Fuel 103 (2013) 430-436

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

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

M. Flues, I.M. Sato, M.A. Scapin, M.E.B. Cotrim, I.M.C. Camargo*

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP Av. Professor Lineu Prestes, 2242, Cidade Universitária, CEP 05508-000, São Paulo, SP, Brazil

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.

ARTICLE INFO

Article history: Received 15 March 2012 Received in revised form 31 August 2012 Accepted 15 September 2012 Available online 4 October 2012

Keywords: Coal Ash Metals mobility

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.

© 2012 Elsevier Ltd. All rights reserved.

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% SiO₂), alumina (5–35% Al₂O₃), ferric oxide (10–40% Fe₂O₃) 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 condensevolatilization 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



^{*} Corresponding author. Tel.: +55 11 31339315; fax: +55 11 31339249. *E-mail address:* icamargo@ipen.br (I.M.C. Camargo).

^{0016-2361/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.fuel.2012.09.045

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 showed 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. Only 20% is considered bottom ash and the remainder as fly ash (80%), comprising different particle sizes; the bag filter ashes are considered the smallest particles.

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 (WDXRFS). 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 EDTA 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.

$$\% \text{ available} = \frac{100 * \text{available metal concentration}}{\text{total metal concentration}}$$
(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

Table 1

 pH_{KCI} range and average for six coal and ashes samples, collected during one year from the Figueira coal plant.

	рН _{ксі}	
	Range	Average
Coal	4.7-6.3	5.3
Bottom ash	9.3-10.4	9.9
Cyclone ash	10.0-13.6	12.1
Bag ash	10.4-13.3	11.9

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 oxyanion compounds, such as AsO_4^{3-} and MOQ_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:

The available concentrations in coal and ash, for major and trace elements, showed the following decreasing sequence concentration:

Availableconcentrationcoal:Majorelements: $Ca \ge Fe > Al \ge Mg \gg Ti$;Trace elements: $Zn > Mn > As > Mo \ge$ Pb > Ni > Cu > Cd > V > Cr > Co.Availableconcentrationinash:MajorCu > Cd > V > Cr > Co.

 $\begin{array}{l} \mathsf{Ca} \geq \mathsf{Al} \geq \mathsf{Fe} > \mathsf{Mg} > \mathsf{Ti}; \ \mathsf{Trace \ elements:} \ \mathsf{As} > \mathsf{Zn} > \mathsf{Mn} > \mathsf{Mo} \geq \mathsf{Pb} > \mathsf{Cr} > \mathsf{V} > \mathsf{Cu} \geq \mathsf{Cd} > \mathsf{Ni} > \mathsf{Co}. \end{array}$

The available concentrations in coal and ash were different from the total metal concentration. This result points to different metal links for coal and ash matrices, therefore the matrices have dissimilar availability sequence.

The variability of the metals concentrations, for each collected coal and ash samples during one year, was evaluated by relative standard deviation from six samples data. The results showed variability from 11% to 21%. The Al, As, Cd, Fe, Mg, Mo and Zn available concentration showed a variability of 50% in coal. In bottom ash, Cu showed variability over 50%, while in cyclone ash, the Cr, Pb and Zn, and in bag ash, the Al, Co, Cr, Pb and V showed variability over 50%. The variability observed in the available concentration in coal, bottom ash, cyclone ash and bag filter ash did not follow the same behavior, indicating that the elements were bound in different ways in coal and in ashes. Therefore, metals probably could reduce or enhance their availability to environment from one fraction to another.

There are few published data about metal concentration of Brazilian coals. In Table 4, the results of Depoi et al. [24] and Levandowski et al. [25], coals from Rio Grande do Sul State (RS), Santa Catarina State (SC) were compared with coal from Figueira, Paraná State (PR). The data showed higher Zn, Cd and As concentration in Figueira's coal than in the other ones. The As high content in the Figueira's coal comes from the high occurrence of pyrite in the Paraná coal.

3.1. Coal and ash metal mobility

According to Carlson and Adriano [26], the most notable feature of ash leachate is the extreme variation in pH range, which can vary from 4.5 to 12. The ash leachate pH determines the solubility of the various trace metals bonded on the surface of the ash particles. Most leach solutions also present high soluble salt concentrations, usually with Ca^{2+} and $SO4^{2-}$ as the dominant cation and anion, respectively. Therefore, depending on the pH different elements will be leached from the coal and ashes.

