Toxic elements mobility in coal and ashes of Figueira coal power plant, Brazil

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HIGHLIGHTS

- The results showed a high total concentration for As and Zn in coal and fly ashes.
- Arsenic and Mo showed high mobility in ash.
- Arsenic could be considered the most critical element to be leached from ashes.

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ABSTRACT

During operation, the coal power plant produces solid waste (bottom and fly ash) and uncontrolled ashes disposal could lead to environmental contamination. Major and trace elements (Al, Fe, Ti, Ca, Mg, As, Cd, Cr, Co, Cu, Mn, Mo, Ni, Pb, Zn, V) were determined in coal and ashes of the power plant of Figueira (Brazil) and their mobility evaluated by total and available metal concentration ratio. The total concentration was determined by WDXRF technique and the available concentration (after extraction with EDTA) by ICP-OES technique. The results showed a high total concentration for As and Zn (average 270 and 391 mg kg\(^{-1}\)) in coal and (average 974 and 1330 mg kg\(^{-1}\)) in fly ashes. The high mobility of As (>70%), followed by Mo (>55%) and next by Mn, Zn, Cd, Pb (30–5%) in ash can cause environmental impact. Arsenic could be considered the most critical element to be leached from ashes.

1. Introduction

Coal has a high concentration of trace elements when compared to geological materials. During coal combustion, ashes enriched with 3–10 times in trace elements concentration are produced [1–3]. The major components in coal ashes are silica (20–60% SiO\(_2\)), alumina (5–35% Al\(_2\)O\(_3\)), ferric oxide (10–40% Fe\(_2\)O\(_3\)) and calcium oxide (2–10% CaO).

During combustion, the elements are not released; this fact is confirmed by the same concentration ratios found in ash and original coal. The trace elements have a tendency to concentrate in the small fine particles of the coal ashes (fly ash) during the condensate-volatilization process. The selective volatilization results in the enrichment of the same elements, while others deplete. The elements behavior depends on their geochemical association with the coal and the combustion condition, what defines their leaching ability in ash. The trace elements mobility also depends on ash physic-chemical characteristic, mainly pH. The trace elements are easier leached from acid ashes, leading to soil pollution and consequent groundwater contamination [4,5].

In coal power plants, the treatment and disposal residues, mainly ashes, continue to be a serious problem, mainly in Brazil, where the coal has high ash content (20–50%). Usually, the coal combustion residues are stored at the plant site or on-site disposal, and only a small part of them have commercial use (30%). In Brazil, the main application of coal ash is for cement and concrete manufacture [6,7]; a small part is used as a road-bed stabilizer, building materials plus glass and ceramic composite. A large fraction of coal ash produced from Brazilian power plant does not find a commercial application and is usually stored in piles, dumped in the vicinity of the power plant or managed to empty coal mine galleries. Typically the coal ash piles make boundary with many ecosystem compartments such as air, water and soil, and thus giving rise to environmental contamination.

The determination of leaching inorganic pollutant in solid waste, such as coal and ash is an important topic for further industrial applications and solid waste management. Environmental contamination caused by coal ash disposal and also their further industrial application require the knowledge of their total metal concentration besides the available metal fraction to other environmental compartments. The total metals concentration applied for environmental evaluations lead to an over estimation of the contamination, once it is well known that a significant fraction of metals is immobilized in the solid matrix.

In a natural environment, the leaching of pollutants from ash matrix is carried out by chelating agents as humic acids. The structure of these complexes is affected significantly by solubility and

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mobility of metals in solid waste. Garrabants and Kosson [8] used the ethylenediaminetetraacetic acid (EDTA) as a leaching agent to predict soil and solid waste metal availability. The arsenic, cadmium, copper, manganese and lead leaching ability with EDTA was compared to their availability, determined by standardized test at pH 7 and 4 (adjusted with nitric acid). A significant greater availability was observed using the EDTA method. The EDTA was also used to determine biogeochemically available metal fractions of estuarine suspended particulate matter [9]. Janos et al. [10] also applied EDTA in the metals leaching studies in ashes. Hong et al. [11] observed that many chelating agents solutions, such as EDTA, NTA (nitrilotriacetic acid) and DPTA (diethylenetriamine pentaacetic) are more efficient in leaching process than HCl for fly ash waste.

