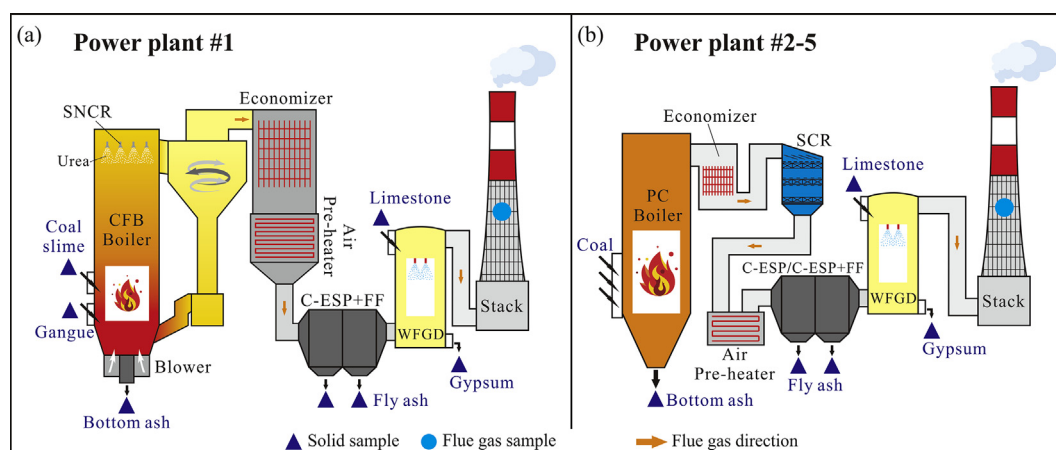


Fig. 2. Schematic diagram and sampling sites of CFPPs with CFB boiler (a) and PC boilers (b).

and boiling points (1196–3520 °C, with most REY over 1500 °C) of REY, noting that they might exist as part of minerals in coal, all REY in stack flue gas were believed to exist in the solid form.

In addition, information about the daily consumption/production of solid materials (t/d), daily flue gas emissions ( $\times 10^4$  m<sup>3</sup>/d), daily average PM content (mg/m<sup>3</sup>) in the stack flue gas, and actual operation power of boilers (MW) for each CFPP was collected.

## 2.2. Analysis methods

Solid materials including feed fuel (pulverized gangue and coal slime for CFB boiler #1, pulverized coal for PC boilers #2–#5), limestone, bottom ash, fly ash, and FGD gypsum were air-dried before grinding into small powder (<0.150 mm). Results for all of the solid samples are presented on an air-dried basis. Proximate analysis for feed coal samples was performed according to the Chinese national standard method.<sup>24</sup> Carbon (C), hydrogen (H), and nitrogen (N) contents in feed coal samples were determined by an elemental analyzer (Vario MACRO Cube, Elementar, Germany) and total sulfur (S) was measured based on the Eschka method.<sup>25</sup> Calorific values were determined by GB/T 213-2008.<sup>26</sup>

Trace elements in solid samples were digested according to a method developed by Qi and Grégoire<sup>27</sup> and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Analytik Jena, German) in the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Briefly, 50 mg of solid sample or a quarter of the filter was digested using 1 mL of concentrated HF and 1 mL of concentrated HNO<sub>3</sub> in PTFE-lined stainless-steel bombs, heated to 190 °C for 24 h. Insoluble remaining residues, if present, were dissolved using 6 mL of 40 vol% HNO<sub>3</sub> heated to 140 °C for 5 h. Following the digestion phase, 200 ng of

rhodium in liquid solution was added and mixed. Finally, 0.4 mL of the digest was transferred to a centrifuge tube, to which 10 mL Milli-Q water (18.2 MΩ cm, Millipore Inc.) was added. Rhodium was used as an internal standard to correct for matrix effects and instrumental drift. All the reagents used were trace metal grade, and HF and HNO<sub>3</sub> were double distilled to remove possible impurity.

## 2.3. Quality assurance and quality control

The accuracy of the proximate and ultimate analyses was checked using certified reference materials (CRMs) of gangue (ZBM110A, GSB 06-2182-2008-1), anthracite (ZBM095, GSB 06-2105-2007), and bituminous coal (ZBM113, GSB 06-2114-2007), and recoveries of these reference materials were in the range of 95%–105%. Certified reference materials of coal (NIST SRM 1632d; NIST SRM 1635a), fly ash (NIST SRM 1633c), and limestone (JLs-1; Jdo-1) were digested and analyzed simultaneously with solid samples to ensure the analytical accuracy of trace elements. The recoveries of REY in different CRMs were in the range of 90%–110%, and the procedure method blank was as low as 0.01 mg/kg. The blank of REY in the Teflon filter was negligible.