The available percentage of metals mobility in the Figueira's coal and ash was calculated by expression (1). A metals available percentage sequence is listed in Table 5. The majority of elements presented higher availability in coal (between 98% for Ca and 1% for Al) than in ashes (between 70% for As and <1% for Al and Fe), where As and Mo showed higher availability in ash.

The trace elements Co and V were not presented in Fig. 1, since the available percentage and the enrichment factor for them could not be calculated due to their concentrations are lower than the limit of quantification (LQ).

Arsenic, Ca and Mo had the highest availability (>40% in ash, Table 5), As also showed high available concentration (1323 mg kg⁻¹, Table 3). Zn, Mn, Pb e Cd were less available in ash (<30%) and, in addition, Zn showed high available concentration (360 mg kg⁻¹) while Mn and Pb showed values below 139 mg kg⁻¹. Al and Fe availability percentage, in coal and ash, were low (<5%), but their available concentration is still high (between 17–758 mg kg⁻¹), what could be explained to the high Al and Fe content in coal (total concentration ~ 20.000 mg kg⁻¹).

The As availability is attributed to its structure FeAsS, arsenopyrite, found in coal, which is quite stable, when inside coal, therefore less available to be leached. The total concentration of As in Figueira's coal is high (around 270 mg kg⁻¹) and its geochemical distribution in coal is homogeneous. The variation among the six coal

Table 2

Total and available concentration of metals (major elements) in coal and ash samples collected during one year from the Figueira coal power plant.

Elements	Coal	Total concentration (%) Ash			Coal	Available concentration (mg kg ⁻¹) Ash		
		Bottom	Cyclone	Bag		Bottom	Cyclone	Bag
Al	1.6-2.8	3.4-4.9	6.8-7.9	8.0-9.9	15-492	117-214	80-251	117-758
Ca	0.1-0.2	0.3-0.6	0.8-1.3	0.7-1.4	980-1896	1602-3544	2862-8364	2900-8472
Fe	1.7-2.7	3.9-11.5	3.9-7.5	4.1-5.9	133-2138	163-252	93-238	17-197
Mg	0.1-0.2	0.2-0.3	0.3-0.5	0.4-0.5	48-413	52-80	30-82	55-141
Ti	0.1-0.2	0.2-0.3	0.4-0.5	0.4-0.6	3.2-5.0	12-18	13-26	15-47

M. Flues et al./Fuel 103 (2013) 430-436

Table 3	
Total and available concentration of metals (trace elements) in coal and ash samples collected during one year from the Figueira coal p	ower plant.

Elements	Coal	Total concentration (mg kg ⁻¹) Ash		Coal	Available concentration (mg kg ⁻¹) Ash			
		Bottom	Cyclone	Bag		Bottom	Cyclone	Bag
As	239-328	127-296	380-667	889-1915	7-53	114-321	277-654	618-1323
Cd	10-25	11-28	18-33	32-57	0.8-2.1	0.1-0.2	0.1-1.2	1.2-4.3
Со	nd	nd	nd	nd	0.79-4.7	0.31-0.49	0.25-0.59	0.42 -0.79
Cr	57-75	74-101	99-125	135-181	0.3-1.5	0.3-1.6	0.5-7.0	2-18
Cu	20-31	31-68	37-73	50-88	1.0-6.3	1.4-5.7	0.6-2.4	1.5-3.9
Mn	76-134	239-445	224-714	219-625	36-98	50-139	44-100	26-44
Mo	20-34	17-43	24-54	68-107	5-29	11-20	20-37	29-96
Ni	30-41	50-74	48-85	63-95	1.1-11	0.6-1.1	0.5-1.3	0.7-2.2
Pb	50-107	66-92	95-217	258-627	16-33	5-12	5-17	9-97
Zn	271-711	434-649	674-1081	1309-2453	9-216	64-161	62-326	115-360
V	LQ-110	LQ-293	LQ-231	LQ-207	0.4-2.6	3.0-4.8	3.1-9.9	4.4-14.7

LQ: limit of quantification; nd: not detectable; LQ (V-total): 4 mg kg⁻¹.

samplings was only 14%. After the coal burning, As associated to sulfur is released from the structure of coal and has a tendency to be adsorbed on the ash slight particles, increasing its availability from 25% in coal to 70% in ash. The As structure composition, in natural coal, influences the availability during the mining, combustion and in ashes disposal; therefore, As could show high or low mobility to different ecosystems compartments. The As 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_4^{2-} , 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 occured for Mn and lower for Zn and Ni [28]. Sanchez et al. [29] observed that fly ash from the Candiota (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 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 (\Box) 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 most major elements behavior. 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 \ge Pb \ge 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.