The aim of this work is to evaluate trace elements mobility in coal and different types of ashes produced by the Figueira coal power plant and to predict probable elements which might contribute to the environmental contamination.

2. Materials and methods

2.1. Site

The “Figueira” CPP (Coal Power Plant) has a 10 MWe capacity and has been working since 1963, but only in 1998 the cyclone and bag filters were installed in the plant. It is located in Figueira County, in the north of Paraná State, in Brazil. The county has 9612 inhabitants, an extension of 115 km² and the main activity is the extraction and exploitation of coal.

From available plant data, the amount of coal burned from 1986 to 1997 was 25,440 t year⁻¹. Since 1999, the data have shown an increase of coal consumption by the plant of 60,000 t year⁻¹ [12]. No data are available about the amount of ash generated. However, it is known that the local coal has 26% of ash and also presents a high amount of pyrite (7%) [13]; this information allowed to calculate ash production to be ca. 6614 t year⁻¹ and an extension of 115 km² and the main activity and bag filters were installed in the plant. It is located in Figueira County, in the north of Paraná State, in Brazil. The county has 9612 inhabitants, an extension of 115 km² and the main activity is the extraction and exploitation of coal.

2.2. Coal and ash samples sampling and treatment

Pulverized coal, bottom and corresponding captured fly ashes (cyclone and bag filter) samples were supplied by the CPP during 2001–2002. The sampling was carried out every two months, obtaining 24 samples a year. In each sampling, 1 kg of bottom and fly ashes plus pulverized coal was collected following ABNT norm, 1987 [14]. All sampling was performed on the same day, grounded, homogenized, air dried and sieved.

2.3. Determination of pH

The pH was determined in a 1:2.5 soil:liquid (w/v) ratio with 1 mol l⁻¹ KCl solution [15].

2.4. Metal determination

2.4.1. Total concentration

The total metal content of the major and trace elements was determined by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The coal and ash samples were prepared in pressed pellets, where in the 1.8 g of sample was added 0.2 g powder wax (analytical grade, HOECHST), mixed and homogenized in Mixer/Mill and after all pressed using a hydraulic press.

An X-ray fluorescence spectrometer from RIGAKU Co., model RIX 3000, was used and the Fundamental Parameters method was applied [16,17]. All the elements were determined by analyzing triplicate measurements. The Fundamental Parameters method was evaluated, according to ISO 17025 [18] and EURACHEM/CITAC [19] norms, using standard reference material SRM 2689 – Coal Fly Ashes, from NIST (National Institute of Standards & Technology).

The precision of the methods is considered satisfactory when RSD% (relative standard deviation) values are below 10%. The RSD% values for major elements determination (Al, Mg, Ca, Ti and Fe) presented values between 1.3 and 5.9% and for trace elements determination (Cr, Mn, Ni, Zn, As and Pb), 1.6–6.1 RSD% values, expect for Cd determination (25.0%), showing a good repeatability of the method.

The accuracy of the method was evaluated by Z-score test and values of |Z| < 2 are satisfactory. The Z-score values for major elements determination presented |Z| < 1, showing adequate accuracy for the determination of all elements. The Z-score values did not calculated for trace elements determination, since their values, in SRM 2689 material, are indicative.

The LQ (limit of quantification) for major elements presented following values: Al: 0.1; Mg: 0.001; Ca: 0.005; Ti: 0.002; Fe: 0.027% and for trace elements were Co: 5; Cr: 4; Cu: 2; Mn: 4; Mo: 5; Ni: 3; Zn: 2; As: 2; Cd: 6; Pb: 2; and V: 4 mg kg⁻¹.

2.4.2. Available concentration

The samples by CPP extraction were done in duplicate; 2 g of coal or ash sample was shaken for 1 h at 10 rpm (vertical rotation) with 40 ml of 0.05 mol l⁻¹ EDTA-NH₄ (pH 7). The sample was centrifuged, filtered by 0.45 μm pore membrane, and acidified with HNO₃ to pH 2, according to the methodology proposed by Ure et al. [20]. Blanks were prepared similarly to the ash and coal samples and for all procedures analytical grade reagents were used.

