Trace Elements in Coal, Coal Combustion Products and Soil from Coal-Fired Power Plant Area Evaluated By Neutron Activation Analysis

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Article Info

Abstract

The concentrations of trace elements were determined in coal, fly ashes from baghouse and cyclone filter, and bottom ash from the Figueira thermal power plant (FPP) by a neutron activation analysis technique. Study of the enrichment factor indicated that coal ashes were moderately enriched for all elements, except for Zn that exhibits significant to very-high enrichment. The mobilization of elements was observed in the zeolite products obtained from the three coal ashes. With regards to the amount present in each type of ash, most of the elements were present at same level in zeolites, with the exception of As which exhibited much lower concentration. The trace element concentrations of two soil samples collected in the vicinity of the FPP was also investigated. The results indicate that the FPP contributes mainly to the Zr and Ba pollution in nearby soils, particularly Zr pollution.

Keywords: Coal; Coal ashes; Zeolite; Soil; Trace elements; Neutron activation analysis

Introduction

The use of coal as an energy source and the impacts of the hazardous elements released from coal combustion have become a great concern to life preservation and sustainability. Despite the nature of non-renewable fuel and its potential for pollution, coal plays a vital role in electricity generation worldwide [1].

Trace elements are present in coal in either organic or inorganic association. During the combustion, the inorganic elements are usually enriched in the coal combustion products (CCPs) produced by coal-fired power plants due to the removal of organic material and water [2-5].

The quantity of trace elements in CCPs, in general, depends on the combustion conditions and the type of particulate control device used, and its collection efficiency as a function of particle size, the concentration of the element in the coal, the physical and chemical properties of the element itself, as well as, their mineralogical form [6-8].

Some of these CCPs can reach soils and plants by wet or dry deposition in the vicinity of the coal-fired power plant. Toxic elements in soils can enter the human body through the consumption of contaminated food crops or water or the inhalation of dust [9-11].

Brazilian coals are richer in ash (content of 20–50 wt.%) and poorer in carbon when compared to worldwide coal [12]. Only ~ 30% of fly ash is applied as raw material for cement production. The remaining solid wastes are disposed in landfills, in nearby abandoned or active mine sites. Consequently, the coal ash piles increase continuously, and this uncontrolled waste disposal site may lead to environmental contamination [13-14].

In a previous study, activity concentration of natural radionuclides in coal, coal combustion by-products, zeolitic material from ashes and soil samples collected in the vicinity of the Figueira coal-fired power plant was determined due to the radiological implication [15]. In this paper, the presence of inorganic trace elements in the same samples was also evaluated by neutron activation analysis.

Materials and Methods

Materials

All the reagents used for experimental studies were of analytical grade. The samples of coal, fly ash from baghouse filter (FB), fly ash from cyclone filter (FC), and bottom ash (BA) were collected at the Figueira coal-fired power plant (FPP) located in Paraná State, Brazil, following *ABNT NBR* 10007/87 [16]. Two deformed soil samples were collected using a hoe at a distance of 500 m from the coal fired power plant. Soil sample 1 (Soil-1) was in the center of a pasture area and Soil sample 2 (Soil-2) was near the Laranjinha river. The soil samples (10 kg) were collected at 30-cm depth, dried at room temperature for two weeks and stored in plastic bags for further analysis [17]. Physical and chemical characterizations of soil samples were *described previously [18]*.

Synthesis of Zeolites from Coal Ashes

The zeolites were prepared by hydrothermal activation of 20 g of coal ash at 100 °C in 160 ml of 3.5 mol L^{-1} NaOH solution for 24 h. The zeolitic materials were repeatedly washed with deionized water to remove excess sodium hydroxide until the washing water had pH ~ 10, then it was dried at 80 °C for 12 h. Zeolites synthesized were named: zeolite from bottom ash (ZBA), zeolite from fly ash from cyclone filter (ZFC), and zeolite from fly ash from baghouse filter (ZFB). A detailed characterization of the zeolites was described elsewhere [19].