	Rio Grande do Sul			Santa Catarina	Paraná		
	Charqueada ^a	Candiota ^a	São Jerônimo ^a	Capivari de Baixo ^a	Figueira ^a	Figueira ^b	Figueira ^c
Concentratio	$n (mg kg^{-1})$						
As	10.0	8.95	3.99	13.0	166	280-554	239-328
Cd	0.38	0.40	0.13	0.55	1.83	3-4	10-25
C	68.9	24.2	21.6	76.3	30.6	24-31	57 -75
C	5.09	7.29	3.17	6.33	3.82	6-7	pu
Cu	13.9	12.4	12.9	16.1	11.2	17–19	20-31
Mo	2.39	2.08	1.83	2.63	42.9	22-64	20-34
Ni	24.2	13.6	9.59	31.4	21.2	16-18	30-41
Pb	23.7	17.9	8.59	20.8	475	88-147	50-107
Zn	61.2	56.7	27.7	86.3	204	573-931	271-711
Mn	70.2	180	51.6	82.7	45.9	153-180	76-134
Concentratic	(%) uv						
Ca	1.03	0.55	0.54	0.50	0.56	0.66-0.95	0.1-0.2
AI	14.6	9.53	10.6	11.0	4.90	4.65-5.34	1.6-2.8
Fe	1.87	2.58	2.16	2.12	3.84	3.19-5.27	1.7-2.7
^a Depoi [24]. ^b Levandowsl ^c Average val	ki [25]. ue of the present work: nd: no	ot detectable.					

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 chalcophiles. 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 adsorpted at the

Metals concentration in Brazilian coals from Rio Grande do Sul (RS), Santa Catarina (SC) and Paraná (PR) states

 Table 5

 Metals availability sequence (in percentage) for Figueira coal and ash.

Assailahilitas managanta ma

	Availability percentage					
	High > 40%	Median 5–30%	Low < 5%			
Coal Ash	Ca > Mn > Pb As > Mo > Ca	$\label{eq:model} \begin{array}{l} Mo \geqslant Zn \geqslant As \geqslant Ni \geqslant Cu > Cd > Mg \\ Mn > Zn > Cd > Pb \end{array}$	$\begin{array}{l} \mbox{Fe} > \mbox{Cr} > \mbox{Ti} > \mbox{Al} \\ \mbox{Cu} \geqslant \mbox{Cr} \geqslant \mbox{Mg} \geqslant \mbox{Ni} > \mbox{Ti} \geqslant \mbox{Fe} \geqslant \mbox{Al} \end{array}$			



Fig. 1. Total concentration ranging of trace elements (As, Cd, Cr, Cu, Mn, Mo, Ni, Pb, Zn) in coal (cv), bottom (cd), cyclone (c) and bag filter (m) ashes.

top soil. Initially, the foresee showed a contamination of As at the top soil and with the time goes, the high mobility such as Cd and Zn, can migrate from the soil upper lawyer the groundwater.

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.

Acknowledgments

This project received financial support from FAPESP (Fundação de Amparo a Pesquisa de São Paulo). All coal and ash analyses were carried out at the Laboratory of Chemical and Environmental Analyses (Laboratório de Análises Químicas e Ambiental), IPEN-CNEN/ SP. We are grateful to Cambui Coal Company (Companhia Carbonifera Cambui) for the permission to carry out this project.

