J Radioanal Nucl Chem (2017) 311:1235–1241
DOI 10.1007/s10967-016-5026-8

A Brazilian coal fly ash as a potential source of rare earth elements

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Received: 14 June 2016 / Published online: 3 September 2016

Abstract Rare earth elements (REEs) have several applications and their market demands have increased. Recently, coal fly ash (CFA) has been considered as a source of these elements. The purpose of this study was to evaluate the REEs content in a CFA from a Brazilian coal power plant by instrumental neutron analysis, to classify it according to commercial purposes and to assess the weathering impact in the REEs content, since it is held in fields nearby the power plant. The results pointed no significant REEs leachability and indicated this CFA as a promising REEs source.

Keywords Brazilian coal fly ash · Rare earth elements · Neutron activation analysis · Raw material

Introduction

Rare earth elements (REEs) are present in our daily life in many technological applications from electronic displays to green energy technologies. Nowadays, REEs supply has faced off some challenges. China is the main supplier of REEs in the world, controlling more than 90 % of rare earth elements market. Since 2009, Chinese government has imposed some export restrictions [1, 2]. In this context, prospection of new mineral deposits and the reopen of old mines have been considered. As an alternative, many countries have intensified a pursuit for new ores, industrial wastes or post-consumer materials with considerable REEs content to be used as secondary raw materials [3–5].

Recently, coal fly ash (CFA) has been considered a source of REEs and the offspring of this new use of this industrial waste has intensified the number of studies on determination of REEs content aiming their extraction [6–11].

CFA worldwide production is estimated on 415–600 million ton annually and is considered as an environmental concern [12]. In Brazil, only fifty percent of coal ashes generated are reutilized [13].

On the last couple of years, Brazilian southeast region has faced a serious drought and hydroelectricity is the main source of power in this region of the country [14]. Because of that, coal power plants have been operating in their maximum capacity and have enhanced the production of CFA reaching around 3 million ton per year [15]. Several studies on its reutilization have been conducted [16–20] but, so far, none considering Brazilian CFA as a possible source of REEs. The aim of this study was to perform a preliminary estimative of the potential use of Figueira power plant CFA as a source of REEs based on the approach adopted by Seredin and Dai [6]. These authors suggested the evaluation of coal and coal ashes as lanthanides and yttrium (REY) raw material based on current market trends of individual REY. They have divided the REEs into critical (Nd, Eu, Tb, Dy, Y and Er), uncritical (La, Pr, Sm and Gd) and excessive (Ce, Ho, Tm, Yb and Lu) and proposed a proportion of the critical and excessive elements (critical/excessive) denominated as "outlook index". Besides that, a long-term column leaching experiment simulating a slight acid rain was performed to evaluate the weathering impact on some REEs content in CFA, since ashes are usually stored in uncovered fields on the power plant vicinity.

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Experimental

Coal fly ash sampling and preparation

Three CFA samples were collected from bag filters from the Figueira Coal Power Plant (CPP) of Paraná State, Brazil (Fig. 1), during 6 months. At every 2 months, 1 kg of CFA was collected. The samples were mixed and homogenized. Sampling procedure and sample preparation were described previously [21].

Leaching experiment

Fifty grams of CFA were packed into acrylic columns (inner diameter of 8 cm) and supported by a 5 cm layer of inert sand or soil. The CFA columns were leached with a dilute solution composed of HNO_3 and H_2SO_4 (pH 4.5) in order to simulate an acid rain over 336 days. The solution volume (6.3 L) used was based on monthly rainfall data from 1933 to 2008 for the city of São Paulo [22]. The experiment was conducted on 10 replicates.

Sample preparation for rare earth elements determination

The particle size of the CFA was measured using a laser based particle size analyzer, namely a Malvern MSS Mastersizer 2000 Ver. 5.54 and the result indicated that the majority of particles (90 %) lies below 62.6 µm. Based on these results, no sieving was performed CFA to INAA sample preparation. Non-leached (NL) samples and leached samples were separately homogenized and oven dried at 40 °C for 48 h. Nearly 50 mg for short irradiation and 100 mg for long radiation of powdered samples and the Polish reference certified material fine fly ash (ICHTJ-CTA-FFA-1) were accurately weighted in polyethylene bags. Aliquots of 50 µL of a rare earth multi-element solution (SPEX CMLS-1) were transferred to small sheets of analytical filter paper (Whatmann No. 42). After drying, these papers were placed onto polyethylene bags and wrapped in aluminum foil. The La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb and Lu content was analyzed in the ashes before and after leaching.