Neutron Activation Analysis

Instrumental neutron activation analysis (INAA) was applied to

determine As, Br, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Sc, Se, Ta, Zn, Zr, and rare earth elements Ce, Eu, La, Lu, Nd, Sm, Tb, and Yb concentrations in samples. For this multi-elemental analysis, approximately 150 mg of samples and reference materials (NIST 1646a Estuarine Sediment and USGS STM-2 Table Mountain Syenite, and synthetic standards prepared by pipetting appropriate aliquots of standard solutions (SPEX CERTIPREP) onto small sheets of Whatman No. 41 filter paper) were accurately weighed and sealed in pre-cleaned double polyethylene bags for irradiation. Samples and reference materials were irradiated for 8 h in a thermal neutron flux of 10^{12} cm^{-2} s^{-1} in the IEA-R1 nuclear research reactor at IPEN (Instituto de Pesquisas Energéticas e Nucleares, Brazil). Counting was done at different time frames, depending on the radionuclide half-life produced during the irradiation. Gamma Spectrometry was performed by using an EG&G Ortec Ge Highpure Gamma Spectrometer detector (AMETEK Inc., USA) and associated electronics, with a resolution of 0.88 and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The analysis of the data was done by using an in-house gamma ray software, VISPECT program, to identify the gamma each energy transition.

The uncertainties of the results were calculated by error propagation. Methodology validation was performed by analyzing the same reference materials cited above. The results presented are mean values (mg kg^{-1}) for the duplicate and standard deviation for concentrations of elements. The relative standard deviations and relative errors were lower than 10% for most of the elements determined.

Results and Discussion

Concentration of T Elements in Coal and Coal Combustion Products

Table 1 shows the concentrations of trace elements in the feed coal and fly ash, cyclone ash and bottom ashes from FPP. The concentrations of elements As, Ba, and Zr are much higher than those of other elements for the coal. For ash samples, besides these elements, Zn also presented one of the highest concentrations.

Table 1: *Concentration of trace elements in coal and CCPs (mg Kg^{-1}).*

	Coal	BA[1]	FC[2]	FB[3]
As	129.82 ± 6.9	203.19 ± 7.93	289.44 ± 15.31	1298.28 ± 57.31
Ba	173.13 ± 34.37	1119.79 ± 145.42	732.02 ± 91.65	754.96 ± 104.02
Br	2.98 ± 0.26	0 ± 0	9.3 ± 0.69	0 ± 0
Ce	47.55 ± 1.63	139.52 ± 4.85	137.54 ± 4.62	133.04 ± 4.62
Co	6.05 ± 0.17	18.81 ± 0.51	23.57 ± 0.53	22.57 ± 0.62
Cr	35.15 ± 1.57	103.76 ± 5.3	92.77 ± 4.34	111.87 ± 5.63
Cs	2.64 ± 0.38	14.31 ± 13.36	9.24 ± 0.77	16.37 ± 15.33
Eu	0.96 ± 0.04	2.59 ± 0.08	2.72 ± 0.08	4.04 ± 0.15
Hf	2.99 ± 0.06	8.22 ± 0.22	10.34 ± 0.15	8.78 ± 0.24
La	22.54 ± 0.43	65.97 ± 1.78	70.94 ± 1.31	78.72 ± 2.13
Lu	0.48 ± 0.02	1.31 ± 0.07	1.36 ± 0.06	1.01 ± 0.05
Na	0.24 ± 0.01	0.65 ± 0.01	0.89 ± 0.02	0.91 ± 0.02
Nd	20.33 ± 1.7	79.42 ± 4.6	71.46 ± 3.45	57.71 ± 3.91
Rb	32.08 ± 2.41	110.22 ± 7.87	77.55 ± 5.16	76.19 ± 5.73
Sb	4.33 ± 0.42	7.18 ± 0.76	10.34 ± 1	32.31 ± 3.4
Sc	7.7 ± 0.06	21.18 ± 0.15	21.3 ± 0.15	30.73 ± 0.22
Sm	5.87 ± 0.23	17.35 ± 0.6	17.88 ± 0.69	24.69 ± 0.86
Ta	0.58 ± 0.08	0.96 ± 0.15	1.99 ± 0.27	1.03 ± 0.11
Tb	0.76 ± 0.17	1.89 ± 0.26	2.11 ± 0.26	3.35 ± 0.48
Th	6.9 ± 0.41	20.45 ± 1.17	19.75 ± 1.16	21.47 ± 1.23
U	17.64 ± 1.55	55.8 ± 3.1	70.81 ± 5.83	120.73 ± 12.44
Yb	3.07 ± 0.27	8.59 ± 0.83	7.51 ± 0.6	10.77 ± 0.9
Zn	46.93 ± 3.27	847.57 ± 38.28	1359.21 ± 62.28	4293.76 ±188.11
Zr	330.11 ± 66.99	504.1 ± 87.31	1275.71 ± 93.21	1736.96 ±282.78

