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Chemical, mineralogical and environmental characterization of combustion by-products generated from mineral coal used for electricity production

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Abstract

The coal combustion by-products, bottom ash (BA), fly ash from cyclone filter (CA) and fly ash from bag filter (FA), generated in a Brazilian thermoelectric power plant, were characterized by X-ray fluorescence, X-ray diffractometry and leaching and solubilization tests. The material retention systems used in the Brazilian power plant from where these by-produtcts were sampled are showed in Figure 1.

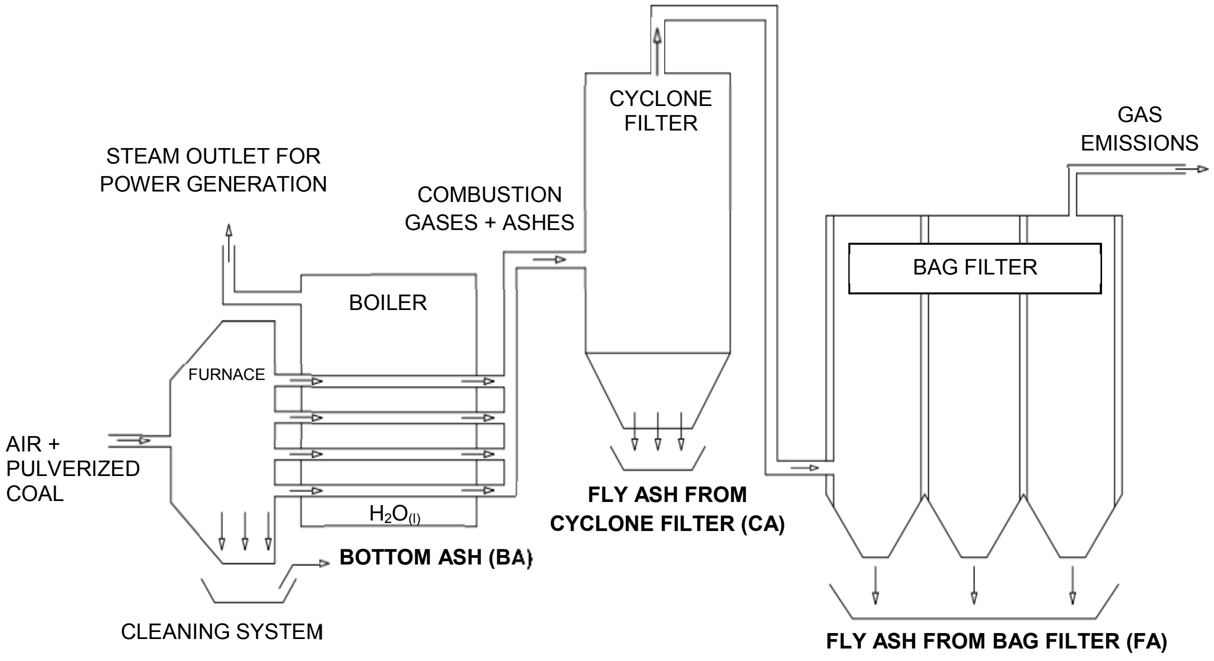

Figure 1 - Coal ash retention systems from Brazilian coal-fired power plant.

The three types of coal ashes presented similar chemical composition, with a total content of main oxides (SiO_2, Al_2O_3 and Fe_2O_3) above 72% and were classified as class F (according to ASTM). The analysis of ash enrichment factor showed that arsenic, zinc and lead concentrate mainly on FA, whereas the elements that presented the greatest enrichment in the bottom ash (BA) and therefore present low volatility are K and Mg. All ashes presented quartz, mullite and magnetite as crystalline phases. In the leaching and solubilization study, the FA sample was considered hazardous and classified according to Brazilian regulation as Class I solid waste, whereas CA and BA samples were considered non-hazardous and not inert solid wastes and classified as Class II-A. Therefore, FA sample from this Brazilian power plant must be discarded only after treatment or stringent disposal criteria must be followed to avoid contamination on site.

Key words: Mineral Coal; Coal Combustion By-products; Materials Characterization.