Elemental determination by instrumental neutron activation analysis (INAA)

For INAA, two types of irradiation, using two separate subsamples, were carried out at the IEA-R1 nuclear research reactor, one for long-lived isotopes and the other for short. First, samples and standards (ICHTJ-CTA-FFA-1 and SPEX-CMLS-1) were irradiated during 8 h, approximately, at a thermal neutron flux of 3.5–5 10^{12} n cm^{-2} s^{-1} for La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb and Lu determination. Uranium content was also measured to evaluate interference of fission products, such as La and Ce. The counting was divided in three series: the first one 7 days after irradiation, the second one 15 days after irradiation, and the third one after 2 months. The counting times varied from 1 to 2.5 h. The interference of ^{153}Gd in the determination of ^{153}Sm was evaluated by calculating the ratio of the 103.2 keV and the 94.5 keV peak of ^{153}Gd. The contribution of ^{153}Gd in the peak of 103.2 keV of ^{153}Sm was negligible (less than 1 %), under the irradiation and counting conditions employed. In the second irradiation, samples and standards were irradiated during 15 s. After a decay time of 10 min, approximately, Dy was measured, and the counting times varied from 5 to 15 min. The elements Er, Pr and Ho were not detected, even measuring few hours after the short irradiation. The induced gamma-ray activity was measured in a gamma-ray spectrometer consisting of a Ge-hyperpure detector and analysed by

Fig. 1 Location of Figueira–Paraná coal power plant (CPP), Brazil

CANBERRA S-100 system software. The detector used had a resolution (FWHM) of 1.9 keV for 1332 keV gamma rays of ^{60}Co.

Data quality control

For the statistical accuracy evaluation, the E_n-number [23] was used. The En-number is defined by the Eq. (1):

$$E_n = \frac{X_{\text{Lab}} - X_{\text{Cert}}}{\sqrt{{U_{\text{Lab}}}^2 + {U_{\text{Cert}}}^2}} \quad (1)$$

where the numerator gives the absolute difference between the experimental result (X_{Lab}) and the assigned value (X_{Cert}) of elemental concentration, and U_{Cert} and U_{Lab} are the expanded uncertainties ($k = 2$) of the recommended assigned and experimental mass fraction, respectively. Table 1 presents the analytical results of three replicates as well as the assigned values with confidence level of 95 %, considering the certified reference material ICHTJ-CTA-FFA-1. All the calculated E_n-number were below 1, showing that the results were satisfactory within 95 % confidence level.

Uranium fission products interference correction

Uranium concentration in the CFA samples was measured and the mean obtained was 332 ± 15 µg g^{-1}. This high content of U may cause a super estimative on ^{140}La, ^{141}Ce, ^{143}Ce, ^{147}Nd and ^{153}Sm contents because of uranium fission products interference [24, 25]. Ribeiro et al. [25] recently evaluated these interference factors in U rich samples at the IEA-R1 reactor and the factors obtained (in µg of element/µg of U) by these authors were applied in the present study, as it was performed in the same reactor and the irradiation and counting conditions were similar. The interference factors used were as following: (0.0021 ± 0.0001) for ^{140}La for a decay time equal to 168 h, (0.250 ± 0.006) for ^{141}Ce, (0.187 ± 0.018) for ^{147}Nd and (0.0521 ± 0.0003) for ^{153}Sm. In each sample, the lanthanide concentration due to the uranium fission was calculated using the mentioned factors and the obtained value was subtracted from the lanthanide concentration determined.

Table 1 Concentration of Ce, Dy, Eu, Gd, La, Lu, Nd, Sm, Tb, Tm and Yb in the certified reference material ICHTJ-CTA-FFA-1 (µg g^{-1}) and E_n-number

Element	This study	Values of the certificate	E_n-number
Ce	121 ± 7	120 ± 7	0.05
Dy	8.4 ± 0.8	9.09 ± 1.45	0.32
Eu	2.31 ± 0.09	2.39 ± 0.06	0.42
Gd	9.2 ± 1.8	10.6 ± 2.6	0.21
La	57 ± 3	60.7 ± 4.0	0.45
Lu	0.63 ± 0.06	0.658 ± 0.043	0.22
Nd	59 ± 7	56.8 ± 3.7	0.15
Sm	10.4 ± 0.8	10.9 ± 0.6	0.29
Tb	1.25 ± 0.15	1.38 ± 0.14	0.39
Tm	1.04 ± 0.18	0.705 ± 0.200	0.80
Yb	3.7 ± 0.9	4.24 ± 0.19	0.30

Results and discussion

Leachability of La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm and Lu

Table 2 presents the analytical results of some REEs content in CFA before and after leaching. The associated uncertainty is the standard deviation of the correspondent replicates.

