

# Characterization, Potential Uses and Soil Leaching of Urban waste/Agricultural residue Ash Mixtures produced from Fluidized Bed Combustion

**D. Vamvuka<sup>\*</sup>, S. Alexandrakis, V. Papadakis**

Department of Mineral Resources Engineering, Technical University of Crete, Greece

<sup>\*</sup> corresponding author, Tel: +30 2821 37603, Fax: +30 2821 69554, e-mail:

[vamvuka@mred.tuc.gr](mailto:vamvuka@mred.tuc.gr)

## Abstract

In the context of exploitation of urban wastes for recycling, valorification, or energy production, present study aimed at investigating the environmental impact and potential uses of ashes produced from co-combustion of such wastes with an olive byproduct in a fluidized bed unit. Bottom and fly ashes were characterized by physical, chemical and mineralogical analyses. Column leaching tests, simulating field conditions, were conducted and key parameters of soil/ash leachate solutions were measured. The results showed that fly and bottom ashes were alkaline, with low electrical conductivity and cation exchange capacity and enriched in Ca, Si, P, K, Mn, Zn, Sr and Cr. The principal mineral phases identified were calcite, quartz, fairchildite, hydroxyapatite and whitlockite magnesian. The elements with higher mobility leached through a soil of quartzitic nature were Na, Mg, Cr and Sr. However, none of the measured values exceeded legislation limits for land disposal. All ashes could be used as secondary building materials, liming agents or soil ameliorants in blends with other byproducts.

**Keywords:** urban wastes; fluidized bed; ashes; leaching

## Introduction

Municipal solid wastes (MSW, urban refuse, garbage) and biosolids (sewage sludge) are generated by urban communities in large quantities in all countries. In European Union up to ~90kg dry MSW and 30kg dry biosolids are produced per capita yearly from waste treatment plants (1). The rising volume of urban wastes is becoming a matter of public concern. Land disposal is no longer viable, due to environmental and health impacts related to pathogens, heavy metals and other pollutants, as well as the limited number of available sites and high cost (2). Therefore, a more extensive investigation and sustainable management of such wastes are required. There is no question about the physical availability of these materials, but the question is how to best utilize them and consider them as “urban ores” rather than urban wastes. The Waste Framework Directive of European Union set the hierarchy of the policy for recycling and reuse (1). As such, thermal treatment for energy production seems an attractive solution, in compliance with the low-economy strategy of European Union (3), by destroying hazardous constituents, reducing disposal volume and increasing economic returns to rural communities.

Among thermal processes, incineration represents the main stream method for the management of unsorted urban wastes in many industrialized countries (4,5). Fluidized bed

combustion is considered the most efficient technology at large scale, since this process is flexible towards variations in fuel properties, achieves high efficiencies and low pollutant emissions (6,7). Despite these advantages, all systems produce solid residues, around 25% of mass input, with various characteristics, depending on type of feedstock used and operating conditions (4,7-9). These characteristics are very important, as they may create technical problems (slagging, fouling, corrosion of surfaces), which reduce plant availability and increase power cost, but also determine the potential exploitation of ashes in various applications and their environmental monitoring (4,7,10,11).

Some mineral species of ashes, such as Ca, Mg, K, P, Fe, Zn and Cu, may have a vitalizing effect as nutrients upon recycling to agricultural or forest soils or alternatively cause eutrophication problems (12), while others such as Al, Si and Ca may be valuable as additives for construction materials (4). In addition, heavy metals in ashes are especially dangerous, because of their persistence and toxicity (13). If mismanaged upon landfill disposal, which is still a common practice, they could threaten human health and the environment, due to leaching into soil and ground water (14,15).

The particular properties of each ash flow in a thermal plant and also between thermal plants using different technologies, makes difficult to establish management practices of general use (16). Several countries have already defined ash management guidelines for each ash flow (7). Furthermore, the utilization of urban wastes in energy systems may pose serious limitations, due to their heterogeneity and variable composition, such as high moisture, volatiles and hazardous species unlike other biomass materials (17-19). Their twofold nature (biogenic and inorganic) influences the elemental and mineralogical composition and therefore their suitability for various applications, as well as the leachability and biological availability of their components (20). Consequently, blending these wastes with higher quality woody residues with lower content of organic and inorganic pollutants, such as agricultural wastes, which are available in large quantities especially in South European countries, could be particularly advantageous. However, when mixtures of fuels are used, a satisfactory synergy and data on final ash materials for proper monitoring and environmental protection are required.

