



## Heavy metal characterization of CFB-derived coal fly ash

Nikolaos Koukouzas\*, Chrisovalantis Ketikidis, Grigorios Itskos

Centre for Research and Technology Hellas, Institute for Solid Fuels Technology and Applications, 357-359 Mesogeion Avenue, GR-152 31, Halandri, Athens, Greece

### ARTICLE INFO

#### Article history:

Received 5 July 2010

Received in revised form 24 October 2010

Accepted 25 October 2010

Available online 20 November 2010

#### Keywords:

Circulated Fluidized Bed (CFB)

Fly ash

Heavy metals

Leaching tests

Hard coal

### ABSTRACT

The present study investigates the heavy metal content of coal fly ash (FA) samples coming from three different sampling points (secondary cyclone, cooler and filter) of a pilot plant combustion facility. The combustion experiments were carried out in a 0.1 MW Circulated Fluidized Bed (CFB) boiler using South African coal, with the addition of limestone for sulfur capture. FA was tested for the presence of selected heavy metals using inductively coupled plasma optical emission spectrometry (ICP-OES); batch leaching tests were conducted as well. The samples were also characterized in terms of their microstructure, chemical and mineralogical composition, total surface area and particle size distribution. Most of the studied metals (Cd, Cr, Cu, Ni, Mn, Zn) showed enrichment in the fine, filter FA particles, while Pb was mostly concentrated in the cooler sample. Regarding leaching characteristics of the examined samples, Cr was found to occur in considerable amounts. Although the use of CFB technology for the combustion of solid fuels steadily gets bigger worldwide, only a very limited number of studies have environmentally assessed CFB-coal FAs to date. Thus, the current study aims to contribute toward building a more integrated knowledge on the environmental impact of this abundant power production by-product.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

The rate of implementation of Circulated Fluidized Bed (CFB) technology for the combustion of solid fuels continuously increases, mainly thanks to its environmental-friendly impact (reduced emissions of NO<sub>x</sub> and in situ desulfurization ability) [1–6]. Thus, the global amounts of CFB-derived coal fly ash (FA) steadily increase. However, only a limited number of studies have environmentally assessed such FAs to date [7–10]. Management and landfill of fly ash from coal-fired power plants are of major environmental concern, mainly because of potential contamination caused by the possible release of harmful elements. Indeed, due to the high quantities of FA that are globally produced, and cannot get totally absorbed by market, a common practice continues to be stockpiling in mine dumps or specific disposal mounds [11]. As fly ash contains elevated soluble major and trace elements that could adversely affect plant and soil quality, rain and other waterways provide a pathway for potentially toxic trace elements to re-enter the food chain and human life cycle from these disposal sites [12].

The physical and chemical characteristics of fly ash, combined with the operational parameters of the power plant and the disposal environments in which the ashes are placed, control the leaching susceptibility of these wastes and determine the potential for contamination to groundwater aquifers [13]. In order to simulate

the leaching behavior of CFB-fly ash in different environmental conditions and to reduce deviation between measurements in the fields and the laboratories, two standard leaching tests were selected to be applied in this study. Given the relevance of the leaching properties of fly ash in terms of waste management, the main objectives of this study were to identify some of the constituents of environmental concern included in the fly ash samples, to evaluate the leaching characteristics of heavy metals from the samples selected, and to assess their environmental characteristics taking into account the new EU regulations on landfilling.

### 2. Materials and methods

#### 2.1. Preparation of raw ash samples

The tested solid samples were derived from firing South African coal with the addition of limestone for sulfur capture (Ca/S: 1.85, load: 100%). Table 1 shows the proximate and ultimate analysis results of the fired coal as well as its heating value. South African coals are generally hard, normally presenting high calorific content and low ash content. Coal fired for the purposes of this study had a net heating value of approximately 6400 kcal/kg.

Pilot plant experiments were conducted at a 0.1 MW CFB reactor operated by VTT (the Technical Research Centre of Finland) at atmospheric pressure. The Riser diameter was 0.17 m and its length 8.0 m. Bed material was natural sand, with particle sizes ranging between 0.1 and 0.3 mm and mean diameter 0.20 mm. Representative FA samples from three different points were collected: at the secondary

\* Corresponding author. Tel.: +30 210 6501771; fax: +30 210 6501598.

E-mail addresses: [koukouzas@certh.gr](mailto:koukouzas@certh.gr) (N. Koukouzas), [ketikidis@lignite.gr](mailto:ketikidis@lignite.gr) (C. Ketikidis), [itskos@certh.gr](mailto:itskos@certh.gr) (G. Itskos).

**Table 1**  
Average characteristics of feedcoal (air-dried basis).

<i>Proximate analysis and heating values</i>	
Ash (%)	<15
Volatiles (%)	23–26
Fixed carbon (%)	44–60
Gross heating value (kcal/kg)	6500–6700
Net heating value (kcal/kg)	~6400
<i>Ultimate analysis</i>	
C (%)	68–72
H (%)	3.5–4.5
N (%)	1.5–1.65
O (%)	6.5–8.5
S (%)	0.80

cyclone, the cooler (gas cooling system, probe-assisted sampling) and the filter (bag house) of the facility; five samples were collected by each point and the average values of the analyses are given as the respective final results. Bed temperature was approximately 860 °C; points of temperature in second cyclone and filter were in the region of 900 and 850 °C respectively.