For a statistical evaluation of REEs concentration variation in the ashes, before and after leaching, the ANOVA single factor analysis was applied. The results indicated no statistical difference between REEs concentration before and after leaching at 95 % confidence level. This apparently reflects the fact that REEs in CFA are usually associated with the glass phase and, in a less proportion, with the ferromagnetic fraction, so few REEs leachability was expected. Other authors [26–28] also verified a very low REEs leachability in an open system experiment in coal fly ashes from other power plants located at the South of Brazil.

REEs total concentration in Figueira CFA

Table 3 presents the concentration of REEs measured by INAA for Figueira CFA. As there were no statistical differences between CFA before and after leaching, the reported value is an average of all the analyzed replicates (16) and the uncertainty is their standard deviation. The same table presents REEs content reported in two other studies in Figueira CFA [29, 30], as well as in CFA from two other coal power stations in southern Brazil (Jorge Lacerda-SC and Candiota-RS) [27, 28] and also the world coal ash mean [31].

REEs total concentration in Figueira CFA detected in the present study was distributed in the following order: Ce > La > Nd > Dy > Gd > Sm > Yb > Lu > Eu > Tb > Tm. As reported previously [29, 30] to Figueira CFA, a similar distribution was observed for Ce, La, Nd, Dy, Gd, Sm and Yb with some variation in Lu, Eu, Tb and Tm distribution. Although the sampling period and batches of Figueira CFA analysed were not the same, comparing the results of this study with the mentioned ones (Table 3), the sum of the measured REEs contents reported was similar, since 541 ± 32 µg g^{-1} was determined and the

Table 2 Concentration of Ce, Dy, Eu, Gd, La, Lu, Nd, Sm, Tb, Tm and Yb obtained in the Non Leached CFA and Leached CFA after 336 days slightly acid leaching

Element	Non Leached CFA (*n* = 10) (μg g^{-1})	Leached CFA(n = 10)
La		
Mean	116 ± 4	119 ± 5
Median	115	120
Range	112–122	110–125
Ce		
Mean	206 ± 17	207 ± 17
Median	208	209
Range	197–216	197–216
Nd		
Mean	112 ± 30	130 ± 33
Median	100	127
Range	89–166	93–181
Sm		
Mean	15.9 ± 2.4	17.8 ± 1.1
Median	16.8	18.0
Range	12.8–18.1	16.2–19.4
Eu		
Mean	4.35 ± 0.20	4.31 ± 0.11
Median	4.35	4.30
Range	4.05–4.60	4.11–4.50
Gd		
Mean	23.1 ± 3.8	22.5 ± 3.8
Median	22.8	22.9
Range	21.0–25.5	20.7–23.4
Tb		
Mean	4.02 ± 0.50	4.00 ± 0.40
Median	4.00	3.95
Range	3.60–4.40	3.40–4.60
Dy		
Mean	25.1 ± 2.3	26.3 ± 1.8
Median	26.2	26.3
Range	22.6–27.2	22.9–28.6
Tm		
Mean	2.05 ± 0.26	2.08 ± 0.27
Median	2.00	2.19
Range	1.85–2.22	1.65–2.54
Yb		
Mean	11.8 ± 1.6	12.4 ± 1.5
Median	11.4	12.0
Range	10.3–13.8	10.7–14.7
Lu		
Mean	4.49 ± 0.20	4.48 ± 0.21
Median	4.45	4.50
Range	4.31–4.80	4.20–4.80

n Number of replicates

mean value reported by those authors ranged from 517 to 582 μg g^{-1}. Figueira CFA presented the highest measured REEs content compared with Jorge Lacerda complex and Candiota CFAs. According to the selected data presented in Table 3, REEs content in south Brazil CPP CFA was distributed in the following order: Figueira Jorge Lacerda Complex Candiota. REEs content of Candiota CFA was lower than the world coal range and Jorge Lacerda and Figueira CFAs presented higher REEs content. The REEs content in the present study was 1.7 higher than world coal ashes.

REEs distribution in Figueira CFA

In Fig. 2, concentration of the studied elements in Figueira CFA were normalized to upper continental crust (UCC) according to Taylor and McLennan [32].