## 3. Results and discussion

### 3.1. Fuel properties

Results of the proximate and ultimate analyses are illustrated in Table 2. Differences in feed fuel are found between CFPP #1 with CFB (gangue and coal slime) and CFPPs #2–#5 with PC in terms of moisture content (higher by 2.89%–9.06% based on air-dried), ash yield (higher by 43.93%–45.15%), fixed carbon (lower by 29.47%–33.19%), carbon content (lower by 41.86%–47.24%), and calorific

Table 2  
Proximate and ultimate analysis of fuels.

| Power plants | Fuel type  | Proximate analysis (wt%) |                 |                 |                  | Ultimate analysis (%) |                 |                 |                 | Q <sub>net,ad</sub><br>(MJ/kg) |
|--------------|------------|--------------------------|-----------------|-----------------|------------------|-----------------------|-----------------|-----------------|-----------------|--------------------------------|
|              |            | M <sub>ad</sub>          | V <sub>ad</sub> | A <sub>ad</sub> | FC <sub>ad</sub> | C <sub>ad</sub>       | H <sub>ad</sub> | N <sub>ad</sub> | S <sub>ad</sub> |                                |
| #1 (N = 4)   | Gangue     | 2.89 ± 0.42              | 18.77 ± 0.27    | 45.15 ± 2.83    | 33.19 ± 2.87     | 47.24 ± 3.43          | 3.21 ± 0.13     | 0.85 ± 0.05     | 0.45 ± 0.07     | 19.29 ± 1.28                   |
| #1 (N = 4)   | Coal slime | 9.06 ± 3.18              | 17.53 ± 0.63    | 43.94 ± 4.18    | 29.47 ± 1.69     | 41.86 ± 1.96          | 2.96 ± 0.15     | 0.82 ± 0.03     | 0.29 ± 0.04     | 17.03 ± 0.79                   |
| #2 (N = 4)   | Bituminous | 1.08 ± 0.12              | 18.07 ± 1.47    | 30.68 ± 2.47    | 50.17 ± 3.90     | 62.38 ± 2.48          | 3.19 ± 0.28     | 1.07 ± 0.07     | 0.64 ± 0.05     | 24.47 ± 1.03                   |
| #3 (N = 4)   | Bituminous | 0.66 ± 0.12              | 15.05 ± 0.62    | 39.56 ± 1.92    | 44.72 ± 1.52     | 51.21 ± 1.49          | 3.04 ± 0.06     | 0.85 ± 0.04     | 2.50 ± 0.23     | 20.74 ± 0.46                   |
| #4 (N = 3)   | Anthracite | 1.43 ± 0.16              | 8.77 ± 0.99     | 38.08 ± 6.53    | 51.73 ± 7.36     | 52.56 ± 10.46         | 3.64 ± 0.57     | 1.18 ± 0.23     | 3.41 ± 0.70     | 21.89 ± 4.05                   |
| #5 (N = 6)   | Anthracite | 2.74 ± 0.21              | 9.10 ± 0.78     | 31.72 ± 5.65    | 56.43 ± 6.17     | 57.99 ± 2.94          | 2.90 ± 0.12     | 0.94 ± 0.06     | 2.73 ± 0.18     | 22.86 ± 1.12                   |
| Min-Max      |            | 0.66–9.06                | 8.77–18.77      | 30.68–45.15     | 29.47–56.43      | 41.86–62.38           | 2.90–3.64       | 0.82–1.18       | 0.29–3.41       | 17.03–24.47                    |
| Mean ± SD    |            | 2.98 ± 3.11              | 14.55 ± 4.53    | 38.19 ± 6.03    | 44.29 ± 10.77    | 52.21 ± 7.35          | 3.16 ± 0.27     | 0.95 ± 0.14     | 1.67 ± 1.36     | 21.05 ± 2.65                   |

Note: M, moisture; V, volatile; A, ash; FC, fixed carbon; C, carbon; H, hydrogen; N, nitrogen; S, sulfur; Q<sub>net</sub>, net heat value; subscript “ad”, air-dried basis.