1. Introduction

Coal is the most widely source used for electricity generation in the world (BP Statistical Review of World Energy, 2015). In Brazil, this source is responsible for only 2.5% of energy production (ANEEL, 2015), but this percentage tends to increase due to the operation of new plants, which are being built to supply the growing energy demand.

After the burning of coal in thermal plants, in addition to the generation of heat and combustion gases, there is also the formation of different types of Coal Combustion By-products (CCBs), which are: botton ash, fly ash from cyclone filter and fly ash from bag filter.

The botton ash, which has the largest granulometry when compared to the others two kinds of ashes, is withdrawn from the system through the bottom of the furnace by a cleaning system which has a container of water. The intermediate size ash is collected in a cyclone filter. The ashes of smaller particle size (fly ash) are retained by a bag filter, which is placed after the cyclone filter.

The objective of this study is to evaluate the chemical and mineralogical characteristics of the CCBs generated from mineral coal used for electricity production in a Brazilian thermal plant, as well as classify environmentally these wastes so that sustainable practices of disposal can be adopted in the future in order to avoid local environmental impacts.

2. Materials and Methods

2.1. Ash samples

Three types of coal ashes (bottom ash, fly ash from cyclone filter, and fly ash from bag filter) were collected directly from the ash retention system specifical for each ash (before mentioned) and labeled in this study as BA, CA and FA, respectively.

2.2 Chemical composition

The semi-quantitative chemical composition of the coal ash samples was determined by a X-ray fluorescence equipment (Bruker – Model S8 Tiger X-ray Fluorescence Spectrometer).

2.3 Mineralogical composition

The CCBs samples were placed in a glass sample holder and analyzed by X-ray diffraction (Rigaku – Multiflex X-ray Diffractometer) using Cu Kα radiation at 40 kV and 20mA. The scan rate was 0.02°/s and ranged between 5 – 90 º (2θ). Crystalline phases identification was made by using Search-Match computer program and by searching the powder diffraction file database from International Centre for Diffraction Data (ICDD), with the help of Joint Committee on Powder Diffraction Standards (JCPDS) files for inorganic compounds.

2.4 Leaching and solubilization tests

The ashes environmental classification was carried out by leaching and solubilization tests according to the Brazilian regulations NBR 10005: 2004 and NBR 10006: 2004, respectively. For the leaching tests, 10 g of coal ash sample was stirred with acetic acid solution (pH 4.93 ± 0.05) for 18 h at 30 rpm (Ética – Mod. 430 Agitator). After filtration, the leachable compounds were extracted, and the elements of interest were analyzed (ABNT, 2004). For the solubilization tests, 25 g of coal ash sample was placed in contact with 100 mL of ultrapure water. The suspension was stirred for 5 min and after it was allowed to stand for seven days at room temperature. After filtration, the solubilized extracts were analyzed (ABNT, 2004). For both the leaching and solubilization tests, the concentration of Hg was determined by graphite furnace atomic absorption cold vapor spectrometry (CV-AAS – PerkinElmer – A Analyst – 800) while the concentrations of all others elements were determined by inductively coupled plasma optical emission spectrometry (ICP-OES – Spetro – Arcos).

3. Results and Discussion

3.1 Chemical Composition

The chemical compositions of the CCBs (by % weight) are given in Table 1. There were no significant variations among the contents of the main oxides present in the ashes. The sum of main oxides (SiO_2+ Al_2O_3+ Fe_2O_3) was 72.6, 75.4 and 80.7% for BA, CA and FA, respectively. These ashes were classified as Class F type according to the American Society for Testing and Materials (ASTM C618).

The contents of Si and Al were above 60% for all samples indicating that these materials can be used for the synthesis of alternative adsorbent materials (Querol et al., 2002; Ahmaruzzaman, 2010; Fungaro et al., 2009; Izidoro et al., 2012; Ciocinta, et al., 2013).