The extracted solution was analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, from SPECTRO ANALYTICAL INSTRUMENTS, model SpectroFlame M120 E). The elemental concentration was determined using analytical curve obtained by multi-element standard solution (from MERCK) following method 6010C [21]. The precision and accuracy of the methodology were evaluated using the SRM 8704 from NIST. It was solubilized following the method 3051A [22], preparing six replicas. The precision, in RSD% values, varied from 1.9% to 10.2% for trace elements (As, Cd, Cr, Mn, Ni, Pb and V), except for Co (19.7%), and 0.6% to 10.1% for major elements (Al, Ca and Mg), except Fe (14.2%) and Ti (17.7%). The accuracy, in Z values, varied from 0.1 to 1.8, except Al (2.5) showing satisfactory accuracy for elemental determination. The limits of quantification, mg kg⁻¹, were 0.005 (Cd, Cr), 0.010 (As, Pb), 0.020 (Co, Cu, Mg, Ti), 0.030 (Mo, V), 0.050 (Mn, Ni), 0.10 (Ca, Zn), 0.20 (Al) and 0.50 (Fe).

2.5. Determination of the available percentage of metals in coal and ashes

The available percentage of metals (expression (1)) represents the amount of metals that can be leached from the coal and ashes to the environment.

% available = \frac{100 \times \text{available metal concentration}}{\text{total metal concentration}} \quad (1)

3. Results and discussion

The pH values for coal and ashes are given in Table 1. The results showed slightly acid coal (average of 5.3), what is expected once this region coal has a high concentration of pyrite, while
ashes showed alkaline pH (9.9–12.1). The acidic characteristic of coal makes the availability of some metals easier, while alkaline property of ashes makes possible the availability of oxygen compounds, such as AsO_4^{3-} and MoO_4^{2-} [23].

The available and total concentration of metal evaluation in coal and ashes were carried out. The term available corresponds to the coal and ashes metal concentration obtained by extraction with EDTA, and specifies the metal availability from coal and ashes to soil and to other environmental compartments. The total concentration corresponds to total metal content in coal and ashes.

The results obtained for the total and available concentration of the major and trace elements in the pulverized coal, bottom ash and fly ash are listed in Tables 2 and 3, respectively. A high total concentration of Zn and As were observed in Figueira coal and the same pattern was observed in ashes. The highest available concentration in coal samples was observed for Zn and Mn, while in ash samples the highest available concentration was observed for As.

Tables 2 and 3 data, the total metal concentrations in coal and ash samples, arranged in decreasing sequence, showed the same behavior for the major and trace elements:

Table 2

<table>
<thead>
<tr>
<th>Elements</th>
<th>Coal</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total concentration (%)</td>
<td>Available concentration (mg kg^{-1})</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>Cyclone</td>
</tr>
<tr>
<td>Al</td>
<td>1.6–2.8</td>
<td>3.4–4.9</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1–0.2</td>
<td>0.3–0.6</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7–2.7</td>
<td>3.9–11.5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.1–0.2</td>
<td>0.2–0.3</td>
</tr>
<tr>
<td>Ti</td>
<td>0.1–0.2</td>
<td>0.2–0.3</td>
</tr>
</tbody>
</table>
the bag filter ash, which had the finest particles.

3.2. Metals enrichment factor in ash

One part of the geochemical behavior of the elements, during coal combustion and in ashes disposal; therefore, As could show high or low mobility to different ecosystems compartments. The behavior for these processes is a reason of concern, due to its high toxicity and tendency of accumulation in the environment. An additional factor contributes for the high mobility of oxyanion compounds, such as AsO$_4^{3-}$ and MoO$_2$$^{4-}$, is the ashes alkaline pH (Table 1).

Different leaching studies, applying diverse leaching methods were carried out in Brazilian coal and ashes. In coal from Leão (RS), high mobility for Cr and Mn, and moderate for Pb, Co, Ni and Cu were observed [27]. Ashes from Charqueadas (RS), pH around 4, presented high concentration of Cr and Zn in leaching solution, but the highest mobility occurred for Mn and lower for Zn and Ni [28]. Sanchez et al. [29] observed that fly ash from the Candida (RS) coal power plant is acid (pH between 4 and 5), and Ni and Cr showed the highest enrichment factor in fly ash. The leaching tests showed high mobility for Mn followed by Cu, Co and Pb. Depoi et al. [24] carried out extraction of elements in ashes from South of Brazil using water. They showed than As and Mo are more extracted of ashes than Cu, Cr, Pb, Zn in extract with pH between 8 and 10. The present study showed that Figueira’s coal, (average pH: 5.3, Table 1), presents a high mobility for Mn and Pb, while the ashes (pH: 9.9–12.1, Table 1) show a high mobility for As and Mo. The above data confirm that different composition and pH of coal and ashes lead to different elements mobility.