## 2.2. Fly ash characterization

The (%) concentration of the major elements in the solid residues was determined by means of X-ray fluorescence (XRF), using a Spectro X-Lab 2000 Energy Dispersive spectrometer applying the samples in a pressed powder form. The collected samples were tested for the presence of the following elements: Pb, Cd, Ni, Cr, Cu, Zn, Mn, Co and As. For determining the trace element concentration, microwave-assisted acid digestion (MW-AD) of FA samples, followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) examination, was applied. As coal contains an appreciable amount of inorganic matter, which mainly consists of aluminosilicate [14], a combination of bulk HNO<sub>3</sub>, HCl and HF was employed for digestion; H<sub>3</sub>BO<sub>3</sub> was afterwards added for removing HF from the reaction mixture. MW-AD was carried out by using a CEM MDS 2000 oven. ICP-AES measurement was performed using a Perkin-Elmer Optima 4300 DV instrument. Digestion procedure included weighting a 0.1 g portion of each FA sample and transferring it into a pressure-resistant PTFE vessel. Then, the acid mixture (3 ml HF, 2 ml HCl and 2 ml HNO<sub>3</sub>) was added. Samples were evenly spaced in the microwave oven carousel and the digestion program was set as listed in Table 2 (Stage 1). The vessels were afterwards removed and carefully vented in a fume hood after they were cooled in a water bath, at room temperature. An amount of 25 ml H<sub>3</sub>BO<sub>3</sub> was afterwards added to each sample. The vessels were returned to the microwave and the second processing was applied to the samples under the conditions described in Table 2 (Stage 2). It is mentioned that H<sub>3</sub>BO<sub>3</sub> was added for the removal of HF because its presence in the sample solution normally poses problems for atomic spectrometry instruments, since the ICP torch and injector are usually quartz made.

The particle size of the ashes was measured with a Malvern Mastersizer-S particle size analyzer using the wet dispersion method in water. Morphology was observed using a JSM-6300 JEOL scanning

**Table 2**  
Microwave-assisted digestion program.

Settings	Stage 1	Stage 2
Power (%)	100 (for 12 vessels)	85 (for 12 vessels)
Pressure (psi)	120	50
Time <sup>a</sup> (min)	25	25
Tap time <sup>b</sup> (min)	15	10

<sup>a</sup> Time interval required to reach the set point of pressure.

<sup>b</sup> Time where the sample remains at the set pressure.

electron microscope (SEM) equipped with an Energy Dispersive X-ray Spectrometer with an Oxford Link ISIS system operated with the typical accelerating voltage of 20 kV. The samples were carbon coated and analyzed using the backscattered electron mode (BSE).

## 2.3. Batch leaching tests

Leachability of heavy and toxic elements was determined in deionized water by applying the European standard test: EN 12457-2 (2002) [15], as well as in CH<sub>3</sub>COOH/NaOH buffer solution (pH = 2.88 ± 0.05) with the application of the U.S. EPA TCLP Method 1311 (1992) [16]. The pulp pH was determined in a suspension of fly ash in deionized water at 25 °C and 2% w/v pulp density. Filter fly ash samples, which were found to have the highest heavy metal content among the types of CFB coal fly ash, were selected to undergo the batch leaching tests which were carried out based on the principles laid out in standard procedures. The extract was transferred into a bottle and stored in a cool dry place for further analysis by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) in the case of Pb, Cd, Ni, Cr, Cu and Mn (minimum reporting limit: 1 ppb) and by Flame Atomic Absorption Spectroscopy (FAAS) in the case of Zn (minimum reporting limit: 50 ppb). In the applied tests, the suspension made by the leaching agent and the solid sample was continuously agitated, and it is assumed that equilibrium was reached by the end of the test. The tests used different leaching agents, leaching solution to solid sample (L/S) ratios, contact times, and pH (Table 3). The TCLP 1311 [15] test uses a relatively weak acid (acetic acid), while the EN 12457-2 [14] test uses the weakest leaching agent (deionized water).

## 3. Results and discussion

### 3.1. Characterization of raw fly ash

Table 4 shows the average chemical composition of the ash samples along with their loss on ignition (LOI) content. Table 5 shows the average specific surface area of the samples as well as the temperature values before and after each sampling.

First of all, it should be mentioned that the temperature at the sampling point of filter FA (bag filter) is apparently much lower than the respective ones at cyclone and cooler. Fly ash samples from cyclone and cooler are intensely siliceous; percentage presence of SiO<sub>2</sub> was by 24% and 23% higher than filter ash respectively. Regarding Al<sub>2</sub>O<sub>3</sub> of cyclone and cooler FA, it was by 35% and 22% higher than filter ash respectively. Reasonably, filter ash was clearly more calcareous than the other two types of samples. In fact, due to the over 10% presence of CaO, filter ash is classified as Class C ash according the ASTM C618, while cyclone and cooler FA lied within the Class F classification margin. CaO of fly ash is attributed to the calcareous minerals of feedcoal (mainly calcite) [17]. CaO (both total and free) is mostly generated through the thermal disruption of calcite (CaCO<sub>3</sub>), a fraction which can be autogenic and give monocrystals as it is first burned in the boiler and it is afterwards reformed as microcrystalline secondary calcite during FA particles-flue gases co-transfer to the chimney [17]. Fe<sub>2</sub>O<sub>3</sub> in coal fly ash, mainly owes its presence to the mineral hematite of feedcoal; Fe<sub>2</sub>O<sub>3</sub> (%) of