(1) bottom ash; (2) fly ash from cyclone filter; (3) fly ash from baghouse filter

Overall, the elements that showed the highest concentrations were As, Ba, Zn and Zr. The high concentrations of As and Zn comes from the high occurrence of pyrite in the Paraná coal [20]. Coal can contain barium in concentrations of up to 3,000 mg kg^{-1} being that barite is the main form of occurrence [21]. The presence of zirconium in coal is predominantly controlled by REE-bearing trace phases such as $ZrSiO_4$ [22].

The contents of trace elements in ashes depend on several factors, such as, the concentration and the geochemical distribution of the elements in the coal, the combustion and pollution control technologies used, among others. Elements can be classified into groups based on the analysis of trace element concentrations in fly

and bottom ashes, enrichment or depletion of these concentrations in relation to the coal and their behavior during combustion [2,23]. The enrichment factor (EF) was used to elucidate the behavior of the trace elements during the coal combustion [2]. The concentrations in ashes can be normalized using a nonvolatile element, whose concentrations in the coal and in the ashes samples are accurately known. The non-volatile element selected for calculation of EF was Ce because it is one of the elements very stable in the geochemical environment of the crust and also present similar concentration in all particle sizes of the ashes [23]. Thus, the EF may be calculated from:

$$EF = \frac{[X]s/[M]s}{[X]c/[M]c} \quad (1)$$

where $[X]s$ and $[X]c$ represent the mass of element X in the sample and coal, respectively, and $[M]s$ and $[M]c$ represent the content of the matrix element (Ce) in the sample and coal, respectively.

Figure 1 showed the EF values of the elements for the CCPs. The EF values for almost all elements in the fly ash from the baghouse filter sample were higher than those in the cyclone or bottom ash samples. The As, Cs, Sb, U, Zn, and Zr were highly enriched in fly ashes, especially Zn. As already mentioned, As and Zn are probably associated with sulfides and could be classified as chalcophiles. The sulfide, in turn, is correlated to a high percentage of arsenical pyrite in coal [20,24]. Barium, Nb, and Rb were elements enriched in bottom ash and Br, Hf, and Ta in cyclone ash.
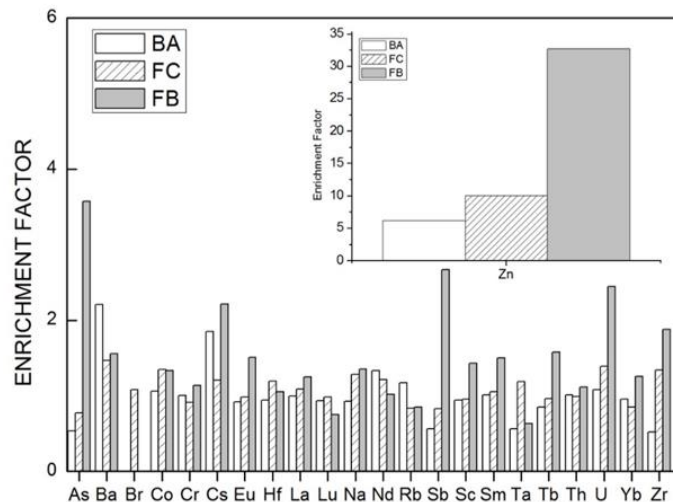

Figure 1: Enrichment factor value of elements in bottom ash (BA), fly ash from cyclone filter (FC) and fly ash from baghouse filter (FB). Inset: Enrichment factor value of Zn.