There is a lot of information in literature on the characterization of municipal solid wastes (MSW) or sewage sludge (SS) ashes (4,21,22), but very limited on fly and bottom ashes produced from fluidized bed systems (6). Micro-analytical techniques have been used to study the distribution of major and trace elements and determine the importance of affinity-based binding mechanisms in separate cyclone ash particles from MSW combustion (6). Several studies have focused on the co-combustion of MSW or SS with coal in fluid bed systems (23,24), industrial wastes (25) or wood (26). Distribution of trace elements and leaching characteristics were investigated (25). Different standard leaching procedures (EN12457-3, AFNORX31-211) (23,25) or acid leaching (26) have been applied, making the results difficult to compare. Column leaching tests, simulating field conditions from disposal of urban waste fly ashes, without any pre-treatment, have not been conducted so far to the best of authors' knowledge. Also, there is lack of data on the environmental impact of ashes produced from mixtures of such wastes with agricultural residues in fluidized bed systems.

In Crete, the largest Hellenic island, the annual increase of the energy demand is very high (8.5%), due to prosperous tourism industry, creating big problems in the power supply. The limited suitable sites for the disposal of urban wastes on one hand and the penalties to European Union in reference to the environmental regulations on the other, demand the exploitation of these wastes for recycling, valorification or energy production. In this context and based on the

previous analysis, current work aimed at investigating the environmental impact and potential uses of ashes generated from co-combustion of untreated MSW and SS with an olive byproduct in a fluidized bed unit. Thus, bottom and fly ashes were characterized by physical, chemical and mineralogical analyses. The leaching behaviour of various species in a local soil was examined through column leaching experiments and key parameters of the percolating soil solutions, such as pH, electrical conductivity, chlorine, sulphate and phosphate ions, major and trace metals, were measured.

## **Materials and Methods**

### ***Production of ash materials***

Two urban wastes from the region of Chania on the island of Crete and one agricultural residue abundant in Crete and Mediterranean countries in general, were selected as raw materials for this study. The urban wastes were sewage sludge (SS) from the liquid waste treatment plant of the city of Chania and municipal solid waste (MSW) from the local enterprise of solid wastes management, both collected from representative samples during a whole year. The agricultural residue was olive stone (OS) provided by a local olive oil factory. After air drying, homogenization and riffing, representative samples were ground to a particle size  $< 425\mu\text{m}$  and characterized according to the European standards CEN/TC335, by proximate analysis, ultimate analysis and heating value.

For combustion tests, mixtures of urban wastes with OS were prepared with mixing ratios up to 50% of wastes by weight in the mixture. The system was a bubbling fluidized bed reactor, with an inner diameter (ID) of 70mm and a total height of  $\sim 2\text{m}$ , described in detail in a previous work (5). The bed material was Na-feldspar  $\text{NaAlSi}_3\text{O}_8$  with an average particle size of  $283\mu\text{m}$ . The experiments were performed at various feed rates and excess air ratios and temperature profiles along the reactor height, efficiency and flue gas emissions have been reported in a previous article by the authors (5). Present study aimed at evaluating fly and bottom ashes through physical, mineralogical, chemical and soil leaching experiments. Bed material and fly ashes collected from the tangential flow type cyclone, from tests with feeding rate  $0.72\text{kg/h}$  of 1-3mm particles and excess air ratio 1.4, after being drained and weighed were analyzed for particle size distribution (PSD), pH, electrical conductivity (EC), cation exchange capacity (CEC), unburned carbon, major and trace elements, mineral phases and species leachability through the soil.

### ***Soil and ash characterization***

The soil used for the leaching tests was collected from the area of Chania in Crete. The  $< 2\text{mm}$  fraction was analysed by the hydrometer method for the proportions in sand, silt and clays. pH and EC of soil and ashes were measured using a Solid:Liquid ratio of 1:10, with a Hanna 211 pH meter and Hanna Benchconductivity EC215, respectively. Cation-exchange capacity was measured by applying the ammonium acetate method (27).