**Table 3**  
Comparison of batch leaching tests applied.

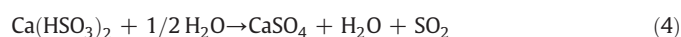
Test conditions	TCLP 1311	EN 12457-2
Leachant	Acetic acid	De-ionized water
Liquid to solid ratio	20	10
Leaching time (h)	18	24
pH control	2.88	Not a factor
Agitation method	Tumbler	Tumbler
Temperature (°C)	25	25
Number of extractions	1	1

**Table 4**  
Major oxides (wt.% on a dry basis) and fineness of the tested fly ash samples.

Ash fraction/Oxides	Cyclone fly ash	Cooler fly ash	Filter fly ash
SiO <sub>2</sub>	47.48	46.92	36.02
Fe <sub>2</sub> O <sub>3</sub>	2.08	2.97	5.08
Al <sub>2</sub> O <sub>3</sub>	33.95	28.24	21.96
TiO <sub>2</sub>	1.11	0.93	0.86
CaO	5.53	8.30	10.79
MgO	1.53	0.61	1.23
SO <sub>3</sub>	3.15	3.24	2.89
P <sub>2</sub> O <sub>5</sub>	2.40	2.49	2.18
Na <sub>2</sub> O	0.38	0.66	0.95
K <sub>2</sub> O	0.70	1.80	2.24
Loss on ignition (LOI)	1.70	3.50	15.60
Fineness (%; +45 μm)	12.5	8.5	6

filter ash was more than double the respective amount of cyclone ash and much higher than that of cooler ash as well. The previously described differentiation in the chemical composition of ashes is attributed, not only to the variation in thermal conditions of sampling points, but also to the their different particle size distributions; the direct interconnection of particle size and concentration of specific oxides is already well-verified in the case of pulverized coal combustion technology (PCC) [18].

Increased percentage presence of SO<sub>3</sub> in the tested ash samples is attributed to the limestone-assisted desulfurization process during coal firing in the CFB pilot plant. Actually, desulfurization reactions driven by CaCO<sub>3</sub> and CaO are likely to have led to the formation of CaSO<sub>4</sub> (Reactions 1–4 [18]), due to the bonding between sulfur oxides and calcium. It should also be mentioned that increased LOI of filter sample may also be a result of the experimental thermal disruption of calcite.



Experimentally obtained values of specific surface area (SSA) of the tested ash samples are directly linked to their particle fineness; increased SSA of particular (partially unburned) FA particles may also be attributed to the porosity formed within their mass due to volatile release within the boiler. It should be mentioned that increased SSA of FA inductively leads to its lower transportation cost when utilized in commercial applications.

Results of the heavy metal analysis of the samples are presented in Table 4. Trace elements were almost equally distributed between cyclone and cooler ash. Concentration of heavy metals was highest in filter ash, except for Pb that was found to be intensely present in the cooler ash. As shown in Table 3, the cyclone operates at high points of temperature, between 760 °C and 820 °C. The cooler operates at temperature points between 280 °C and 760 °C. The temperature at which filter ash is precipitated is again lower than those in the cooler ash (130–150 °C). At those levels of temperature, desublimation and condensation of volatile metals and their compounds [19] take place

**Table 5**  
Specific surface area (m<sup>2</sup>/g) of samples and temperature at each sampling point.

Ash fraction	Cyclone fly ash	Cooler fly ash	Filter fly ash
BET/N <sub>2</sub> specific surface area	4.1	12.1	17.9
Temperature (°C) before /after sampling point	820/755	755/277	152/131

or it is already completed [20–22]. Thus, the heavy metal content in the filter ash seems to be elevated compared to the respective content of the cyclone ash or cooler ash. The results of the current research study are compared with the ranges of heavy metal concentration reported in the literature for fly ash. Data were collected at power plants burning fuel of equal rank and applying the same combustion technology (Table 6).

Kouvo and Backman [23] report that emissions of heavy metals are not necessarily related to the trace metal concentration of the fuel used. The emission is rather a result of a complex system combining (a) the bed history and its metal concentrations due to it, i.e. the saturation state of the metal of interest in the bed, (b) incineration temperature, (c) fuel ash content and composition, (d) fuel density and (e) chlorine and sulfur content of the fuel that is known to have an influence on volatilization of the trace metals. As aforementioned, trace elements were found to be enriched in the finer filter particles except for lead, which is abundant in the coarse cyclone ash. It is worthwhile noticing that the lead capture of the bed sand gets its maximum value of 72% at the incineration temperature of around 700 °C. At lower and higher incineration temperatures, the capture (Reactions 1–4) decreases [24,25].