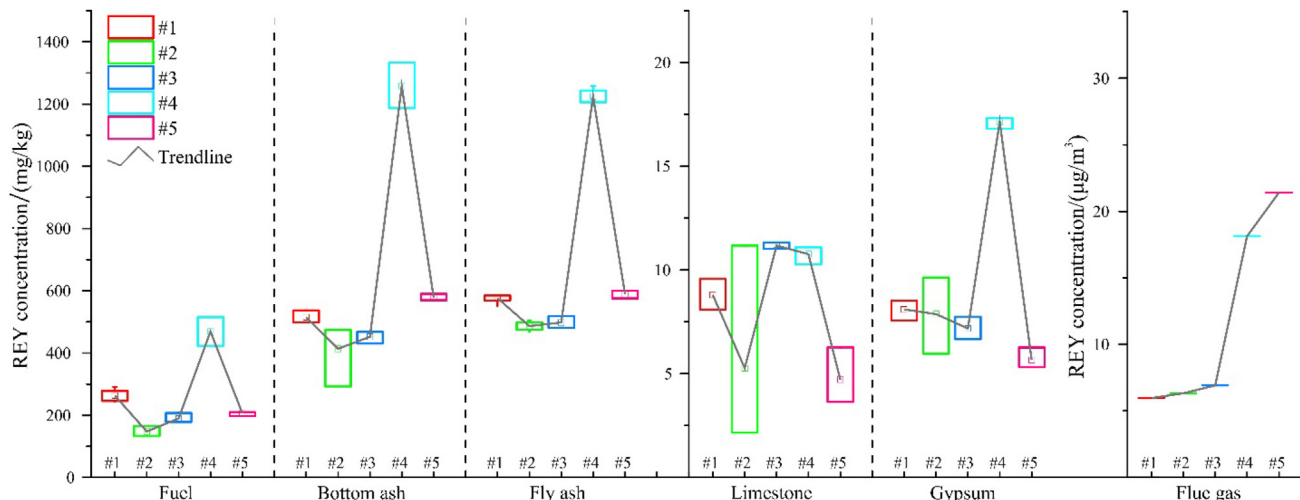


Fig. 3. Comparison of total REY contents in solid samples and flue gas from the five CFPPs.

value (lower by 17.03–19.29 MJ/kg). In addition, lower volatile matter (by 8.77%–9.10%) in feed fuel is observed from CFPPs #4–#5, and the sulfur content (2.50%–3.41%) from CFPPs #3–#5 is higher than that from the other CFPPs. The calorific values of feed fuel in the five CFPPs are in the range of 17.03–24.47 (average 21.05) MJ/kg, belonging to the low to medium range of known values for coals in China.<sup>28</sup> Feed fuels in CFPPs #1–#2 and CFPPs #3–#5 are classified as low-sulfur and medium-high sulfur coal,<sup>29</sup> respectively.

### 3.2. Partitioning patterns of REY among fuel and combustion products

REY concentrations in solid samples and stack flue gas are illustrated in Fig. 3 and Table S1. High REY concentrations are found for the feed coal (147–469 mg/kg, on the whole coal basis), bottom ash (413–1257 mg/kg), and fly ash (486–1225 mg/kg). Partitioning trends of REY among different solid samples in the five tested CFPPs are similar and the highest REY contents occurred in coal ( $469 \pm 46$  mg/kg), bottom ash ( $1257 \pm 60$  mg/kg), and fly ash ( $1225 \pm 23$  mg/kg) from CFPP #4 (Fig. 3), indicating that REY concentrations of bottom ash and fly ash are inherited from the characteristics of coal. REY content in bottom/fly ash of this study is much higher than that in European CFPPs (246–481 mg/kg,<sup>30</sup>) and slightly higher than that from South Africa (402–599 mg/kg,<sup>9</sup>). The high REY contents are also reported in CCPs of three CFPPs in Guizhou (e.g., two > 400 mg/kg, and one > 1000 mg/kg).<sup>31,32</sup> Coal

mines in Guizhou are mainly located in the west and northwest of the province (Fig. 1(a)), which covers the locations of CFPPs #1–#4. The REY contents of coal in Guizhou demonstrate a decreasing trend from north to south (Fig. 1(b), unpublished internal data), resulting in REY concentration in coals from CFPP #2, which is situated in the southernmost side, being only 147 mg/kg. In contrast, an average REY concentration of 469 mg/kg is found for coals from CFPP #4, located in the central–north area (Table S1). This suggests that combustion ashes derived from coal in the central to north part of Guizhou may represent a better REY resource than in other parts of Guizhou. This trend is confirmed by high REY (750 mg/kg) fly ash found in another CFPP in south Sichuan, which is located to the north of Guizhou.<sup>33</sup> REY in feed coals of all five investigated CFPPs exceeded the global average of 68.47 mg/kg and the average of Chinese coal (135.89 mg/kg).<sup>11,13</sup> During deposition, REY enriched sediments with strong adsorption capacity (e.g., clay, shale, and organic matter),<sup>34</sup> became incorporated with the accumulating peat and resulted in higher REY contents in coals with elevated ash and sulfur.

REY concentrations in limestone, gypsum, and flue gas are very low, with ranges of 4.7–11.2 mg/kg, 5.7–17.1 mg/kg, and 5.91–21.41  $\mu\text{g}/\text{m}^3$ , respectively. The influence of flue gas input to gypsum is somewhat discernible (Fig. 3). For example, the concentration of gypsum (17.1 mg/kg) from CFPP #4 increases compared with that in limestone (10.8 mg/kg) because the REY content in fly ash is the highest. In addition, the concentration of