The contents of CaO, K_2O and SO_3 were between 1.5 and 3.6%. The iron and sulfur compounds (Fe_2O_3 and SO_3) are derived from the pyrite (FeS_2) usually present in the feed coal. The presence of S in CCBs shows that not all the sulfur present in the pyrite can be converted into SO_2 and SO_3 gases after the coal combustion.

TABLE 1 – Chemical composition (wt%) of coal ash samples

Components	BA	CA	FA
SiO_2	45.4	46.0	49.2
Al_2O_3	17.0	16.2	21.6
Fe_2O_3	10.2	13.2	9.86
CaO	2.76	3.57	2.06
K_2O	2.46	2.20	2.74
SO_3	1.46	1.54	1.65
TiO_2	0.863	0.86	1.20
MgO	0.936	0848	1.02
Na_2O	0.942	1.01	1.23
ZnO	0.136	0.222	0.682
MnO	0.084	0.099	0.061
P_2O_5	0.039	<0.001	0.097
Cr_2O_3	0.055	0.062	0.048
PbO	<0.001	0.02	0.049
As_2O_3	0.026	0.034	0.16
ZrO_2	0.063	0.067	0.099
Rb_2O	0.012	0.011	0.014
SrO	0.02	0.022	0.029
NiO	<0.001	0.009	0.011
CuO	0.012	0.015	0.022
Y_2O_3	0.016	<0.001	0.028
V_2O_3	0.06	0.053	0.082
MoO_3	0.014	0.016	0.03
BaO	0.038	<0.001	<0.001
SiO_2/Al_2O_3	2.47	2.57	2.19

Low variations in the amounts of the presented compounds can occur due to the different exposure time of each waste to the heat from the flue gas that comes from the furnace, which allows that some volatile elements to separate from the solid phase and migrate to the gaseous phase. The

SiO_2/Al_2O_3 ratios were calculated for coal ashes and the values ranged from 2.19 to 2.57.These values are consistent with other studies (Shiguemoto et al., 1993, Izidoro, 2013).

In order to understand how the main elements present in the coal behave during the combustion, in which type of waste they are more likely to concentrate and which elements are more or less volatile, the Enrichment Factor (EF) was calculated. Through EF, the concentrations of the different elements can be normalized using as reference a non-volatile element for which their concentration is known in both coal and ash. The use of EF is more convenient than the direct comparison between the concentrations of the elements. The non-volatile elements most used in this calculation are Al, Ce, Fe, la, Si and Ti, among others. In the present study, Al was chosen as the non-volatile element (Pires & Querol, 2004; Font et al., 2012).

The EF was calculated for bottom ash (EF_{BA}), for the ash from cyclone filter (EF_{CA}), and for the fly ash from bag filter (EF_{FA}) by equations (1), (2) and (3), respectively:

$$EF_{BA} = [C_{oBA}/CAl_{BA}] / [C_{oCoal}/CAl_{Coal}] \quad (1)$$

$$EF_{CA} = [C_{oCA}/CAl_{CA}] / [C_{oCoal}/CAl_{Coal}] \quad (2)$$

$$EF_{FA} = [C_{oFA}/CAl_{FA}] / [C_{oCoal}/CAl_{Coal}] \quad (3)$$

Where, C_o is the concentration of a given element and CAl is the concentration of aluminum in the concerned waste (BA, CA or FA) or in the feed coal (Gordon & Zoller, 1973; Pires & Querol, 2004; Font et al., 2012).

By using this normalization system, the enriched elements in the ashes will reach an EF > 1. On the other hand, the most impoverished elements will have an EF < 1 (Font et al., 2012). A comparison among the EFs determined for each ash can also be made to verify in which waste the concerned element concentrates more and verify its volatilization. Figure 2 shows the EFs calculated for the different chemical elements present in the ashes.