Trace elements vaporization behavior is closely related to their partitioning in emission streams and their different enrichment phenomena [2,6,23]. The elements enriched in fly ash from baghouse and cyclone ash are those partially volatilized during coal combustion with later re-condense onto the smallest particles [25]. The low-volatile elements that present a weak segregation and non-volatile elements can be found also bottom ash.

The CCPs were classified in the "moderate enrichment" category based on EF values (2-5), with the exception of Zn, which classifies the CCPs between "significant enrichment" and "very high enrichment" (EF value > 5-40) [26].

The effective utilization of coal ashes is strongly desired from environmental and economical point of view. The disposal costs would be minimized, less landscape would be reserved for its disposal and the by-products may be used as raw materials. According to its mineralogical and chemical composition, coal ashes can be used as raw material for synthesis of zeolites using hydrothermal method. Among various uses, zeolites can be applied to wastewater treatment and CO_2 reduction [27-28].

The concentration of the trace elements of zeolitic materials is displayed in Table 2.

Table 2: Concentration of trace elements in zeolite from bottom ash (ZBA), zeolite from fly ash from cyclone filter (ZFC), and zeolite from fly ash from baghouse filter (ZFB).

Trace element	ZBA	ZFC	ZFB
		(mg Kg^{-1})	
As	61.94 ± 3.39	34.53 ± 2	46.17 ± 2.16
Ba	801.6 ± 121.92	825.86 ± 100.63	837.37 ± 141.57
Br	11.38 ± 0.87	10.08 ± 0.71	15.98 ± 0.84
Ce	135.84 ± 4.87	143.36 ± 4.81	161.75 ± 5.76
Co	20.82 ± 0.57	24.51 ± 0.54	23.13 ± 0.67
Cr	109.69 ± 5.55	98.28 ± 4.07	137.43 ± 6.79
Cs	8.81 ± 8.23	4.57 ± 0.68	9.88 ± 9.49
Eu	2.92 ± 0.09	2.85 ± 0.09	4.1 ± 0.13
Hf	9.09 ± 0.17	10.26 ± 0.15	9.5 ± 0.18

La	72.6 ± 1.97	69.83 ± 1.29	76.98 ± 2.09
Lu	1.29 ± 0.06	1.35 ± 0.06	2.49 ± 0.12
Na	4.97 ± 0.11	3.85 ± 0.09	6.97 ± 0.16
Nd	65.63 ± 3.3	67.89 ± 2.89	87.31 ± 5.47
Rb	0 ± 0	9.64 ± 2.84	0 ± 0
Sb	4.38 ± 0.47	4.58 ± 0.45	9.48 ± 1
Sc	22.37 ± 0.16	21.64 ± 0.15	33.19 ± 0.23
Se	0.92 ± 1.32	2.7 ± 1.18	0 ± 0
Sm	18.67 ± 0.65	17.59 ± 0.67	24.9 ± 0.87
Ta	0.48 ± 0.08	1.25 ± 0.15	1.43 ± 0.13
Tb	1.95 ± 0.21	2.15 ± 0.26	3.69 ± 0.52
Th	21 ± 1.22	20.54 ± 1.2	26.71 ± 1.53
U	56.99 ± 3.15	69.3 ± 5.66	103.36 ± 5.81
Yb	8.93 ± 0.77	7.8 ± 0.64	14.29 ± 1.19
Zn	914.17 ± 41.17	1132.84 ± 51.97	3249.39 ± 142.65
Zr	643.57 ± 180.34	1330.84 ± 123.72	1863.35 ± 250.52

There are few studies in the literature on the transfer of undesirable elements from ash into zeolite [29-30]. The majority of authors assessed only major elements.