At ~730 °C, most sulfur will react with oxygen to form either SO<sub>2</sub> (g) or SO<sub>3</sub> (g); Between 730 and 910 °C, most sulfur will react with CaO to form CaSO<sub>4</sub> (s). Most lead will react with sulfur to form PbSO<sub>4</sub> (s) at temperatures below about 730 °C. Between 730 and 820 °C, most lead will form PbO (s); and above 820 °C lead will be in the form of PbO (g). Moreover, a significant difference between the combustion temperatures in various combustion systems, i.e. ~1500 °C in PCC and ~850 °C in FBC (Fluidized Bed Combustion) systems, indicates different properties of the ashes [26]. Because of the lower temperature, fewer amounts of trace elements are in the vapor phase in FBC. In addition, a portion of the Ca in limestone is unutilized and remains in ash as CaO [27]. Another portion of Ca reacts with the acidic components of the ash, thus changing its leachability. In the presence of limestone, a change in the distribution in favor of the solid phase was observed for Pb. The results suggest that little Pb will be emitted in the vapor phase. If released to the environment [26] this element will most likely be in the stack gas as part of the dust which was not removed in the system.

The samples that have the highest trace element concentration were also those with the finest particles, captured at the bag house of the facility. The fine particles in coal ash play an important role above their weight concentration because of their large active surface area [28]. This is significant both in terms of leaching and physical

**Table 6**  
Comparison of values of heavy metal concentrations obtained in this study with those reported in literature (mg/kg; d.w.).

Element	Ash fraction			Bed ash and fly ash Lecuyer et al., 2001 [10]	Barthoňová et al., 2007 [8]	
	Cyclone fly ash	Cooler fly ash	Filter fly ash	Local lignite/hard coal	Bituminous coal Fly ash	Bottom ash
Pb	70	80	20	0.2–74	168	53
Cd	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	0.03–2.0	nr <sup>b</sup>	nr <sup>b</sup>
Ni	100	115	135	16–79	108	48
Cr	139	170	254	4.0–92	115	88
Cu	65	65	95	4.4–66	159	91
Zn	54	49	85	19–155	nr <sup>b</sup>	nr <sup>b</sup>
Mn	348	325	393	nr <sup>b</sup>	nr <sup>b</sup>	nr <sup>b</sup>
Co	33	31	43	nr <sup>b</sup>	nr <sup>b</sup>	nr <sup>b</sup>
As	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	7.6–135	29	9.4

<sup>a</sup> Not detected by means of AAS.

<sup>b</sup> No reference.

properties. In this context computerized scanning electron microscope feature analysis was applied to characterize these particles. Figs. 1–3 show SEM micrographs of the fly ash samples. According to Paya et al. [29], the typical vesicular structure is attributed to the volatilization process of the low molecular weight fraction from the original coal particles is observed.

Unfused mineral particles were mostly quartz (Fig. 1a and b) and were readily recognized in reflected light by their low reflectance and polishing relief (they are harder than most of other constituents of fly ash). They were relatively large particles, occupying the silt-size range (4–150  $\mu\text{m}$ ), and many displayed the sub-angular to sub-rounded morphologies.

Figs. 2 and 3 show highly irregular skeletal or spongy particles. Particles of this type were also commonly visible as cavity fillings within large fragments. Investigation with SEM at magnifications of 6000 (Figs. 2b and 3b) revealed the presence of numerous micron-sized bubbles and cavities dispersed throughout the material. These fine bubbles probably contain structural water that was liberated during decomposition and partial fusion of hydrous minerals [30].

As shown in Fig. 4 fly ashes show bi-modal particle size distributions (also observed in the past by Jankowski et al. [31]), with the main peak at 4  $\mu\text{m}$  for filter fly ash, at 12  $\mu\text{m}$  for cooler fly ash and at 15  $\mu\text{m}$  for cyclone fly ash respectively. In all cases a secondary peak is observed between 0.2 and 0.3  $\mu\text{m}$ . The particle size distribution is an important property of fly ash, with the smaller particles having greater surface areas. Size distribution is important during the interaction of the ash with different solutions, since it

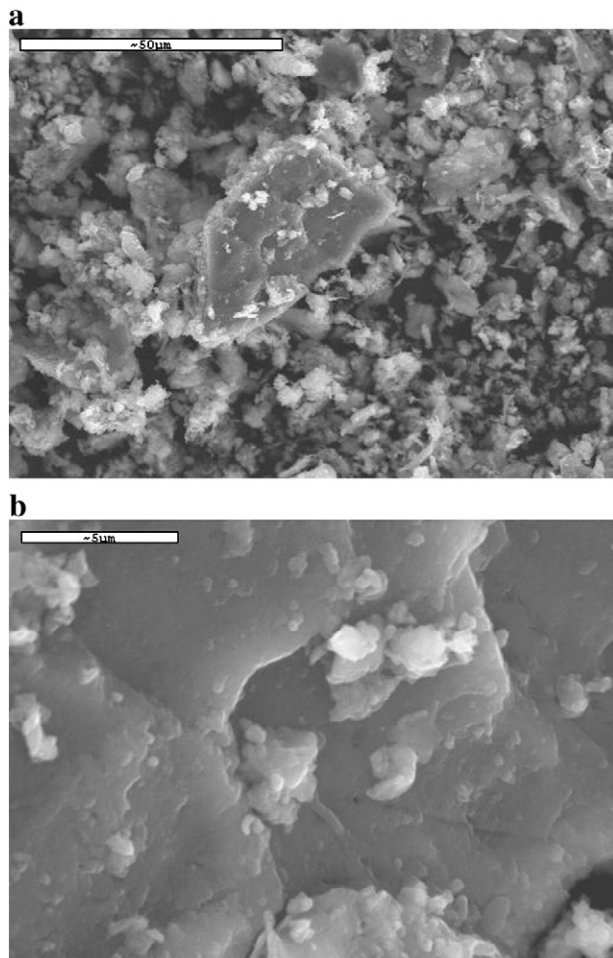


Fig. 1. Micro morphology of cyclone fly ash: magnified (a)  $1 \times 10^3$  and (b)  $6 \times 10^3$ .