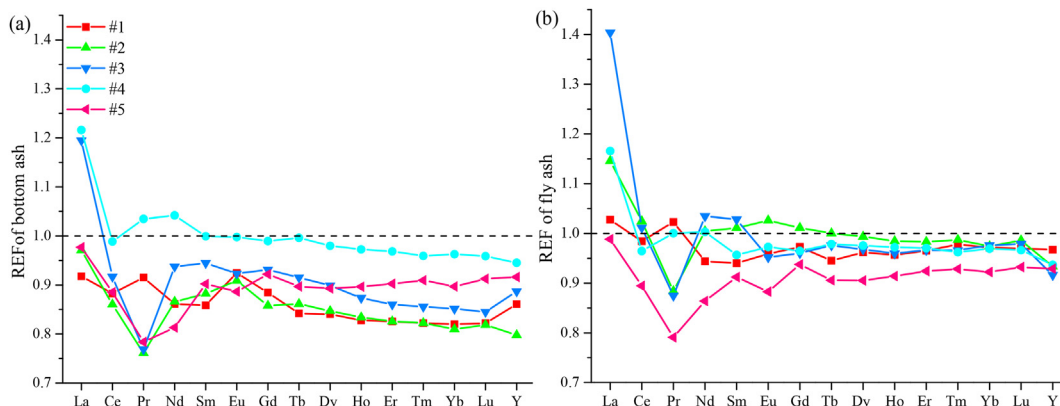


Fig. 4. The relative enrichment factor (REF) of REY in bottom ash (a) and fly ash (b) in the five CFPPs.



**Fig. 5.** REY distribution patterns in fuel (a), bottom ash (b), fly ash (c), limestone (d), and gypsum (e) from the five CFPPs (relative to REY in the upper continental crust (UCC)<sup>40</sup>). \* From Ketris and Yudovich<sup>11</sup>; \*\* From Dai et al.<sup>14</sup>; \*\*\* From Dai et al.<sup>13</sup>

flue gas is also higher than that of others except CFPP #5, because the PM content in CFPP #5 (36.4 mg/m<sup>3</sup>, Table S2) is 2.5–3.5 times higher than that of the others (10.3–14.8 mg/m<sup>3</sup>).

In order to reveal the REY enrichment in bottom ash and fly ash compared to the feed fuel, relative enrichment factor (REF)<sup>35</sup> was calculated as follows:

$$REF = \frac{REY_{ash} \times A_{ad}}{REY_{fuel}} \quad (1)$$

where REF is the relative enrichment factor, REY<sub>ash</sub> REY concentration in bottom or fly ash, A<sub>ad</sub> ash yield of feed fuel, and REY<sub>fuel</sub> REY concentration in feed fuel.

REY are regarded as non-volatile elements and are approximately evenly distributed in bottom ash and fly ash.<sup>35,36</sup> REF values of REY in bottom ash and fly ash of this study are in the range of 0.86–1.02 and 0.91–1.04, respectively (Fig. 4 and Table S3). However, slightly higher REF values are found in the fly ashes compared with the bottom ashes. For example, REFs of 0.98 for fly ash versus

0.88 for bottom ash occur at CFPP #1, 1.01 versus 0.86 are found at CFPP #2, and 1.04 versus 0.94 are found at CFPP #3. This indicates that a bit more REY are partitioned into fly ash than bottom ash. This redistribution may be due to the different affinity of combustion ash to REE that results from the particulate size, the ash constituents, and the encapsulated minerals in ashes.<sup>37–39</sup> In addition, the enrichment curve changes gradually from high levels of light rare earth elements (LREE, La–Eu) to low levels of heavy rare earth elements (HREE, Gd–Lu + Y), indicating that LREE, especially La, is more likely to fractionate into the combustion ashes during the combustion process (Fig. 4(a, b)).

According to the average concentration of REY in the upper continental crust (UCC),<sup>40</sup> the normalized REY distribution patterns are illustrated in Fig. 5. Slight enrichments of HREE are seen in most samples ( $La_N/Yb_N = 0.92 < 1$ ). The REY distribution pattern of coal from Guizhou is much different from that of Chinese coal and the world coal in terms of Tm (Fig. 5(a), Table S1). Although a distinctly positive Tm anomaly is observed in world and Chinese coal,<sup>13,14</sup> the coal from Guizhou does not reflect this, probably due to the low concentration (0.4–1.2 mg/kg) of Tm in the feed coal of this study (Table S1) and the associated analysis uncertainties. High ash yields (>43%) in gangue and coal slime from CFPP #1 (Table 2) are reflected by LREE enrichment (LREE/HREE = 8.29). For coal from CFPP #4, the extremely high REY concentrations with a positive Ce anomaly ( $Ce/Ce^* = 1.28$ ) and negative Eu anomaly ( $Eu/Eu^* = 0.52$ ) are more likely as a function of depositional environment, such as rock characteristics of the sediment source areas, gas-hydrothermal fluid from magmatic activity, and/or seawater.<sup>41</sup> The distribution patterns of REY in bottom ash (Fig. 5(b)) and fly ash (Fig. 5(c)) are similar to that of feed coal, particularly for CFPP #4. This is also seen in the global average REY in coal and the corresponding ash (Fig. 5(a, b, c)). Limestone and gypsum (Fig. 5(d, e)) have similar REY distributions with moderate Ce negative anomaly and significant Y positive anomaly, suggesting that most REY in WFGD gypsum are inherited from limestone. In addition, as the product of WFGD, gypsum is affected by the fly ash to a certain extent since the WFGD process captured some fly ash. For example, gypsum from CFPP #4, produced by the reaction of limestone and flue gas in WFGD, has more obviously enriched REY than that from the other CFPPs (Fig. 5(e)).