Comparing the values of the three zeolitic materials with the relative coal ashes, no significant differences are detectable for most of the elements (Figure 2). Therefore, zeolites synthesized retained most of the elements present in the ash. The exception was As which is an element highly soluble in alkaline environment and was thus leachable from ashes in the synthesis process. This behavior of arsenic was observed in a previous study [30].

On the other hand, the content of some elements, mainly Lu, Nd, and Ta, recorded in zeolite ZFB was higher than that present in the ash. It is possible that these elements are enriched during the synthesis due to their lower solubility in alkaline medium when compared to others elements.
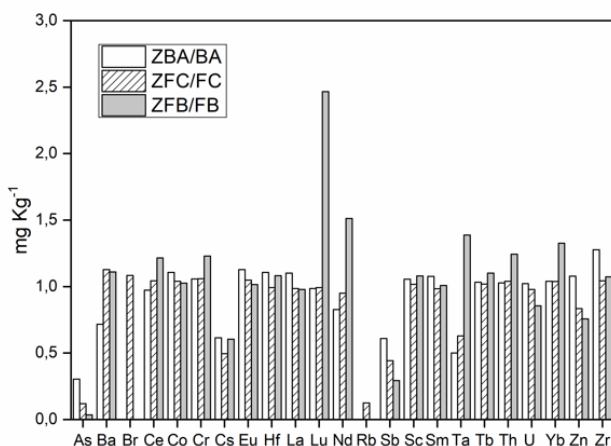

Figure 2: Ratio *of element concentration in zeolite synthesized and in the raw coal ash: bottom ash (ZBA/BA); cyclone filter (ZFC/FC); baghouse filter (ZFB/FB).*

The conversion of coal fly ash to zeolite reduces the potential toxicity of the raw material because the most toxic trace elements are encapsulated in the newly formed mineral structure.

The distribution of elements during zeolite synthesis from coal fly was reported in a previous study [29]. Zeolites were synthesized by means of the two different 2-step synthesis routes. In the 2-step without fusion, Mn, Mg, Ca, Ti, S, Ba, Ce, Co, Cu, Sr, Y, and Zn present in the ash were fully incorporated into the Na-P1 zeolite. In the fusion assisted process nearly all elements report to the ash were not found in the zeolite A produced.

The mobilization of trace elements was also observed in zeolite Na-P1 and zeolite 4A synthesized by integrated two-step alkaline hydrothermal process [31]. The zeolite Na-P1 formed in first stage contained most of the impurities present in the initial raw fly ash. Zeolite 4A, formed in second stage, retained a far lower amount of elements compared to the initial concentrations in the ash. Both zeolites were enriched in several elements, such as Ni in zeolite Na-P1 and As in zeolite 4A.

Determination of Trace Elements in Soil Samples

In order to investigate the environmental impact due to coal-fired-power plant activity, the trace element concentrations present in soil samples collected near FPP were determined. Table 3 listing trace element concentrations for Soil-1 sample (collected in the center of a pasture area) and Soil-2 sample (collected near Laranjinha River). Figure 3 illustrates the results divided into trace elements, which are the constituents with concentration below 20 (Figure 3a), and elements with amounts above 25 mg Kg^{-1} (Figure 3b).