3.2. Metals enrichment factor in ash

The As depletion on bottom ash probably occurs by volatilization and later condensation processes on fly ash matrix, because of the decreasing flue-gas temperature. As heterogeneous condensation is a surface area phenomenon, As should be enriched on the thin fly ash particles. In smaller extension, the same behavior is expected for Pb and Cd elements. According to Beck [2], the maximum enrichment occurs on the smallest fly ash particles, apparently due to volatilized compounds re-condensing onto particle surfaces. Since smaller particles have the largest surface to volume ratio, they exhibit the highest enrichment.

Considering the total concentration of all elements in the six samplings, the ratio bag filter ash/coal was determined. The same enrichment factor was observed for the majority of the elements with ratios around 2–3; only elements As, Pb, Zn and Ca showed a higher enrichment factor for the bag filter ash/coal (ratio ~5). The enrichment factor sequence for the trace elements was: As $\geq$ Pb $\geq$ Zn $>$ Mn $>$ Mo $>$ Cu $>$ Cr $>$ Cd $>$ Ni.

According to Coles et al. [3], trace elements in coal are in geological equilibrium in nature. During exploration and combustion process of coal, the physical chemical properties of the elements and their chemical form change in coal and ashes. Therefore, the trace elements in coal and ashes can be more mobile and, consequently, they can increase the risk of environmental pollution.

Chemical and physical properties of the coal change when pulverized and burned at temperatures around 1500 °C. The contained toxic elements can be released to the environment. To understand the post combustion distribution of elements is useful to know each element association with the coal inorganic or organic phases. One part of the geochemical behavior of the elements, during coal formation as well as their chemical behavior during combustion can be explained under groups:

**Group I** is composed by elements such as Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, rare earth elements (Ce, Dy, Eu, La, Nd, Sm, Tb and Yb), Sc, Ta, Th and Ti; they showed little or no enrichment on the small fly-ash particles. Mason [30] classifies these elements as lithophiles. Usually, the lithophilic elements are associated with alumino-silicate minerals. It would be expected that these elements were distributed in the alumino-silicate matrix of the fly ash.

**Group II** is composed by elements such as As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn, where the enrichment factor increases with decreasing particle size. Mason [30] classifies these elements as chalcophiles. The chalcophilic elements are associated with sulfide minerals; they are, as a rule, volatilized during combustion and later condensed onto the smallest fly-ash particles.

**Group III** is composed by elements such as Ba, Be, Co, Cr, Cu, Ni, Sr, U and V and they have intermediate behavior between Groups I and II.

The asymmetry distribution for the several trace elements in coal and ashes in the samples and the enrichment factor, coal to ash, was evaluated by a box plot graphic representation, using the total concentration (Fig. 1). This methodology allows a visualization of the results dispersion in different samples, the range of data variation, the average (–) and the median (–), as well as the comparison between different elements. Fig. 1 showed that, in general, all trace elements have a tendency to enhance their concentration in the same sequence coal $<$ bottom ash $<$ cyclone filter ash $<$ bag filter ash. The highest concentrations were observed in the bag filter ash, which had the finest particles.

According to Coles et al. [3], some of the more volatile trace elements are preferentially re-condensed on smaller particles. Given that As is the most volatile element, is quite depleted on bottom ash and tends to enhance on fly ash. In the coal combustion, most of the alumino-silicate minerals (mostly clay) form a melt and drop out as slag, following the main major elements behavior.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Total concentration (mg kg$^{-1}$)</th>
<th>Available concentration (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coal</td>
<td>Ash Bottom</td>
</tr>
<tr>
<td>Cd</td>
<td>10–25</td>
<td>11–28</td>
</tr>
<tr>
<td>Co</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Cr</td>
<td>57–75</td>
<td>74–101</td>
</tr>
<tr>
<td>Cu</td>
<td>20–31</td>
<td>31–68</td>
</tr>
<tr>
<td>Ni</td>
<td>30–41</td>
<td>50–74</td>
</tr>
<tr>
<td>V</td>
<td>1Q–110</td>
<td>1Q–293</td>
</tr>
</tbody>
</table>

LQ: limit of quantification; nd: not detectable; LQ (V-total): 4 mg kg$^{-1}$.
In relation to Figueira’s (PR) coal, the As, Pb and Zn showed similar behavior with increasing enrichment factor from coal to the bag ash filter (the smallest ash particles), suggesting that these elements are associated to sulfide, and could be classified as chalcophilous. The sulfide associated in Figueira’s coal is probably correlated to a high percentage of arsenical pyrite (FeAsS).