The PSD of fly and bottom ashes was derived from a diffraction pattern resulting from a laser irradiated suspension of ash and water, using a Mastersizer S laser diffractometer by Malvern Instruments and from dry sieving, using a sieve shaker Analysette 3 PRO of Fritsch, respectively.

Mineralogical analysis of crystalline compounds was conducted with an X-ray diffractometer (XRD), model D8 Advance of Bruker AXS, with application of Cu K $\alpha$  radiation and nickel filter (U=35kV, I=35mA). The XRD scans were performed between 2 and 70 2 $\theta^\circ$ , with increments of 0.02 $^\circ$ /s. A software system DIFFRAC plus Evaluation by Bruker AXS and the JCPDS database were used for data processing and identification of crystalline components.

Chemical analysis of ashes in major and trace elements was performed by an inductive coupled plasma mass spectrometer type ICP-MS 7500cx, coupled with an Autosampler Series 3000, both by Agilent Technologies (detection limits 0.004-0.13ppb, depending on element). The samples were dissolved by a microwave-assisted digestion with HNO<sub>3</sub> acid. The microwave digestion was carried out by using Anton Paar Multiwave 3000 oven. Phosphorous and silicon measurements were conducted using a spectrophotometer type UV-VIS Hach 4000V and an atomic absorption spectrometer (AAS) Analyst-100 of Perkin Elmer, equipped with a graphite furnace assembly (model HGA 800) and a deuterium arc lamp background correction system. For sample preparation, the procedures of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fusion or acid digestion (HCl/HF/HNO<sub>3</sub>) were used, depending on the element under determination.

Prior to these analyses, the ashes were burned in the oven at 300 $^\circ$ C for not altering the mineralogical composition, in order to calculate combustion losses due to unburned carbon.

### ***Leaching of fly ashes through the soil***

Continuous column leaching experiments, simulating the release of components from a soil-ash mixture to a water phase, were adopted in this work, in order to get an estimate of long-term leaching behaviour. To maintain compatibility with field conditions, soil-ash mixtures were prepared at a ratio 95:5 and no extraction with strong acids was applied. Purified water instead, with an amount corresponding to the average annual quantity of rainfall in the area of Crete (~620mm), was percolating through the soil-ash mixture (100g) in a vertical column with an ID of 2.5cm and a height of 20cm. The hydraulic head was kept constant during each test and the ratio of solid to water was 1:0.7, so that to simulate the water saturation capacity of the soil. The column effluent was collected in seven equal volume glass flasks, filtered through a micropore membrane filter and the pH and electrical conductivity of each extract were measured. The chlorine, sulphate and phosphate ions of the leachates were determined according to the Argentometric 3693-SC, Barium chloride 3665-SC and Vanadomolybdophosphoric acid 3655-SC methods respectively, using a UV-VIS spectrophotometer Smart 3 by LaMotte. The filtered leachates were concentrated, transferred to 25mL plastic vials and prepared for chemical analysis.

## **Results**

### ***Characterization of raw fuels***

From the proximate and ultimate analyses of raw fuels in Table 1, it can be observed that all fuels were rich in volatile matter, while the fixed carbon of MSW was extremely low. OS having greater carbon content and lower ash content than urban waste materials presented a higher calorific value, comparable to the upper limit of low rank coals. Chlorine, being related to emissions, fouling and corrosion in boilers, was encountered at very low levels, apart from the MSW sample. The sulphur content of SS was rather high, whereas the concentration of nitrogen

for all samples was generally high, particularly that of SS material. A previous work by the authors (5) showed that to meet legislation for SO<sub>2</sub> and NO<sub>x</sub> emissions, without any extra measures, the share of SS and MSW in the fuel mix should be up to 50% and 10%, respectively. Consequently, these mixtures were used for the leaching experiments.