### 3.3. Mass balance and atmospheric emissions of REY

On the basis of the onsite monitoring information (Table S2) and REY concentrations in different materials, REY flows in input and output samples were calculated, as shown in Table S4. REY input and output are basically balanced in these five CFPPs, e.g., the ratio of output to input of REY is in the range of 90.31%–113.71% (Fig. 6). Feed coal accounts for the majority of input sources (>99.48%) because the consumption and REY concentration of feed coal are both higher than those of limestone. For the output materials, 84.02%–93.71% REY occur in fly ash and 5.73%–15.22% in bottom ash in CFPPs with PC boilers based on total output. The difference of REY concentrations between bottom and fly ash is not significant (Fig. 3, Table S1), but the yield of fly ash is much higher than that of bottom ash (Table S2), with the fly ash being the primary REY output in PC CFPPs. Due to the difference in combustion boiler (CFB) and fuel in CFPP #1 (gangue and coal slime), the increasing yield of bottom ash results in a decreased REY output ratio in the fly ash (68.87%). Being non-volatile elements, less than 0.08% (range: 0.01%–0.08%) of the REY are emitted with the stack flue gas in the studied CFPPs (Fig. 6). Only 0.13–0.50 kg/d REY are released into atmosphere from the five CFPPs (Table S4, #5: 0.50 kg/d > #3, #4: 0.28 kg/d > #2: 0.21 kg/d > #1: 0.13 kg/d).

Emissions factors (EMFs) of REY were calculated as follows:

$$EMF_1 = \frac{M_{REY}}{M_{coal}} \quad (2)$$

$$EMF_2 = \frac{M_{REY}}{P \times t} \quad (3)$$

$$EMF_3 = \frac{M_{REY}}{M_{coal} \times Q_{net,ad}} \quad (4)$$

where  $EMF_1$ ,  $EMF_2$ , and  $EMF_3$  are REY emission factors that are based on the fuel consumption, actual generation power and heat value of fuel, respectively;  $M_{REY}$  is the amount of REY emitted into the atmosphere per day (g/d);  $M_{coal}$  is the consumption of fuel (t/d, based on CFPP statistics);  $P$  is the actual power of tested power plant (on-line monitoring data);  $t$  is running time of a utility boiler (24 h/d);  $Q_{net,ad}$  is calorific value of fuel (MJ/kg).

Based on the above equations,  $EMF_1$ ,  $EMF_2$ , and  $EMF_3$  were estimated to be 38.70–180.11 mg REY/t coal, 24.06–79.37  $\mu$ g REY/(kW·h), and 2.18–7.88 g REY/TJ, respectively (Table S3). Note that REY released into the atmosphere not only settle down to the earth

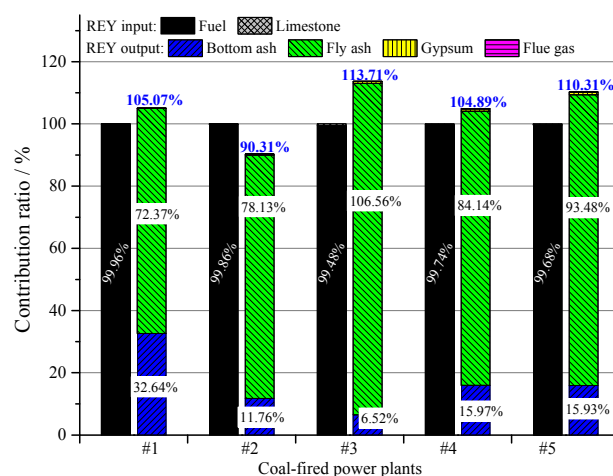


Fig. 6. Proportions of REY in input and output materials of five CFPPs (the output ratio is based on the total input).