References

- Block C, Dams R. Study of fly ash emission during combustion of coal. Environ Sci Technol 1976;10(10):1011-7.
- [2] Beck HI. Radiation exposure due to fossil fuel combustion. Radiat Phys Chem 1989;34:285–93.
- [3] Coles DG, Ragaini RC, Ondov JM. Chemical studies of stack fly ash from a coal fired power plant. Environ Sci Technol 1979;13(4):455–9.
- [4] Theis TL, Wirth JL. Sorptive behavior of trace metals on fly ash in aqueous systems. Environ Sci Technol 1977;11(12):1096–100.
- [5] Roy WR, Griffin RA, Dickerson DR, Schuller RM. Illinois basin coal fly ashes. 1. Chemical characterization and solubility. Environ Sci Technol 1984;18:734–9.
- [6] Fernandes ID, Ferret LS, Khahl CA, Endres JCT, Maegawa A. Cryztaline microstructure modification of Brazilian coal ash with alkaline solution. In: International ash utilization symposium. Proceeding of 1999 international ash utilization symposium, Lexington, Kentucky, USA, October 18–20, 1999.
- [7] Ferret LS, Fernandes ID, Khahl CA, Endres JCT, Maegawa A. Zeolitication of ashes obtained from the combustion of Southern's Brazil Candiota coal. In: International ash utilization symposium. Proceeding of 1999 international ash utilization symposium, Lexington, Kentucky, USA, Octember 18–20, 1999.
- [8] Garrabants AC, Kosson DS. Use of chelating agent to determine the metal availability for leaching from soils and wastes. Waste Manage 2000;20:155–65.
- [9] Whitworth DJ, Achterberg EP, Herzl V, Nimmo M, Gledhill M, Wosfold PJ. Development of a simple extraction procedure using ligand competition for biogeochemically available metals of estuarine suspended particulate matter. Anal Chim Acta 1999;392:3–17.
- [10] Janos P, Wildnerova M, Louckab T. Leaching of metals from fly ashes in the presence of complexing agents. Waste Manage 2002;22:783–9.
- [11] Hong KJ, Tokunaga S, Kajiuchi T. Extraction of heavy metals from MSW incinerator fly ashes by chelating agents. J Hazard Mater 2000;B75:57–73.
- [12] Ministério de Minas e Energia. Sumário mineral 1999. Brasília: DNPM; 1999 [ISSN 0101 2053].
- [13] Flues M, Hama P, Fornaro A. Avaliação do nível da vulnerabilidade do solo devido à presença de termelétrica a carvão (Figueira, PR – Brasil). Quim Nova 2003;26(4):479–83.
- [14] Associação Brasileira de Normas Técnicas. Amostragem de resíduos: procedimento. Rio de Janeiro: ABNT; 1987 [NBR 10007].
- [15] Empresa Brasileira de Pesquisa Agropecuária. Manual de métodos de análise de solo. 2nd ed. Rio de Janeiro: EMBRAPA; 1997.
- [16] Lachance GR, Claisse F. Quantitative X-ray fluorescence analysis. Theory and application. London: John Wiley; 1995.
- [17] Beckhoff B, Kanngiesser B, Langhoof N, Wedell R, Wolff H. Handbook of practical X-ray fluorescence analysis. Berlin: Springer; 2006.
- [18] International Organization for Standardization. General requirements for the competence of testing and calibration laboratories. 2nd ed. Geneva: ISO; 2005 [ISO/IEC 17025(E)].
- [19] EURACHEM/CITAC. Quantifying uncertainty in analytical measurements. 2nd ed. London: EURACHEM; 2000.
- [20] Ure AM, Quevauviller PH, Muntau H, Griepink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the European communities. Int J Environ An Ch 1993;51:135–51.
- [21] United State Environmental Protection Agency, USEPA. Method 6010C; 2007. http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/6010a.pdf. [accessed 30.08.12]
- [22] United State Environmental Protection Agency, USEPA. Method 3051A; 2007. http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3051a.pdf> [accessed 30.08.12]
- [23] Querol X, Umaña JC, Alastuey A, Ayora C, Lopez-Soler A, Plana F. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. Fuel 2001;80:801–13.

- [24] Depoi FS, Pozebon D, Kalkreuth WD. Chemical characterization of feed coals and combustion-by-products from Brazilian power plants. Int J Coal Geol 2008;76:227-36.
- [25] Levandowski J, Kalkreuth W. Chemical and petrographical characterization of feed coal, fly ash and bottom ash from the Figueira Power Plant, Paraná, Brazil. Int J Coal Geol 2009;77:269-81.
- [26] Carlson CL, Adriano DC. Environmental impacts of coal combustion residues. J Environ Qual 1993;22:227-47.
- [27] Teixeira EC, Pestana MHD, Sanchez JD, Fernandes I. Geochemical distribution of metallic elements in the mineral matter of Brazilian coals. Environ Technol 1994;15:989-96.
- [28] Teixeira EC, Binotto RB, Sanchez JD, Migliavacca D, Fachel JMG. Environmental assessment and characterization of residues from coal processing and steel industry activities. Fuel 1999;78:1161-9.
- [29] Sanchez JCD, Teixeira EC, Fernandes ID, Pestana MHD, Machado RP. Estudos da concentração e da mobilidade dos elementos metálicos nas cinzas da Usina Termoelétrica de Candiota. Geochim Brasil 1994;8(1):41-50.
- [30] Mason B. Principles of geochemistry. New York: Wiley; 1966.
 [31] Kaakinen JW, Jorden RM, Lawasani MH. Trace-elements behavior in a coalfired power-plant. Environ Sci Technol 1975;9:862-8.
- [32] McBride MB. Environmental chemistry of soils. New York: Oxford University Press; 1994.