**Table 1.** Proximate and ultimate analyses and calorific value of the samples (% dry weight)

Sample	Volatile matter	Fixed carbon	Ash	C	H	N	O	S	Cl	GCV <sup>a</sup> (MJ/kg)
Olive stone (OS)	73.6	19.3	7.1	49.7	6.6	2.0	34.3	0.33	0.06	20.8
Sewage sludge (SS)	67.2	15.6	17.2	42.4	6.7	8.1	23.9	1.70	0.01	18.8
Municipal solid waste (MSW)	67.6	3.5	28.9	35.3	4.8	1.6	26.4	0.28	0.31	14.7

<sup>a</sup> Gross calorific value

### *Physicochemical properties of solid materials*

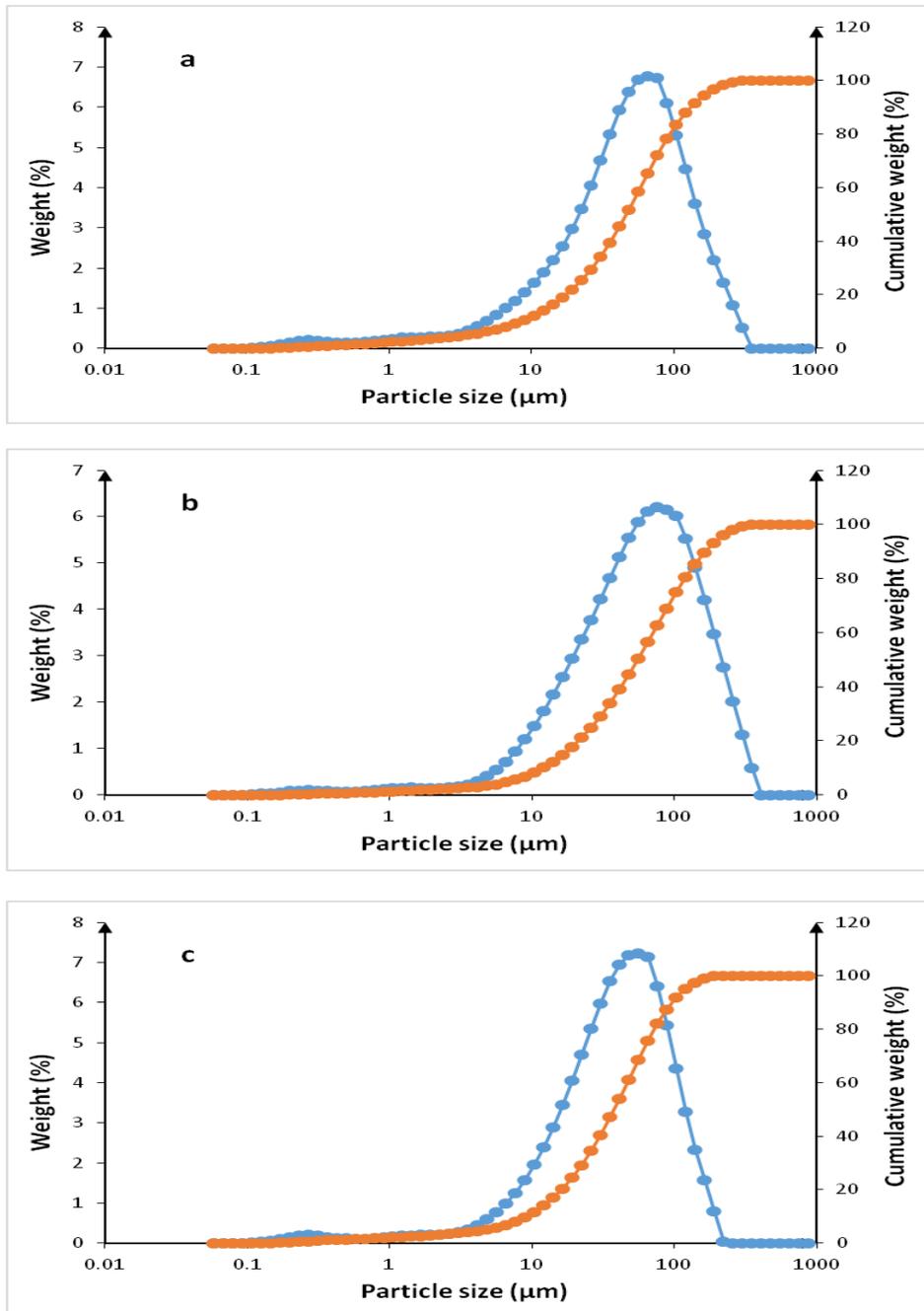
Table 2 shows that the soil was neutral, had very low EC and CEC, the latter mainly due to its small percentage in clays. On the other hand, all ash materials were alkaline (pH between 11.6 and 12.7), with low EC and extremely low CEC. Unburned carbon in ashes was very low during the fluidized bed tests and had a minor effect on combustion efficiency (5). Heat losses deduced from fly ashes had the largest portion in the total loss in ash.