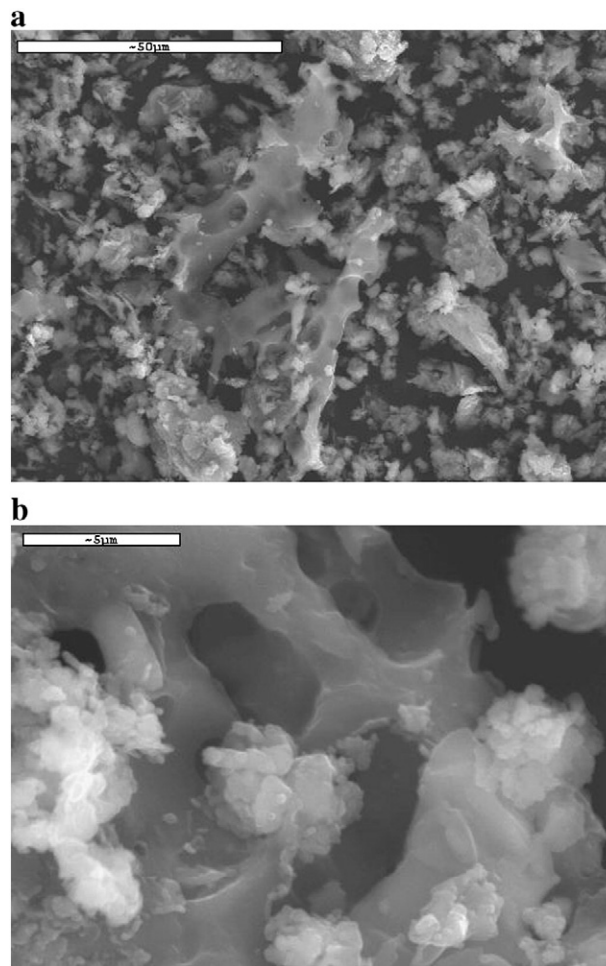


Fig. 2. Micro morphology of cooler fly ash: magnified (a)  $1 \times 10^3$  and (b)  $6 \times 10^3$ .

affects the mobilization of any trace elements on the surface of particles. Itskos et al. [28] report that chemical and physical properties, and subsequently the industrial-utilization potential, greatly vary as a function of the particle size distribution of ashes.

As aforementioned, the fly ash samples were collected at three sampling points: secondary cyclone, cooler and filter (bag house), thus some differences occurred with respect to the chemical and morphological composition of the material. In general, circulating beds use a higher fluidizing velocity and consequently the particles are constantly held in the flue gases, and pass through the main combustion chamber and into a cyclone, from which the larger particles are extracted and returned to the combustion chamber. Because of the recirculation of the bed material, particle residence times are relatively long compared to the gas residence time, and can be measured in tens of seconds [32]. As was shown in Table 4, cyclone ash particles contain less potassium than filter ash particles. This can be explained by the fact that alkali vapor condenses over the filter deposited fly ash rather onto the cyclone ash that circulates in the high temperature flue gas. Additionally, filter ash exhibits lower particle size (Fig. 4) and correspondingly higher specific surface area in comparison to the cyclone ash (Table 5). This sample has therefore a higher adsorptive potential. Concerning filter ash, it is worthwhile mentioning that the flue gas temperature of the bag filter is limited due to the existence of the cooler in order to avoid damage to the bags themselves. This fact can contribute toward trace element capturing, by allowing further condensation of volatile species. It is also possible that a proportion of trace elements remaining in the vapor phase will also be removed due to adsorption by the collected 'dust cake'.