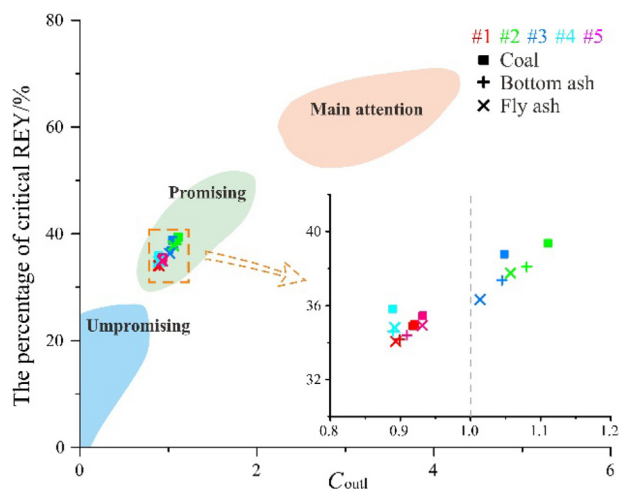


Fig. 7. Classification of REY-rich materials (coal, fly ash and bottom ash) by the outlook coefficient ( $C_{out}$ ) and the percentage of critical elements ( $REY_{def,rel}$ ), modified from Seredin and Dai<sup>18</sup> and Dai et al.<sup>41</sup>

surface nearby the CFPPs and contaminate nearby soil or water, but also can migrate for long distances with atmospheric circulation when existing in the form of fine particulate matter.<sup>20,23,42</sup>

### 3.4. Reclamation potentials of REY from CCPs

Coal has been regarded as a potential and promising supply of some REY,<sup>10,41,43</sup> especially bituminous and low-quality coal (such as gangue, coal slime, and stone coal) with higher mineral matter which concentrate trace elements.<sup>44,45</sup> After combustion, trace elements accumulate in the bottom ash and fly ash (Fig. 3, Table S1), enabling them to become prospective sources of REY.<sup>1,4–6,10,41</sup> According to the level of supply and demand from industry,<sup>46</sup> REY were divided into critical and potential critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu) groups (Table S5). The outlook coefficient ( $C_{out1}$ ), defined as the ratio of the relative amount of critical REY to the relative amount of excessive REY, for REY ores,<sup>8,46</sup> was also applied in the present study:

$$C_{out1} = \frac{(Nd + Eu + Tb + Dy + Er + Y / \sum REE)}{(Ce + Ho + Tm + Yb + Lu / \sum REE)} \quad (5)$$

The REY<sub>def,rel</sub> (the percentage of critical REY) vs.  $C_{out1}$  plot is an important evaluation of the economic significance for high-REY materials.<sup>8,41</sup> There was no significant change in the relative concentration of individual elements during the combustion because of the non-volatile properties of REY.<sup>35</sup> Critical REY accounted for 34.06%–39.37% of the total REY, with  $C_{out1}$  being in the range of 0.89–1.11 (Fig. 7; Table S5). On the basis of REY classification plot,<sup>8,41</sup> all REY-rich materials (coal, bottom ash, and fly ash) in this study belong to the promising REY raw materials.

Compared with the REY deposits formed in nature, recycling REY-rich ash may save significant amount of cost from mining and beneficiation processes. Seredin and Dai<sup>8</sup> reported the reasonable cut-off grade of REO (oxides of REY, sum of La<sub>2</sub>O<sub>3</sub> to Lu<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub>) in fly ash to be 1000 mg/kg. It is worth noting that the REY concentration of bottom/fly ash in this study was up to 1250 mg/kg (Table S1). Extracting REY from REY-rich materials is still in the experimental stage. In the nature, it was found that silicate and aluminosilicate are the dominant REY carrying minerals, accounting for 80% of different kinds of REY-rich materials, followed by carbonates and sulphates.<sup>32,41,47,48</sup> King et al.<sup>49</sup> compared the effect of aqueous acid and alkaline leaching on different types of fly ash and reported that the composition of fly ash had a decisive influence on the extraction efficiencies, and using the most appropriate leaching method could increase the recovery to 85%–100%. Taggart et al.<sup>1</sup> used heated nitric acid to digest fly ash and gained a recovery efficiency of 70%. REY extraction efficiencies as high as 88.15% had been achieved by HCl leaching of desilicated fly ash.<sup>33</sup> Therefore, REY-rich CCPs are potential candidates for REY production, should technology development for REY recovery become economically feasible. In addition, reasonable recycling of REY-rich CCPs will also benefit air quality through reducing pollutant emissions, such as secondary mercury release from fly ash in CFPPs and cement plants.<sup>50</sup>

## 4. Conclusions

Materials (feed fuel, bottom ash and fly ash, limestone, gypsum, and stack flue gas) were sampled from five coal-fired power plants in Southwest China, and REY concentrations and atmospheric emissions were characterized. The following conclusions were obtained:

- (1) REY concentrations differ little between bottom ash and fly ash of the coal combustion, and the total amount of REY from these products account for > 99.18% of REY in total output during the combustion and flue gas treatment process. REY concentrations are higher in this study than previously reported worldwide.
- (2) The ratio of REY output to input in the five CFPPs is in the range of 90.31%–113.71%. Extremely low emissions of REY (<0.08%, 0.13–0.50 kg REY/d) are identified from the stack flue gas. Consequently, MEFs are as low as 38.70–180.11 mg REY/t coal, 24.06–79.37 μg REY/(kW·h), or 2.18–7.88 g REY/TJ.
- (3) The outlook coefficient ( $C_{out1}$ ) of REY reclamation is in the range of 0.89–1.11. Recycling REY from REY-rich CCPs (bottom and fly ash), especially in the central–north Guizhou province, can create industrial and economic values, noting that extraction technology still faces many difficulties in large-scale industrial production.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jre.2019.12.013>.