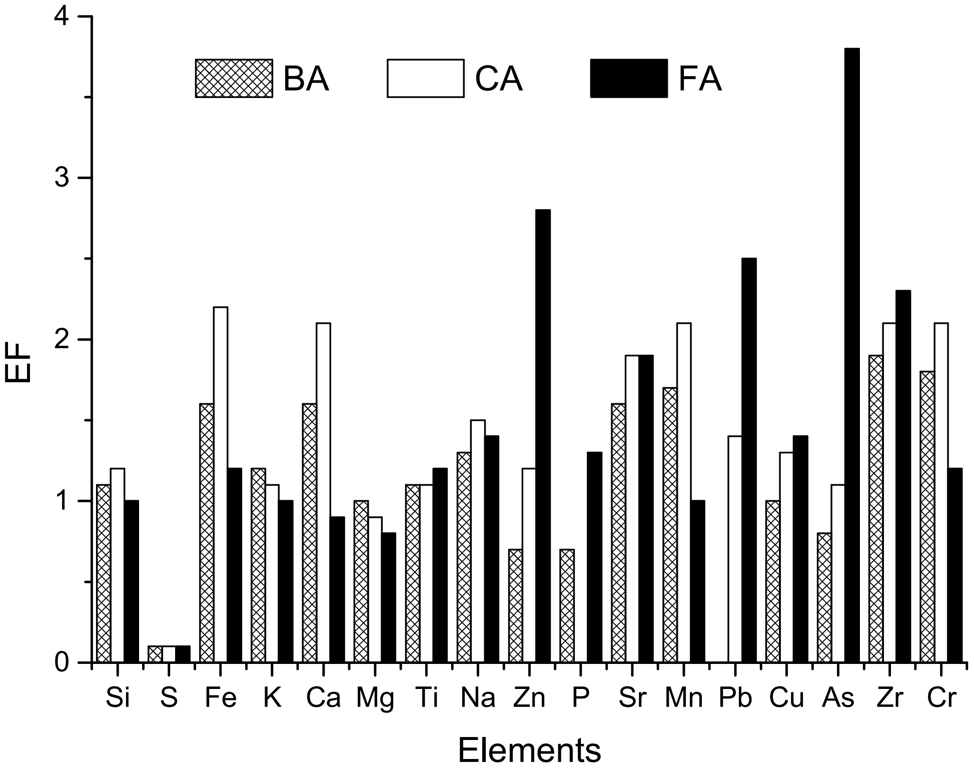

Figure 2 – Enrichment Factor (EF) to the main elements from BA, CA and FA samples.

According to Figure 2, the elements enriched in the fly ash from bag filter (which presented EF > 1) in descending order were as follows: As (FE = 3.8), Zn (2.8), Pb (2.5), Zr (2,3), Sr (1,9), Cu and Na (1,4), P (1,3), Fe, Ti, and Cr (1,2).

The three elements which presented the highest EF in the fly ash (As, Zn and Pb) were impoverished in bottom ash (EF of 0.8, 0.7 and 0 for the elements, respectively), but presented an intermediate value (and higher than 1.0) for the cyclone ash. These results indicate that those elements are still volatile at the cyclone filter temperature and condense inside the bag filter when the temperature decreases, concentrating on the ashes with smaller particle size (FA).

CA sample presented EF > 1 for the following elements: Fe, K, Ca, Ti, Na, Zn, Sr, Mn, Pb, Cu, As, Zr and Cr. Most of these elements are also concentrated in the FA sample and are depleted in the BA sample, with the exception of Ca and Mn, which concentrated more in the CA sample.

The elements that presented the highest enrichment in the bottom ash sample (BA) and, therefore, presented low volatility are K and Mg. Sulfur showed impoverishment for all ash samples, indicating that most part of this element is emitted together with the flue gases. Some variations among the enrichment factors determined for the ashes can be related to the affinity of some elements for the unburnt carbon content of the samples (Font et al., 2012).

3.2 Mineralogical composition

Crystalline phases identified for the ash samples are shown in Figure 3. The three ash samples are composed mainly of quartz, mullite and magnetite (which are also confirmed from their chemical compositions - Table 1). These crystalline phases are typically encountered in this type of material and were identified in other studies (Umaña, 2002, Jha et al., 2008, Lee et al., 2010, Ibanez et al., 2012, Widiastuti et al. ., 2016). All difratograms also presented amorphous phase, which can be attributed to the amorphous silica content in these materials.