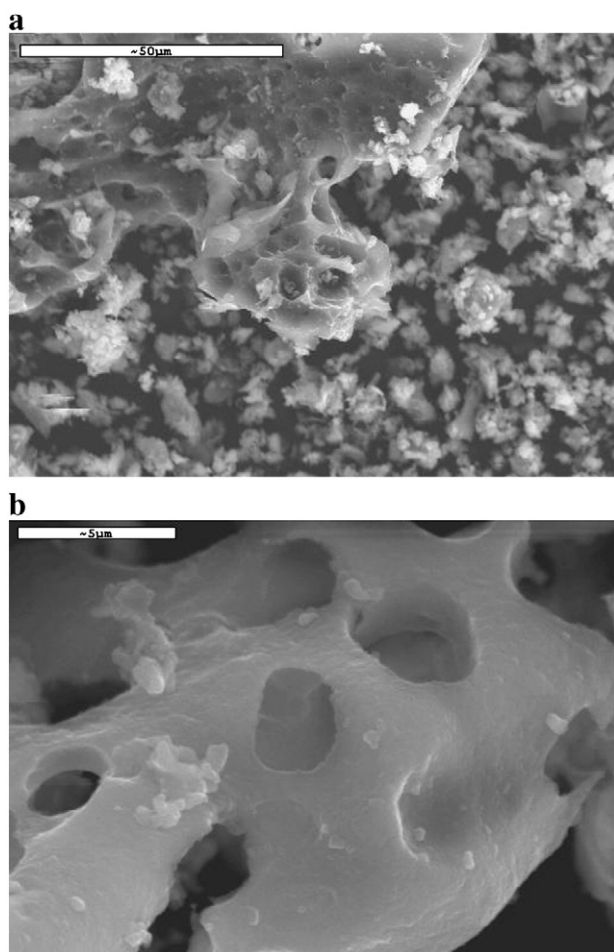


Fig. 3. Micro morphology of filter fly ash: magnified (a)  $1 \times 10^3$  and (b)  $6 \times 10^3$ .

### 3.2. Leaching of heavy metals

Table 7 presents the results of the EN 12457-2 and TCLP 1311 leaching tests for the selected filter fly ash sample. All elements showed higher leaching rates under the TCLP 1311 test than EN 12457-2. This is due to the acidic conditions of the TCLP leaching test. Under these conditions pH has a great impact on mobility of trace elements from fly ash samples. In addition to pH, redox potential, liquid-to-solid ratio and leachant type have a great impact on the stability of leachable trace elements in fly ash under these two leaching tests as well as fly ash structure and properties [33]. On the

**Table 7**  
Leachability of heavy metals from filter fly ash.

TCLP 1311			EN 12457-2		
Element	Leaching capacity (mg/kg; d.w.)	Regulatory level (mg/L)	Element	Leaching capacity (mg/kg; d.w.)	Toxicity limits (mg/kg)
					IW <sup>a</sup> NHW <sup>b</sup> HW <sup>c</sup>
Pb	0.74	0.75 <sup>d</sup>	fPb	0.10	0.5 10 50
Cd	0.10	0.11 <sup>d</sup>	Cd	nd <sup>e</sup>	0.04 1 5
Ni	0.48	11.00 <sup>d</sup>	Ni	nd <sup>e</sup>	0.40 10 40
Cr	0.95	0.60 <sup>d</sup>	Cr	0.62	0.5 10 70
Cu	1.91	1.0 <sup>f</sup>	Cu	nd <sup>e</sup>	2 50 100
Zn	0.99	4.3 <sup>d</sup>	Zn	0.90	4 50 200
Mn	3.07	0.05 <sup>f</sup>	Mn	1.22	

<sup>a</sup> Inert waste.

<sup>b</sup> Non-hazardous waste.

<sup>c</sup> Hazardous waste.

<sup>d</sup> Values according to the US EPA Land Disposal Restrictions.

<sup>e</sup> Not detected by means of AAS.

<sup>f</sup> Values according to the US EPA National Secondary Drinking Water Standards.

other hand, the relative concentration of calcite and clays in coal is one of the most influential factors on the leaching behavior of fly ash. Because of their high pH, ashes that contain free CaO have leaching properties and potential for contamination very different from those ashes where free CaO is non-existent or present at insignificant quantities [34]. The reason for the difference is that the leaching of most trace elements is pH dependent.

As shown in Table 7, the raw material was not leached in an extent higher than the maximum allowed limits imposed by the European legislation for solid wastes. The results showed that there was no any serious leaching of main constituent metals with the exception of Cr regarding both the TCLP and the EN tests. The leaching capacity of this metal is slightly above the toxicity level for inert wastes, but far from being considered as a non-hazardous waste. With respect to the TCLP test, it is worth pointing out that the copper and manganese amount leached show higher values than the respective ones proposed by the US EPA National Secondary Drinking Water Standard. The latter belongs to the non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor or color) in drinking water, since a TCLP EPA maximum for land disposal has not been established. In addition, the results of the analyses indicate that coal ash used herein is very similar to alkaline coal ash produced elsewhere [33] and that, for most toxic elements, it does not present any potential contamination danger. Only chromium approaches limit values, as already mentioned above. Regarding the TCLP 1311 test, the final pH of the leachate is variable depending on the CaO content of the ash

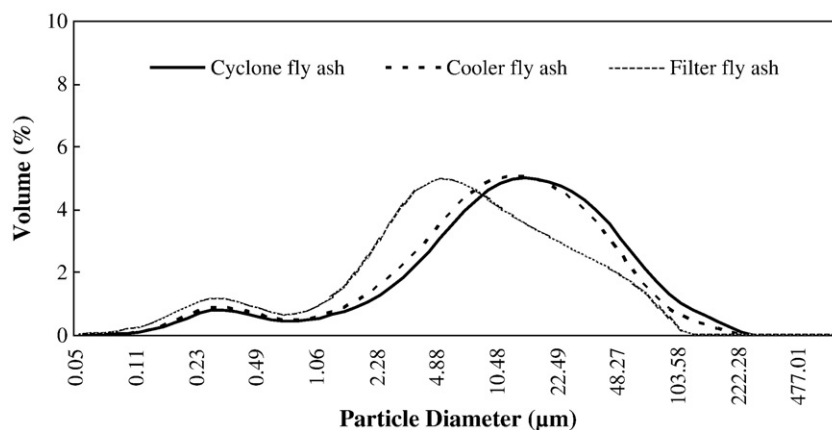


Fig. 4. Particle size distribution of the fly ash samples.

and the comparison between leachates is therefore not strictly accurate and the final pH should always be included in the leaching results. This is due to the sharp changes in solubility of many elements as a function of pH. The TCLP test has a further disadvantage for some elements such as chromium. Less chromium is extracted at very low pH (4 and less) than under slightly acidic conditions (pH 5–7).