Table 3*: Concentration of trace elements in soils samples around the FPP.*

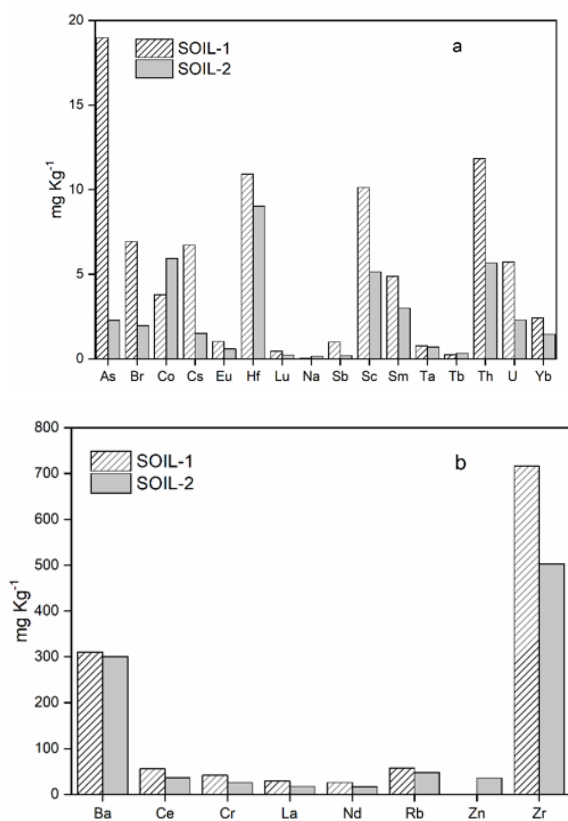| Trace element	SOIL-1 (mg Kg^{-1})	SOIL-2
As	18.98 ± 0.92	2.28 ± 0.19
Ba	310.65 ± 70.27	300.87 ± 41.08
Br	6.93 ± 0.5	1.97 ± 0.16
Ce	55.89 ± 2.13	36.63 ± 1.27
Co	3.79 ± 0.14	5.94 ± 0.16
Cr	41.83 ± 2.67	25.99 ± 1.52
Cs	6.72 ± 6.31	1.51 ± 0.29
Eu	1.03 ± 0.04	0.59 ± 0.03
Hf	10.92 ± 0.2	9.02 ± 0.12
La	29.17 ± 0.8	17.52 ± 0.33
Lu	0.46 ± 0.02	0.23 ± 0.02
Na	0.05 ± 0	0.15 ± 0.01
Nd	25.68 ± 6.92	17.05 ± 0.81
Rb	57.07 ± 4.48	47.88 ± 3.02
Sb	1 ± 0.11	0.19 ± 0.02
Sc	10.13 ± 0.08	5.14 ± 0.04
Sm	4.88 ± 0.17	3 ± 0.12
Ta	0.76 ± 0.11	0.47 ± 0.06
Tb	0.25 ± 0.14	0.33 ± 0.09
Th	11.84 ± 0.68	5.67 ± 0.34
U	5.73 ± 0.48	2.3 ± 0.34
Yb	2.41 ± 0.26	1.45 ± 0.15
Zn	0 ± 0	35.57 ± 2.56
Zr	716.7 ± 119.89	503.3 ± 55.66

Figure 3*: Trace elements in soil samples: (a) concentration below 20 mg Kg^{-1}. (b) concentration above 25 mg Kg^{-1}.*

In general, concentrations of all elements of Soil-1 were higher than Soil-2. Soil-1 present higher organic matter content and higher clay fraction compared to sample of Soil-2 [18], so, can act as an adsorbent and retain elements from ashes.

The elements present in the soils were in two concentration ranges. At the lowest level (0.05-19 mg kg^{-1}), As, Hf, Sc and Th showed the highest concentrations in both soils (Figure 3A). It should be noted that As, which is one of the main elements enriched in ash presented a concentration 8 times higher in Soil-1 than in Soil-2. At the highest level (26-717 mg kg^{-1}), Zr and Ba presented the highest concentrations in both soils (Figure 3B). Zinc, which was the most enriched element in the ashes, was found only in Soil-2 with concentration of 36 mg kg^{-1}. The elements that could be a potential problem for soil contamination are As due to their mobility and toxicity, and with lower risk is Zn [20].

Previous studies regarding soil samples around FPP reported that Co, Cr, Cu, Ni, and Sc were of lithogenic origin, while As, Cd, Hg, Mo, Pb, Sb, U, and Zn showed origin in the coal and ash sources of the area [32].