**Table 2.** Physicochemical properties of solid materials

Sample	pH	Electrical conductivity (mS/cm)	Cation exchange capacity (meq/100g)	Unburned carbon (%)
OS	12.7	3.3	0.12	0.07
OS/SS 50:50	11.6	1.1	<0.1	0.06
OS/MSW 90:10	12.3	1.3	0.10	0.01
Soil	7.1	0.02	0.18	-

The PSD of the cyclone ashes are illustrated in Figures 1a-c. The fly ash of OS constituted from fine particles, ranging between 0.1 and 350µm with 90% of these being below

120 $\mu\text{m}$ . The median particle size of the cumulative distribution curve was 48 $\mu\text{m}$ . The fly ash of OS/MSW mixture presented a similar PSD to OS as the percentage of MSW was low, i.e. 10%. Particle sizes varied between 0.1 and 250 $\mu\text{m}$  with 90% of these being below 90 $\mu\text{m}$ . The median size of the cumulative distribution curve was 35 $\mu\text{m}$ . On the other hand, OS/SS fly ash was coarser, with PSD ranging between 0.5 and 470 $\mu\text{m}$ , 90% of particles had a size of 165 $\mu\text{m}$ , while the median size in this case was 56 $\mu\text{m}$ . Bottom ashes recovered from bed material after the tests were found to consist of coarser particles, between 0.1 and 1.8mm. 90% of these were comprised of size fractions greater than 300 $\mu\text{m}$ .



**Figure 1.** Particle size distribution of (a) OS (b) OS/SS 50:50 and (c) OS/MSW 90:10 fly ashes

The physicochemical properties of ashes are important, because they are directly related to their potential uses, such as pozzolans, absorbents and soil ameliorants, or for land disposal. It is known that pozzolanic properties are more intense when particles are finer and carbon is below 6% (28), whereas higher carbon content increases surface area and sequestration in soil in case of deposition. Also, heavy metals tend to concentrate in small particles, the leachability of which is also higher. However, the leachability of elements and ions through soil/ash mixtures to water is controlled among other factors by the pH, the EC and the CEC of the solid materials involved (14,16,18,29).

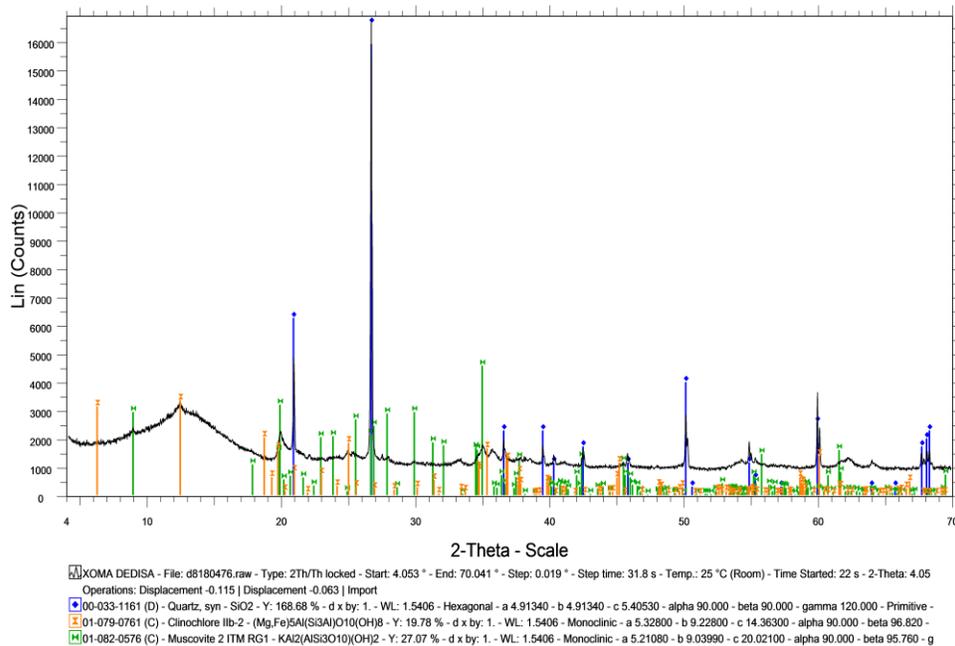
### ***Mineral phases of soil and ashes***