#### 4. Conclusions

The main conclusions of the current research study can be summarized as follows:

- The examined fly ash samples had two particle modes: (a) coarse in the secondary cyclone and (b) fine in the filter fly ash. Those two particle modes were accompanied by inversely proportional values of specific surface area: low in the case of secondary cyclone ash and high in this of filter ash.
- The heavy metal content evaluation of the fly ash samples indicated their enrichment in the fine particles of the filter ash, with the exception of Pb which was mostly concentrated in the cooler ash (due to the lower temperature after the cooler with a concomitant condensation of flue gas in this region). In this context, it is of great importance for the environmental consequences of the heavy metals that conventional particle-removal devices effectively capture the fine fly ash particles, which means that they will also capture the incorporated heavy metals.
- Leaching evaluation of the filter ash samples showed that Cr concentration was in considerable amounts, with respect to the EN conditions. Under the TCLP conditions, Cr exceeded the EPA Land Disposal Restriction Limit while Cu and Mn were found to be on the high level regarding the US EPA National Secondary Drinking Water Standard. In general, trace elements were found to be more mobile under TCLP conditions, the results of which indicated the worst case scenario, due to strongly acidic conditions in comparison to EN 12457-2.
- Chromium should be carefully monitored. In general, leaching experiments showed that the elemental composition of the leachate may not proportionally reflect the elemental composition of the whole ash sample (the rate at which the elements will leach from the ash sample is dependent on the form in which the element is present and the location of the element within the ash matrix or absorbed onto the ash particle surface).

#### Acknowledgments

The authors gratefully acknowledge financial support from the European Commission, Research Fund for Coal and Steel, under contract number RFCR-CT-2005-00009, as well as the Technical Centre of Finland (VTT) for the accomplishment of combustion experiments. Mr Papandreu, Ms Kanellopoulou and Dr Stathopoulos of CERECO are also acknowledged for their valuable contribution towards the experimental determination of heavy metals concentration.

#### References

- [1] N. Koukouzas, Ch. Vasilatos, G. Itskos, I. Mitsis, A. Moutsatsou, Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials, *Journal of Hazardous Materials* 173 (1–3) (2010) 581–588.
- [2] N. Koukouzas, J. Hämäläinen, D. Papanikolaou, A. Tourunen, T. Jäntti, Mineralogical and elemental composition of fly ash from pilot scale fluidised bed combustion of lignite, bituminous coal, wood chips and their blends, *Fuel* 86 (14) (2007) 2186–2193.
- [3] N. Koukouzas, C.R. Ward, D. Papanikolaou, Z. Li, C. Ketikidis, Quantitative evaluation of minerals in fly ashes of biomass, coal and biomass–coal mixture derived from circulating fluidised bed combustion technology, *Journal of Hazardous Materials* 169 (1–3) (2009) 100–107.
- [4] A. Nikolopoulos, D. Papafioti, N. Nikolopoulos, P. Grammelis, E. Kakaras, An advanced EMMS scheme for the prediction of drag coefficient under a 1.2 MWth