## References

1. Taggart RK, Hower JC, Dwyer GS, Hsu-Kim H. Trends in the rare earth element content of U.S.-based coal combustion fly ashes. *Environ Sci Technol*. 2016;50(11):5919.
2. U.S. Geological Survey. *Mineral commodity summaries*. Reston, Virginia; 2018, 2018 <https://pubs.er.usgs.gov/publication/70194932>. Accessed February 26, 2019.
3. Chelgani CS, Hower JC. Estimating REY content of eastern Kentucky coal samples based on their associated ash elements. *J Rare Earths*. 2018;36(11):1234.
4. Dai SF, Finkelman RB. Coal as a promising source of critical elements: progress and future prospects. *Int J Coal Geol*. 2018;186:155.
5. Hower JC, Groppeo JG, Henke KR, Hood MM, Eble CF, Honaker RQ, et al. Notes on the potential for the concentration of rare earth elements and yttrium in coal combustion fly ash. *Mineral*. 2015;5(2):356.
6. Huang ZX, Fan MH, Tian HJ. Coal and coal byproducts: a large and developable unconventional resource for critical materials–Rare earth elements. *J Rare Earths*. 2018;36(4):337.
7. Kuppusamy VK, Holuszko M. Rare earth elements in flotation products of coals from East Kootenay coalfields. *J Rare Earths*. 2019;37(12):1366.
8. Seredin VV, Dai SF. Coal deposits as potential alternative sources for lanthanides and yttrium. *Int J Coal Geol*. 2012;94:67.
9. Wagner NJ, Matiane A. Rare earth elements in select Main Karoo Basin (South Africa) coal and coal ash samples. *Int J Coal Geol*. 2018;196:82.
10. Yang X, Werner J, Honaker RQ. Leaching of rare Earth elements from an Illinois basin coal source. *J Rare Earths*. 2019;37(3):312.
11. Ketriss MP, Yudovich YE. Estimations of Clarks for Carbonaceous biolithes: world averages for trace element contents in black shales and coals. *Int J Coal Geol*. 2009;78(2):135.
12. Lin RH, Soong Y, Granite EJ. Evaluation of trace elements in U.S. coals using the USGS COALQUAL database version 3.0. Part I: rare earth elements and yttrium (REY). *Int J Coal Geol*. 2018;192:1.
13. Dai SF, Ren DY, Chou C-L, Finkelman RB, Seredin VV, Zhou YP. Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. *Int J Coal Geol*. 2012;94:3.
14. Dai SF, Ren DY, Tang YG, Yue M, Hao LM. Concentration and distribution of elements in late permian coals from western Guizhou province, China. *Int J Coal Geol*. 2005;61(1–2):119.
15. World Coal Association. <https://www.worldcoal.org/coal/uses-coal/coal-electricity>; 2019. Accessed February 27, 2019.
16. National Bureau of Statistic of China. *China statistical yearbook*. China Statistics Press; 2018 (in Chin.).
17. Bureau of statistics of Guizhou province. *Guizhou statistical yearbook*. China Statistics Press; 2018 (In Chin.).
18. Chen CL, Fang KH, Zhao ZH, Ye W. *Study on quality and comprehensive utilization of fly ash in Guizhou province*. 4. Fly Ash Comprehensive Utilization; 2012:22 (In Chin.).
19. The National Development and Reform Commission of China. *Annual report on comprehensive utilization of resources in China*. 2014 (in Chin.).
20. Sun GY, Li ZG, Liu T, Chen J, Wu TT, Feng XB. Rare earth elements in street dust and associated health risk in a municipal industrial base of central China. *Environ Geochem Health*. 2017;39(6):1469.
21. Zhao ZH, Zhu SD. Study for development on coal resources in Guizhou province. *China Min Mag (Zhong Guo Kuang Ye)*. 2006;15(3):17 (in Chin.).