The XRD pattern of the soil used for the leaching tests in Figure 2 reflects its quartzitic origin.

**Table 3.** Mineralogical analysis of fly and bottom ashes

Mineral phases	Sample						
	Bed material	OS		OS/SS 50:50		OS/MSW 90:10	
		Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash
Quartz SiO <sub>2</sub>	+	+++	++	++	+	++	++
Calcite CaCO <sub>3</sub>		++	++	+	++	+++	++
Anhydrite CaSO <sub>4</sub>		++	+	+	+	+	+
Albite (Na,Ca)Al(Al,Si) <sub>3</sub> O <sub>8</sub>	+++	+	+	+	++	+	++
Muscovite KAl <sub>2</sub> (Si <sub>3</sub> AlO <sub>10</sub> )(OH) <sub>2</sub>	+	+		+	+	+	+
Microcline KAlSi <sub>3</sub> O <sub>8</sub>	+	+	+	+	+	+	+
Whitlockite magnesian Ca <sub>18</sub> Mg <sub>2</sub> H <sub>2</sub> (PO <sub>4</sub> ) <sub>14</sub>				++	++	+	
Fairchildite K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>		++	+++	+	+	++	+
Hydroxyapatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)		+	++			+	+
Dolomite CaMg(CO <sub>3</sub> ) <sub>2</sub>			++				
Hematite Fe <sub>2</sub> O <sub>3</sub>		+	+	+	+	+	+
Arcanite K <sub>2</sub> SO <sub>4</sub>		++	++	+	+	+	+
Periclase MgO		+	+	+	+	+	+
Aphthitalite NaK <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>						+	+
Epsomite MgSO <sub>4</sub> .7H <sub>2</sub> O						+	+
Dawsonite NaAl(CO <sub>3</sub> )(OH) <sub>2</sub>		+	+				
Sylvite KCl		+	+			+	+
Portlandite Ca(OH) <sub>2</sub>						+	+
Monticelite CaMgSiO <sub>4</sub>						+	+

+++: high intensity ++: medium intensity +: low intensity



**Figure 2.** XRD spectra of soil

The crystalline mineral phases of fly and bottom ashes of OS and its blends with SS and MSW, as identified by XRD, are listed in Table 3. Both OS ashes (maximum fluid bed temperature attained 849°C) were dominated by Ca-based minerals in the form of calcite, anhydrite, fairchildite and hydroxyapatite. Dolomite was concentrated only in bottom ash. The presence of calcium was attributed to its high content naturally occurring in wood. Anhydrite was most probably formed by dehydration of gypsum, as the sulphur dioxide content of flue gases was found to be extremely low. Hydroxyapatite is associated with the use of fertilizers, such as  $\text{NH}_4\text{H}_2\text{PO}_4$  during the cultivation of olive trees. Among silicates, quartz was abundant in both ashes, whereas albite, muscovite and microcline were remnants of elutriated inert bed material in the cyclone, during the experiments. Hematite, periclase and dawsonite were detected in small amounts, however potassium minerals, such as arcanite, fairchildite and to a lesser extent sylvite, were enriched in OS ashes. These sulphate, carbonate and chloride minerals were partly vaporized during combustion and condensed on cyclone ash.