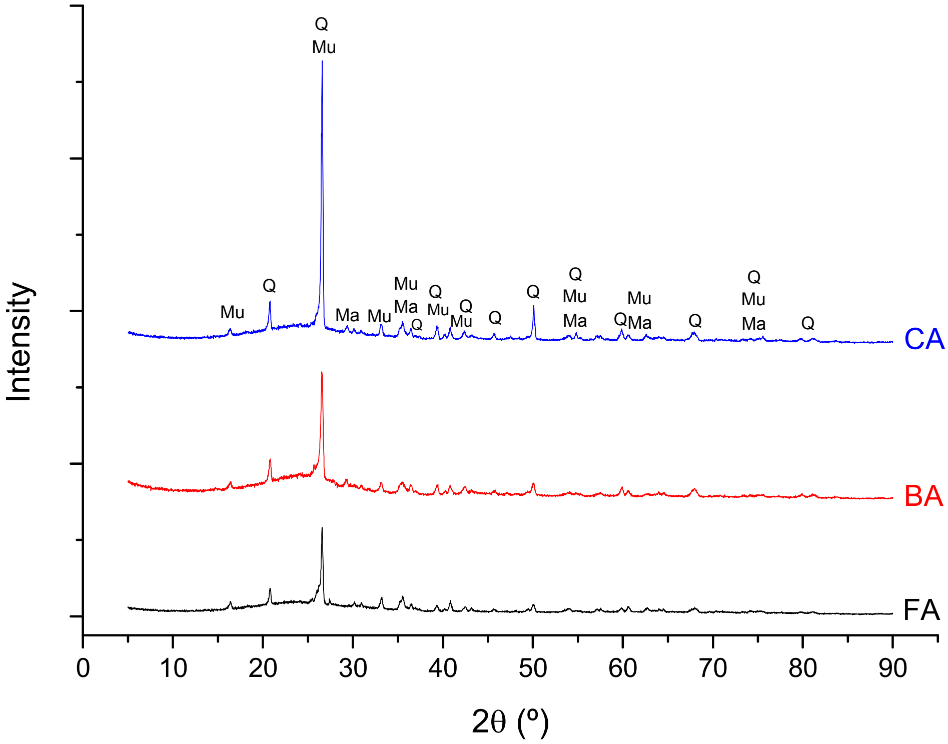

Figure 3 - XRD Patterns of coal ash samples: Q = Quartz (SiO_2), M = Mullite ($Al_{4,8}Si_{1,2}O_{9,6}$) and Ma = Magnetite (Fe_3O_4).

3.3 Leaching and solubilization tests

The concentration of the chemical elements in the ash extracts of the leaching tests (using acetic acid) and solubilization tests (using water) are shown in Tables 2 and 3, respectively, and complement the characterization study of these materials. According to Fungaro et al. (2013), the chemical elements chosen for these tests are those that represent the highest risk to fauna and flora and it is also are used to evaluate the environment behavior of waste materials.

TABLE 2 – Concentration of elements leachated from fly ashes and the allowed limit values

Elements	**Concentration (mg L^{-1})**			**Maximum Limits*(mg L^{-1})**
	BA	**CA**	**FA**	
Ag	<0.010	<0.010	<0.010	5.0
As	0.086 ± 0.001	0.111 ± 0.002	1.27± 0.2	1.0
Ba	0.236 ± 0.001	0.161 ± 0.001	0.0269± 0.0002	70
Cd	0.0266± 0.0002	0.031 ± 0.001	0.2731± 0.0001	0.5
Cr	<0.01	0.014± 0.001	0.039 ± 0.0004	5.0
Hg	<0.001	<0.001	<0.001	0.1
Pb	0.0527 ± 0.0003	0.0527 ± 0.0003	0.047 ± 0.002	1.0
Se	0.107 ± 0.01	0.13 ± 0.2	0.138 ± 0.002	1.0

(*) Established by Norm ABNT NBR 10004 (2004a).