Theis and Wirth [4] studied the behavior of trace metals in fly ash and observed that the adsorption of As, Cr, Cu, Zn were associated to Fe oxide, while Cd and Ni were adsorbed by Mn oxide, contained in the ash coating, and Pb was partially associated to Fe and Mn oxides. Kaakinen et al. [31] suggested that the most volatile elements tend to be enriched more on fly ash surface. According to Theis and Wirth [4] and Kaakinen et al. [31] studies, the results of Figueira’s coal and ashes suggest that the high degree of arsenic concentration were associated to iron, present in arsenical pyrite (FeAsS). Probably, Zn and Pb are also associated to sulfide in pyrite form and like arsenic can be volatile and their condensation on the surface of cooling ash particles could be expected.

3.3. Relation metal–ash–soil

Several toxic metals were associated to coal combustion by products, the most commonly elements of concern are Mo and As, other metals such as Cd and Pb have also been reported due to their toxicity. Elements considered chalcophilic are largely enriched in fly ash and are usually adsorbed on Fe, Mn and Al oxides, present in ash matrix. A potential soil contamination can occur in site disposal by ashes leaching. Metal polluted soils lead to human contamination, either by direct ingestion or through animals and plants. The total metal concentration is not the best way to express the risk of human exposure. The determination of available concentration can be a better way to express the potential toxic concentration available to the environment.

To evaluate the potential risk to soil contamination due to ash disposal, it is important to analyze the results of the total and available concentrations, besides the mobility of the metals in ashes. The major elements are present in a high total concentration in ash, their available concentration is also high, but their mobility in ash is small, except Ca. Considering that the mobility and toxicity of the major elements are low, these elements tend to be strongly connected to ash matrix and contribute with a low risk factor for soil contamination.

On the other hand, the trace elements are present in lower total concentration, but higher available concentration, what established a higher percentage of mobility for these elements (Table 5). These elements tend to be weakly associated to the ash matrix and contribute with high risk factor for the soil contamination due to their leach ability. Based on the trace elements data of Tables 3 and 5, the elements that could be a potential problem for soil contamination are As, Mo and Cd, due to their mobility and toxicity, and with lower risk are the Pb, Zn and Mn elements.

The trace element arsenic is considerate the critical element in ash due to its high available concentration and the availability percentage in ashes. The high toxicity and tendency of accumulation in the environment are a reason for arsenic concern.

According to McBride [32], in aerobic soil the oxidized state (V) for As (arsenate) is more stable. Arsenate shows a similar chemical behavior than phosphate in soils; and it is chemisorbed by Fe and Al oxides. Arsenate is an anion, it is most effectively adsorbed at low pH soil, and consequently its mobility is fairly low in acid soils. Usually, the soil metals adsorption capacity decreases according to the soil acidity, however exception to As and Mo was observed by McBride [32], where their adsorption increases with soil acidity.

When As is leached from ashes and is introduced into the acid soil of Figueira’s [13], this element tend to be adsorbed at the
Zn and Mn elements.

Ashes produced by coal power plants are considered waste and need to be properly disposed to avoid environmental contamination, so it is important to know the mobility of metals in ash. The evaluation of the mobility of the major and trace elements in coal and different types of ashes produced by the Figueira coal power plant showed that As is the most important element of concern to ashes disposal on soil. The results of this study showed a possible soil contamination by As and, in lower extension, by Cd, Mo, Pb, Zn and Mn elements.

4. Conclusion

Ashes produced by coal power plants are considered waste and need to be properly disposed to avoid environmental contamination, so it is important to know the mobility of metals in ash. The evaluation of the mobility of the major and trace elements in coal and different types of ashes produced by the Figueira coal power plant showed that As is the most important element of concern to ashes disposal on soil. The results of this study showed a possible soil contamination by As and, in lower extension, by Cd, Mo, Pb, Zn and Mn elements.

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**References**