22. USEPA. *Test Method 5. Determination of particulate matter emissions from stationary sources*. 1996.
23. Chen D, Liu XW, Han JK, Jiang M, Xu YS, Xu MH. Measurements of particulate matter concentration by the light scattering method: optimization of the detection angle. *Fuel Process Technol.* 2018;179:124.
24. GB/T 212-. *Proximate analysis of coal*. Beijing: Issued by the Chinese General Administration of Quality Supervision, Inspection and Quarantine and the Standardization Administration of China; 2008 (in Chin.).
25. GB/T 214-. *Determination of total sulfur in coal*. Beijing: Issued by the Chinese General Administration of Quality Supervision, Inspection and Quarantine and the Standardization Administration of China; 2007 (in Chin.).
26. GB/T 213-. *Determination of calorific value of coal*. Beijing: Issued by the Chinese General Administration of Quality Supervision, Inspection and Quarantine and the Standardization Administration of China; 2008 (in Chin.).
27. Qi L, Grégoire DC. Determination of trace elements in twenty six Chinese geochemistry reference materials by inductively coupled plasma mass Spectrometry. *Geostand Geoanal Res.* 2000;24(1):51.
28. GB 15224.3-. *Classification for quality of coal-Part 3: calorific value*. Issued by the Chinese general administration of quality supervision, inspection and quarantine and the standardization administration of China. Beijing. 2010 (in Chin.).
29. GB 15224.2-. *Classification for quality of coal-Part 2: sulfur content*. Beijing: Issued by the Chinese General Administration of Quality Supervision, Inspection and Quarantine and the Standardization Administration of China; 2010 (in Chin.).
30. Blissett RS, Smalley N, Rowson NA. An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. *Fuel.* 2014;119:236.
31. Huang C, Wang YB, Huang B, Dong YM, Sun XQ. The recovery of rare earth elements from coal combustion products by ionic liquids. *Miner Eng.* 2019;130:142.
32. Pan JH, Zhou CC, Tang MC, Cao SS, Liu C, Zhang NN, et al. Study on the modes of occurrence of rare earth elements in coal fly ash by statistics and a sequential chemical extraction procedure. *Fuel.* 2019;237:555.
33. Wang Z, Dai SF, Zou JH, Frenc D, Graham IT. Rare earth elements and yttrium in coal ash from the Luzhou power plant in Sichuan, Southwest China: concentration, characterization and optimized extraction. *Int J Coal Geol.* 2019;203:1.
34. White WM. *Geochemistry*. John Wiley & Sons, Ltd.; 2013:275.
35. Meij R. Trace elements behavior in coal-fired power plants. *Fuel Process Technol.* 1994;39:199.
36. Clarke LB, Sloss LL. *Trace elements-emissions from coal combustion and gasification*. London: IEA Coal Research; 1992.
37. Hower JC, Groppo JG, Henke KR, Graham UM, Hood MM, Joshi P, et al. Poned and landfilled fly ash as a source of rare earth element from a Kentucky power plant. *Coal Combust Gasif Prod.* 2017;9:1.
38. Liu JJ, Dai SF, He X, Hower JC, Sakulpitakphon T. Size-dependent variations in fly ash trace element chemistry: examples from a Kentucky power plant and with emphasis on rare earth elements. *Energy Fuels.* 2017;31(1):438.
39. Xu MH, Yan R, Zheng CG, Qiao Y, Han J, Sheng CD. Status of trace element emission in a coal combustion process: a review. *Fuel Process Technol.* 2004;85(2–3):215.
40. Taylor SR, McLennan SM. *The continental crust: its composition and evolution*. London: Blackwell; 1985.
41. Dai SF, Yan XY, Ward CR, Hower JC, Zhao L, Wang XB, et al. Valuable elements in Chinese coals: a review. *Int Geol Rev.* 2016;60(5–6):590.
42. Wang CX, Zhu W, Peng A, Guichreit R. Comparative studies on the concentration of rare earth elements and heavy metals in the atmospheric particulate matter in Beijing, China, and in Delft, The Netherlands. *Environ Int.* 2001;26(5–6):309.
43. Bartonova L, Serencisova J, Cech B. Yttrium partitioning and associations in coal-combustion ashes prior to and after their leaching in HCl. *Fuel Process Technol.* 2018;173:205.
44. Luo KL. Arsenic and fluorine contents and distribution patterns of early paleozoic stonelike coal in the Daba Fold Zone and Yangtze Plate, China. *Energy Fuels.* 2011;25(10):4479.
45. Li ZG, Li XY, Liu JL, Zhang LM, Chen J, Feng XB. Stone coal as a potential atmospheric mercury source in Da-Ba-Shan mountain areas, China. *Int J Coal Geol.* 2019;206:21.
46. Seredin VV. A new method for primary evaluation of the outlook for rare earth element ores. *Geol of Ore Deposits.* 2010;52(5):428.
47. Folgueras MB, Alonso M, Fernandez FJ. Coal and sewage sludge ashes as sources of rare earth elements. *Fuel.* 2017;192:128.
48. Kolker A, Scott C, Hower JC, Vazquez JA, Lopano CL, Dai SF. Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe. *Int J Coal Geol.* 2017;184:1.
49. King JF, Taggart RK, Smith RC, Hower JC, Hsu-Kim H. Aqueous acid and alkaline extraction of rare earth elements from coal combustion ash. *Int J Coal Geol.* 2018;195:75.
50. Li XY, Li ZG, Wu TT, Chen J, Fu CC, Zhang LM, et al. Atmospheric mercury emissions from two pre-calciner cement plants in Southwest China. *Atmos Environ.* 2019;199:177.