TABLE 3 – Concentration of elements solubilized from fly ashes and the allowed limit values

Elements	**Concentration (mg L^{-1})**			**Maximum Limits*(mg L^{-1})**
	BA	**CA**	**FA**	
Ag	<0.010	<0.010	<0.010	0.05
Al	3.4± 0.04	0.79± 0.05	0.27± 0.01	0.2
As	9.95± 0.2	0.17± 0.01	0.7± 0.03	0.01
Ba	0.038± 0.001	0.15± 0.01	0.022± 0.001	0.7
Cd	<0.01	<0.01	<0.01	0.005
Cr	0.36± 0.01	<0.01	0.042± 0.003	0.05
Cu	<0.05	0.074± 0.005	<0.05	2
Fe	0.376± 0.005	0.31± 0.06	<0.1	0.3
Hg	<0.001	<0.001	<0.001	0.001
Mn	0.013± 0.001	0.027± 0.008	<0.01	0.1
Na	190.5± 0.2	92± 2	77± 3	200
Pb	<0.1	<0.1	<0.1	0.01
Se	0.43± 0.03	0.045± 0.001	0.039± 0.001	0.01
Zn	0.093± 0.003	0.21± 0.001	<0.1	5

(*) Established by Norm ABNT NBR 10004 (2004b).

According to Table 2, FA sample was the only one that presented in the leachate solution a concentration (for As) above the allowed limit by Brazilian regulation (1.27 mg L^{-1}, while the limit is 1.0 mg L^{-1}).

Thus, the FA sample is considered hazardous and can be classified as Class I, while CA and BA samples can be classified as Class II (non-hazardous waste). Therefore, the disposal of the ash from the bag filter should be carried out after treatment or be carefully disposed in industrial landfills designed to handle hazardous waste in order to avoid contamination on site.

The solubilization test complements the leaching study and classifies non-hazardous waste as inert or non-inert by NBR 10006 (ABNT, 2004b). This study was performed for all samples (including FA) for comparison.

According to the results showed in Table 3, all samples presented concentration values for Al and As above the allowed limit, whereas only for BA sample the extracted solution also presented high concentrations of Cr and Fe.

It is noteworthy that, when the lead concentration was considered, it was not possible to classify the wastes in the solubilized extract (Table 3), since the equipment detection limit is above the limit of the Brazilian regulation.

Hg determination was below the equipment detection limit (Tables 2 and 3). According to Depoi et al. (2008) the determination of mercury can be impaired due to the absence of an oxidizing agent in the solution able to stabilize this element, as well as due to the increase of temperature in the solution caused by the stirring of suspension during the tests. The classification of the tested materials is summarized in Table 4.

TABLE 4 – Summary of the classification of wastes from coal combustion according to NBR 10005 and 10006 (ABNT, 2004a; ABNT, 2004b).

Sample	Leaching test	Solubilization tests
BA	Class II – Non-Hazardous	Non Inert – Class II A
CA	Class II – Non-Hazardous	Non Inert – Class II A
FA	Class I – Hazardous	–

According to Table 4, although BA and CA samples are considered non-hazardous, they are also non-inert, thus they should be disposed of in landfills or co-processed. It is worth mentioning, as explained by Querol et al. (1996), that coal ashes are not completely inert and can, over time, mobilize trace elements of their mineral fraction. Therefore, stabilization and immobilization studies of toxic elements present in this type of waste are needed in future research.

4. Conclusion

1. Coal combustion by-products (CCBs) presented similar chemical composition, with total content of the main oxides (SiO_2, Al_2O_3 and Fe_2O_3) above 72% for the three samples, and were classified as class F according to ASTM.

2. Ashes enrichment factor analysis showed that As, Zn and Pb concentrate mainly in fly ash from bag filter (FA), whereas the elements that presented higher enrichment in the bottom ash (BA) and therefore present low volatility are K and Mg.

3. All ashes presented quartz, mullite and magnetite as crystalline phases.
4. Leaching and solubilization tests of CCBs showed that FA sample was considered hazardous and classified as class I waste, while CA and BA samples were considered non-hazardous and non-inert wastes and classified as class II-A.
5. Stabilization and immobilization studies of toxic elements present in ashes are needed in future research in order to avoid contamination on waste disposal site.

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