The trace elements which presented the most significant concentrations in soil samples in this work were compared with the results from other studies [32-34]. The concentrations were similar to data reported for sample collected around Laranjinha River (Soil-2 sample).

Conclusions

The present study provides information of trace metals present in coals and CCPs due to operation of FPP and identifying anthropogenic pollution signals. Most elements exhibit moderate enrichment in ashes (2–5 times), with exception of Zn, which was

significantly enriched in all ash samples. Among the trace elements in ashes, As can be considered the most critical element due to its high mobility.

Most of the elements investigated in the zeolites from coal ashes show concentrations close to those measured in the raw material and an important decrease in concentration of As was observed, which will ensure safer application of these synthesized products.

Soil samples collected in the vicinity of the FPP showed high levels of the Zr and Ba, and As, Hf, Sc and Th at lower levels.

The results of this study can be used as database for future assessment of trace elements pollution from FPP and for development of protective measures.

Acknowledgment

References

1. World energy resources.

2. Meij R. Trace element behavior in coal-fired power plants. Fuel Process. Technol. 1994; 39: 199-217.

3. Querol X, Fernandez-Turiel JL, López-Soler A. Trace elements in coal and their behaviour during combustion in a large power station. Fuel. 1995; 74: 331-343.

4. Martinez-Tarazona MR, Spears DA. The fate of trace elements and bulk minerals in pulverized coal combustion in a power station. Fuel Process. Technol. 1996; 47: 79-92.

5. Juda-Rezler K, Kowalczyk D. Size Distribution and Trace Elements Contents of Coal Fly Ash from Pulverized Boilers. Pol J Environ Stud. 2013; 22: 25-40.

6. Xu M, Yan R, Zheng C, Qiano Y, Han J, Sheng C. Status of trace element emission in a coal combustion process: a review. Fuel Process Technol. 2003; 85: 215-237.

7. Vejahati F, Xu Z, Gupta R. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization- A review. Fuel. 2010; 89: 904–911.

8. Nalbandian H. Trace element emissions from coal. IEA Clean Coal Centre; IEA, London, U.K. 2012; 1-89.

9. Lim JM, Jeong JH, Lee JH. Instrumental neutron activation analysis of coal and its combustion residues from a power plant. J Radioanal Nucl Chem. 2013; 298: 201-208.

10. Ćujić M, Dragović S, Dordević M, Dragović R, Gajić B. Environmental Assessment of Heavy Metals around the Largest Coal Fired Power Plant in Serbia, Catena. 2016; 139: 44-52.

11. Huang X, Hu J, Qin F, Quan W, Cao R, Fan M, et al. Heavy Metal Pollution and Ecological Assessment around the Jinsha Coal-Fired Power Plant (China). Int J Environ Res Public Health. 2017; 14: 1589-1601.

12. Kalkreuth W, Holz M, Kern MM, Machado G, Mexias A, Silva MB, et al. Petrology and chemistry of permian coals from the Paraná basin: 1. Santa Terezinha, Leão-Butiá and Candiota coalfields, Rio Grande do Sul– Brazil Int J Coal Geol. 2006; 68: 79-116.

13. Depoi FS, Pozebon D, Kalkreuth WD. Chemical characterization of feed coals and combustion-by-products from Brazilian power plants. Int J Coal Geol. 2008; 76: 227-236.

14. Fungaro DA, Izidoro JC, Santos FS, Wang S. Coal fly ash from Brazilian power plants: chemical and physical properties and leaching characteristics. in: Sarker, P.K. (Ed.), Fly ash: chemical composition, sources and potential environmental impacts. Nova Science Publishers, Hauppauge, Chapter 5. 2013; 145-164.

15. Fungaro DA, Silva PSC, Campello FA, Miranda CS, Izidoro JC. Evaluation of radionuclide contamination of soil, coal ash and zeolitic materials from Figueira Thermoelectric Power Plant. Braz J Rad Sci. 2019; 7: 1-18.