When SS was mixed with OS at a proportion of 50% (maximum fluid bed temperature attained 786°C), Table 3 shows that dolomite, hydroxyapatite, sylvite and dawsonite could not be detected in fly and bottom ashes, instead a new phosphate phase appeared, whitlockite magnesian, possibly due to household detergents [30]. Calcium and potassium minerals were identified in smaller amounts in OS/SS mixture, as compared to OS ashes.

On the other hand, the OS/MSW mixture (maximum fluid bed temperature attained 845°C), apart from the phases which were found in OS ashes, presented also apthitalite and magnesium phases monticelite and eptonite. The latter was probably formed by reaction of periclase (primary or secondary from decomposition of dolomite which was not detected in bottom ash at temperatures higher than 800°C) with  $\text{SO}_2$  of flue gas. Phosphorous and potassium were incorporated in lower quantities in OS/MSW ashes as hydroxyapatite, arcanite and

fairchildite. Finally, portlandite was formed by absorption of moisture by calcium oxide (most probably produced by decomposition of dolomite) after ashing.

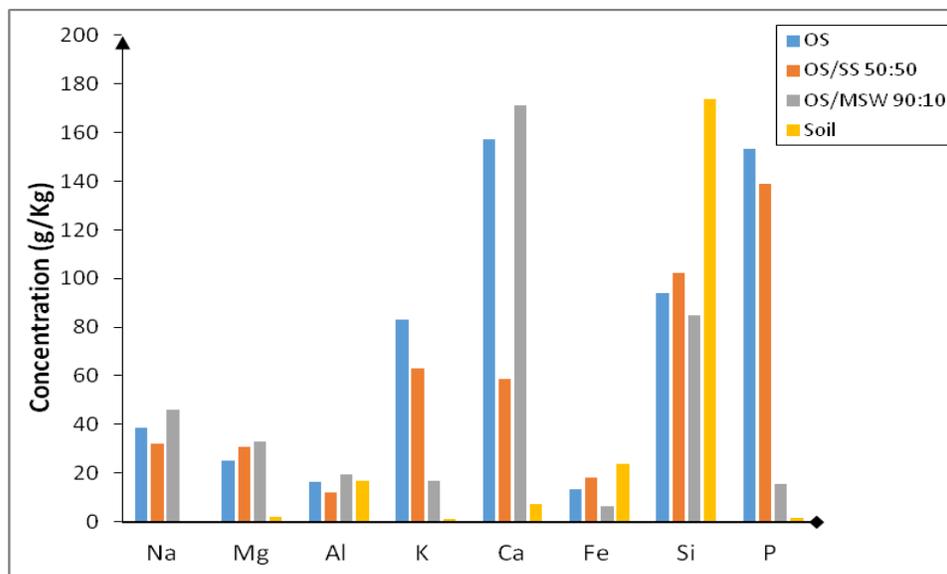
### Major and trace elements of soil and ashes

Figure 3 compares the major elements in soil and fly ashes of the materials studied. As can be observed, OS ash was rich in Ca, Si and P and to a lesser extent in K, in accordance to the XRD analysis previously presented. The higher amounts of P and K with respect to the blended materials, was due to the higher content of P and K originally found in this sample, as well as the partial vaporization of hydroxide, sulphate and chloride species (hydroxyapatite, arcanite, sylvite) identified in the XRD spectra, which condensed on fly ash particles in the upper part of the reactor, when the flue gas was cooled.