The light REEs (LREE), which includes La, Ce, Nd and Sm, have shown similar pattern in UCC normalized curve, their average varying from 3.2 to 4.8 higher than the average of the earths crust. Higher ratios were observed for medium REEs (MREE), Eu, Gd, Tb and Dy, with values ranging from 4.9 to 7.4 and for HREE (heavy REEs), such as Tm, Yb and Lu, whose values observed ranged from 5.5 to 14.0. As mentioned previously, the coal used in Figueira CPP is U-rich type and it also presents high pyrite content (7 %) [33–35]. According to Dai et al. [9], this type of coal may presents positive Eu anomalies and HREE+Y and MREE+Y enrichment. Eu positive anomalies in coal can be estimated by Eq. (2), suggested by Bau and Duski [36]:

$$Eu_N/Eu_N* = Eu_N/[(Sm_N \times 0.67) + (Tb_N \times 0.33)] \quad (2)$$

where Eu_N, Sm_N and Tb_N are the ratio of each element concentration in the investigated samples versus their concentration in the UCC. Eu_N/Eu_N* ratio is commonly used to quantify decoupling of Eu from the other REE + Y (REY), and produces Eu anomalies (positive or negative) in REY distribution [9]. The average of Eu_N/Eu_N* obtained for CFA sample in this present study was 1.06, which indicates Eu positive anomaly. Distribution for Figueira CFA is an H-type (LaN/LuN < 1) according to Seredin and Dai [6] typical of REY-rich coal ashes.

Figueira CFA as REEs raw material estimative

According to Seredin and Dai criterion [6], for a preliminary estimation, the cut-off grade of REY (REE + Y) in coal combustion products for beneficial recovery expressed in REO (rare earth oxides) is ≥1000 μg g^{-1} (0.1 %), or ≥800–900 μg g^{-1} for coal seams more than 5 m in

Table 3 Concentration of Ce, Dy, Eu, Gd, La, Lu, Nd, Sm, Tb, Tm and Yb obtained in the Figueira CFA sample compared with other CFA samples in μg g^{-1}

Element	Figueira			Jorge Lacerda [28][b]	Candiota [27]	World Coal Ash [31]
	This Study	Bentlin [29]	Campaner [30]			
La	118 ± 5	121 ± 1	102 ± 6.47	70.5 ± 4.1	52.7	69
Ce	207 ± 17	238 ± 2	203 ± 5.17	185.9 ± 10.8	113.3	130
Nd	123 ± 16	114 ± 1	98.8 ± 6.66	76.21 ± 4.13	55.2	67
Sm	17.1 ± 1.9	25.0 ± 0.52	23.5 ± 2.96	16.2 ± 0.9	9	13
Eu	4.32 ± 0.14	6.29 ± 0.32	5.7 ± 0.83	2.2 ± 0.2	–[a]	2.5
Gd	22.7 ± 3.8	28.1 ± 1.7	29.7 ± 4.77	16.1 ± 0.9	12.1	16
Tb	4.01 ± 0.39	<0.009	–[a]	2.2 ± 0.2	1.8	2.1
Dy	25.9 ± 2.0	27.6 ± 0.3	36.6 ± 7.01	12.7 ± 1.1	10.5	14
Tm	2.07 ± 0.27	4.39 ± 0.08	–[a]	1.3 ± 0.1	0.74	2
Yb	12.2 ± 1.5	15.7 ± 0.1	17.6 ± 2.87	7.6 ± 0.7	6.3	6.2
Lu	4.48 ± 0.20	2.35 ± 0.03	–	1.3 ± 0.1	1.3	1.2
Sum	541 ± 32	582	517	392	263	323

[a] Not reported by authors

[b] Arithmetic mean of reported results

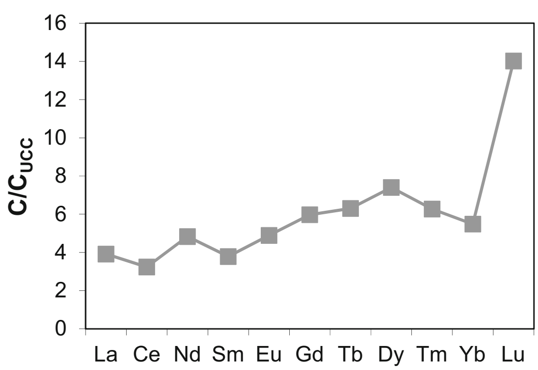

Fig. 2 Rare earth elements normalized to the upper continental crust [32]