16. ABNT NBR 10007, 1987. Associação Brasileira de Normas Técnicas. Amostragem de resíduos: procedimento [BRAZILIAN ASSOCIATION OF TECHNICAL STANDARDS-NBR 10007. Sampling of solid residues]. Rio de Janeiro (in Portuguese).

17. EMBRAPA. National Soil Research Center. Manual of soil analysis methods, 2nd. ed. EMBRAPA-CNPS, Rio de Janeiro (in Portuguese). 1997.

18. CAMPELLO FA. Study of the leaching and stabilization of toxic elements present in coal fly ash. Master's Thesis. Nuclear and Energy Research Institute, São Paulo-SP, Brazil. 2018.

19. Izidoro JC, Miranda CS, Guilhen SN, Fungaro DA, WANG S. Treatment of coal ash landfill leachate using zeolitic materials from coal combustion by-products. Adv Mater Technol Environ Appl. 2018; 2: 177-186.

20. Flues M, Sato IM, Scapin MA, Cotrim MEB, Camargo IMC. Toxic elements mobility in coal and ashes of Figueira coal power plant, Brazil. Fuel. 2013; 103: 430-436.

21. Sulovsk P. Mineralogy and chemistry of conventional and fluidised bed coal ashes. Bull Czech Geol Surv. 2002; 77: 1–11.

22. Kolker A, Scott C, Hower JC, Vazquez JA, Lopano CL, Dai S. Distribution of rare earth elements in coal combustion fly ash, determined by SHRIMP-RG ion microprobe. Int J Coal Geol. 2017; 184: 1−10.

23. Pires M, Querol X. Characterization of Candiota (South Brazil) coal and combustion by-product. Int J Coal Geol. 2004; 60: 57–72.

24. Mason B. Principles of geochemistry. 3rd ed., Wiley, New York. 1966.

25. Coles DG, Ragaini RC, Ondov JM. Chemical studies of stack fly ash from a coal fired power plant. Environ Sci Technol. 1979; 13: 455–459.

26. Sutherland R. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 2000; 39: 611-627.

27. Lee YR, Soe JT, Zhang S, Ahn JW, Park MB, Ahn WS. Synthesis of nanoporous materials via recycling coal fly ash and other solid wastes: A mini review. Chem Eng J. 2017; 317, 821-843.

28. Mallapur VP, Oubagaranadin JUK. A brief review on the synthesis of zeolites from hazardous wastes. Trans Indian Ceram. Soc. 2017; 76: 1-13.

29. Du Plessis PW, Ojumu TV, Fatoba OO, Akinyeye RO, Petrik LF. Distributional fate elements during the synthesis of zeolites from South African coal fly ash. Materials. 2014; 7: 3305–3318.

30. Belviso C, Cavalcante F, Gennaro S, Palma A, Ragone P, Fiore S. Mobility of trace elements in fly ash and in zeolitised coal fly ash. Fuel. 2015; 144: 369-379.

31. Ferrarini SF, Cardoso AM, Paprocki A, Pires M. Integrated Synthesis of zeolites using coal fly ash: element distribution in the products, washing waters and effluent. J Braz Chem Soc. 2016; 27: 2034–2045.

32. Campaner VP. Geochemical dispersion of elements and radionuclides in the atmosphere and soil of an area with mining and

coal-fired thermoelectric power plant activities. MS thesis, State University Campinas. 2013; 143.

33. Flues M, Sato IM, Cotrim MB, Figueiredo Filho PM, Camargo IMC. Evaluation of the influence of a coal plant operation on metal and as concentrations in the soil of Figueira, Pr-Brazil. Quim. Nova. 2008; 31: 25–30

34. Kalkreuth W, Levandowski J, Delgado T, Scheffer R, Maia S, Peralba M, et al. Evaluation of environmental impacts of the Figueira Coal-Fired Power Plant, Paraná, Brazil. Energy Exploration & Exploitation. 2014; 32: 423-470.