- CFBC isothermal flow: Part I. Numerical formulation, *Chemical Engineering Science* 65 (13) (2010) 4080–4088.
- [5] A. Nikolopoulos, K. Atsonios, N. Nikolopoulos, P. Grammelis, E. Kakaras, An advanced EMMS scheme for the prediction of drag coefficient under a 1.2 MWth CFBC isothermal flow: Part II. Numerical implementation, *Chemical Engineering Science* 65 (13) (2010) 4089–4099.
- [6] A. Nikolopoulos, I. Rampidis, N. Nikolopoulos, P. Grammelis, E. Kakaras, Numerical investigation of 3-D transient combustor flow in a 1.2MWth pilot power plant, *Proceedings of the 20th International Conference on Fluidized Bed Combustion*, 2009, pp. 839–844.
- [7] A. Baba, G. Gurdal, F. Sengunalp, Leaching characteristics of fly ash from fluidized bed combustion thermal power plant: case study: Çan (Çanakkale-Turkey), *Fuel Processing Technology* 91 (9) (2010) 1073–1080.
- [8] L. Bartoňová, Z. Klika, D.A. Spears, Characterization of unburned carbon from ash after bituminous coal and lignite combustion in CFBs, *Fuel* 86 (3) (2007) 455–463.
- [9] G. Skodras, P. Grammelis, M. Prokopidou, E. Kakaras, G. Sakellariosopoulos, Chemical, leaching and toxicity characteristics of CFB combustion residues, *Fuel* 88 (7) (2009) 1201–1209.
- [10] I. Lecuyer, S. Gueraud, J.M. Bursi, Different uses of CFB ash-EDF investigations, 42nd IEA-FBC Meeting, Sydney, Nova Scotia, Canada, May 10–11 2001.
- [11] S. Tsimas, A. Moutsatsou-Tsima, High calcium fly ash as the forth constituent in concrete: problems, solutions and perspectives, *Cement & Concrete Composites* 27 (2005) 231–237.
- [12] A. Georgakopoulos, A. Filippidis, A. Kassoli-Fournaraki, Leachability of major and trace elements of fly ash from Ptolemais Power Station, Northern Greece, *Energy Sources* 24 (2202) 103–111.
- [13] D.A. Kopsick, E.E. Angino, Effect of leachate solutions from fly and bottom ash on groundwater quality, *Journal of Hydrology* 54 (1981) 341–356.
- [14] A. Iwashita, T. Nakajima, H. Takanashi, A. Ohki, Y. Fujita, T. Yamashita, Effect of pretreatment conditions on the determination of major and trace elements in coal fly ash using ICP-AES, *Fuel* 85 (2) (2006) 257–263.
- [15] EN 12457-2, Characterisation of waste-leaching-compliance test for leaching of granular waste materials and sludge: Part 2. One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm, European Committee for Standardisation, 2002.
- [16] US EPA, Toxicity Characteristic Leaching Procedure (TCLP), Method 1311, 1992.
- [17] G. Itskos, N. Koukouzas, Ch. Vasilatos, I. Megremi, A. Moutsatsou, Comparative uptake study of toxic elements from aqueous media by the different particle-size-fractions of fly ash, *Journal of Hazardous Materials* 183 (1–3) (2010) 787–792.
- [18] G. Itskos, S. Itskos, N. Koukouzas, Size fraction characterization of highly-calcareous fly ash, *Fuel Processing Technology* 91 (11) (2010) 1558–1563.
- [19] M. Narodoslawsky, I. Obernberger, From waste to raw material - the route from biomass wood ash for cadmium and other heavy metals, *Journal of Hazardous Materials* 50 (1996) 157–168.
- [20] A. Nordin, P. Schager, B. Hall, Mercury speciation in flue gases; a comparison of results from equilibrium calculations with results from laboratory experiments, *Proc. Finnish/Swedish Flame days*, Abo, Finland, 1990.
- [21] D. Tillman, *Trace Metals in Combustion Systems*, Academic Press, CA, USA, 1994.
- [22] A.M. Ure, C.M. Davidson (Eds.), *Chemical Speciation in the Environment*, Chapman and Hall, New York, 1995.
- [23] P. Kouvo, R. Backman, Estimation of trace element release and accumulation in sand bed during bubbling fluidized bed co-combustion of biomass, peat, and refuse-derived fuels, *Fuel* 82 (2003) 741–753.
- [24] T.C. Ho, C. Chen, J.R. Hopper, D.A. Oberacker, Metal capture during fluidized bed incineration of wastes contaminated with lead chloride, *Combustion Science and Technology* 85 (1992) 101–116.
- [25] T.C. Ho, T.C. Chuang, S. Chelluri, Y. Lee, J.R. Hopper, Simultaneous capture of metal, sulfur and chlorine by sorbents during fluidized bed incineration, *Waste Management* 21 (2001) 435–441.
- [26] E. Furimsky, Characterization of trace element emissions from coal combustion by equilibrium calculations, *Fuel Processing Technology* 63 (2000) 29–44.
- [27] M. Hartman, K. Svoboda, Reactions of calcium hydroxide with sulphur dioxide at high temperatures, *International Journal of Chemical Engineering* 24 (1984) 759–764.
- [28] G. Itskos, S. Itskos, N. Koukouzas, The effect of the particle size differentiation of lignite fly ash on cement industry applications, 3rd World of Coal Ash, WOCA Conference - Proceedings, 2009.
- [29] J. Paya, J. Monzo, M.V. Borrachero, E. Ferris, F. Amahjour, Thermogravimetric methods for determining carbon content in fly ashes, *Cement and Concrete Research* 28 (1998) 675–686.
- [30] A.R. Ramsden, M. Schibaoka, Characterization and analysis of individual fly-ash particles from coal-fired power stations by a combination of optical microscopy, electron microscopy and quantitative electron microprobe analysis, *Atmospheric Environment* 16 (1982) 2191–2206.
- [31] J. Jankowski, C.R. Ward, D. French, S. Groves, Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems, *Fuel* 85 (2005) 243–256.
- [32] F.D. Botha, Overview of the fluidized bed combustion process and material, *Proceedings of State Regulation of Coal Combustion By-Product Placement at Mine Sites: A Technical Interactive Forum*, May 4–6 2004, Harrisburg, PA, USA.
- [33] H.A. Van der Sloot, L. Heasman, Ph. Quevauviller, Harmonization of Leaching/Extraction Tests, Elsevier, Amsterdam, 1997.
- [34] Y. Nathan, M. Dvorachek, I. Pelly, U. Mimran, Characterization of coal fly ash from Israel, *Fuel* 78 (1999) 205–213.