thickness. In the same study, these authors have reported coal and coal ashes from specific places in China, Russia and Tajikistan with REO content up to 2.03 %, but the average are mostly between 0.1 and 0.2 %. Some authors [8, 10] have reported total REO between 297 and 579 μg g^{-1} in CFA from Poland and UK. Blissett et al. [8] highlighted CFA as derived samples from industrial processes without costs of mining and exploration associated and suggested further work to access the easy REEs extraction which might reduce the cut-off grade value. Figueira CPP uses coal extracted from the Cambuí mine, where coal seam occurs at 40 m depth subdivided in a lower seam (40 cm thickness) and upper seam (20 cm) [35]. In this study Ce, Dy, Eu, Gd, La, Lu, Nd, Sm, Tb, Tm and Yb content was measured and total REO obtained was 643 ± 37 μg g^{-1}. REEs assessment in Figueira CFA is scarce. Bentlin [29] had measured the lanthanides content in Figueira CFA samples by inductively coupled plasma optical emission spectrometry (ICP-OES), and by transforming this author data in REO, the obtained value was 723 μg g^{-1}, although Y content was also not available. Campaner [30] had measured the REEs Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm and Y content in Figueira CFA by inductively coupled plasma mass spectrometry (ICP-MS, and, by transforming the reported REY content determined by this author in total REO, the value obtained was 933 μg g^{-1}, but Tm, Tb and Lu content was not reported. Seredin and Dai [6] also proposed an index to evaluate the commercial viability of REEs extraction based on REEs content, applying Eq. 3:

$$C_{\text{outl}} = \left(\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y} \Big/ \sum \text{REY}\right) \Big/ (\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu} \Big/ \sum \text{REY}) \quad (3)$$

where C_{outl} is defined as "outlook index", the sum of (Nd + Eu + Tb + Dy + Er + Y) is defined as critical REY, the sum of (Ce + Ho + Tm + Yb + Lu) is defined as excessive REY and $\sum$REY is defined as the sum of all lanthanides +Y. As previously highlighted, the measured REEs concentration in Figueira CFA was similar to the concentration obtained by Bentlin [29] and Campaner [30]. For this reason, the values applied to calculate C_{outl} index, to estimate Figueira CFA as a REEs raw material, were divided as follows: the concentration of La, Ce, Dy, Eu, Gd, La, Lu, Nd, Sm, Tb, Tm and Yb showed on Table 3, performed by INAA, measured in this present study; the mean concentration data of Pr (<0.0012 μg g^{-1}), Ho (2.46 μg g^{-1}) and Er (23.5 μg g^{-1}) reported by Bentlin

[29] and Y (203 μg g^{-1}) as described by Campaner [30], Based on Seredin and Dai [6] evaluation of REY-rich coal fly ashes considering individual REY composition and not only the total REY by the C_{outl} index and critical elements (%), Figueira CFA, can be classified as a promising REEs raw material, since, according to these authors' evaluation, a promising CFA is defined as a CFA with a percentage of REY critical elements from 30 to 51 % and C_{outl} index from 0.7 to 1.9. The value of C_{outl} index obtained in this study was 1.7, the percentage of critical elements in total REY was 50 % and the total REO estimated was 922 μg g^{-1}.

Conclusions

In this paper, Figueira CPP coal fly ash REEs content was determined aiming to evaluate its commercial application. No leachability of the ashes with an acid dilute solution was verified indicating no weathering impact on REEs content in CFA. The main results of this study suggested that this fly ash can be considered a promising REEs source, considering its total REEs content and individual element concentration and distribution. The uranium content in this fly ash is also remarkable, about 120 times higher than UCC values [32], which may indicate this coal fly ash as a potential source also for uranium. Nevertheless, a more detailed study should be done to evaluate the commercial possibilities for uranium.

Modern society has a life style that depends on energy consumption and one of the most important challenges of XXI century is to supply the ascendant demand of energy with renewable sources and to reduce waste generation by not renewable sources. Coal is the worldś most abundant fossil fuel and one of drawbacks on its utilization is the production of ashes waste. The utilization of coal fly ashes as REEs source depends on several issues, as environmental hazards, workers safety, logistic, costs, applicability, extraction methods, particle size, recovery rate etc. Such issues are beyond the scope of this study, but are strongly recommended to be taken into account in future studies.

Acknowledgments The authors gratefully acknowledge the financial support from FAPESP (São Paulo Research Foundation). We are grateful to Cambui Coal Company (Companhia Carbonifera Cambui) for permission to carry out this project. The author C.N Lange thanks for the fellowship from the Brazilian Nuclear Energy Comission (CNEN).

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