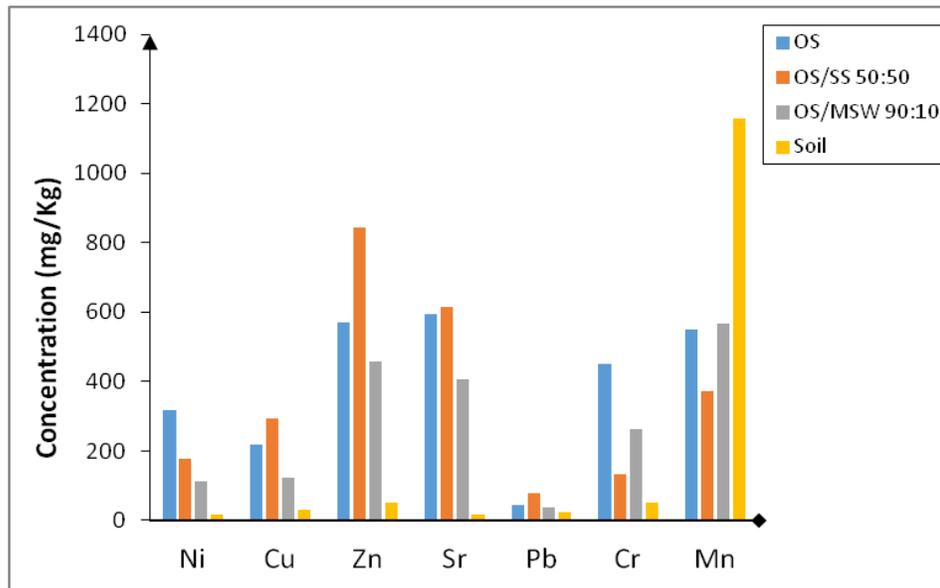
When OS was mixed with SS, it can be seen that the levels of Ca and K were lower as compared to OS ash, which is consistent with the mineralogical analysis. This mixture was rich in Si and P, confirming the presence of quartz and whitlockite magnesian identified through XRD.

In the case of OS/MSW mixture, it is clear from the figure that the concentrations of K and P were significantly lower, in agreement with the mineral phases detected. Furthermore, the higher proportion of Mg in the ash can be explained by the appearance of monticelite and eponite minerals apart from periclase. Ca and Si dominated in the OS/MSW ash. As already discussed, part of Si in all ashes was attributed to some elutriation of the feldspar bed material in the cyclone.

The most abundant element in soil was Si found to be incorporated in quartz, followed by Fe and Al associated with chlorinoclone and muscovite minerals, as shown in Figure 2. Present results are consistent with literature data of chemical analyses of fly ashes from combustion of wastes in fluidized beds, reporting Ca to vary between 85 to 200g/kg, K between 39 to 199g/kg, P between 10 to 109g/kg, Mg between 7.8 to 60g/kg, Si between 102 to 200g/kg, Al between 6.8 to 127g/kg, Fe between 10 to 48g/kg and Na between 6.7 to 52g/kg (6-8,31).



**Figure 3.** Chemical analysis of fly ashes and soil in major elements



**Figure 4.** Chemical analysis of fly ashes and soil in trace elements

The analysis of fly ashes in trace elements is indicated in Figure 4. Toxic heavy metals As, Hg, Cd and Co, ranging between <0.4ppb to 6ppm, were omitted from the graphs. Generally, all ashes were enriched in Zn, Sr and Mn and contained moderate amounts of Cu and Ni. By blending OS with SS, the concentrations of Cu, Zn and Pb were increased, while those of Ni and Mn were decreased, suggesting that the levels of Cu, Zn and Pb were higher in SS waste, as compared to OS residue and the levels of Ni and Mn lower, respectively. The unexpectedly high values of Cr in fly ashes were attributed to contamination with stainless steel attrite in the cyclone, as laboratory ashes prepared according to CEN/TC335 standards were found to contain below 80ppm of Cr. This behaviour has been also confirmed by other studies (16). When OS was mixed with MSW, Figure 4 shows that all trace elements released (except Mn) were found to absorb into fly ash particles in smaller amounts. The

**Table 4.** Comparison of trace element concentrations of fly ashes with literature data

Ref.	Fuel type	Trace element concentration (mg/kg)								
		Cr	Ni	Cu	Zn	Sr	Pb	Co	Mn	As
(7)	Forest residue	50	30	120	200	300	100		1000	10
(36)	Peat-wood	69	51	87	284		31			25
(23)	Coal-SS-MBM	171	29	108	331		33			5.8
(25)	Household-industrial waste	100-1050	35-311	317-16400	5040-26900		108-6920			26-136
(6)	MSW	410	210	7300	9600	380	1500	30	1800	40
(26)	SS-wood	60-71	51	680	1600		88	17	1400-1900	10
This study	OS-SS/OS-MSW	134-450	112-317	123-294	458-845	408-616	37-78	2.8-10.7	371-567	0-6

concentrations of heavy metals in the soil were very low, except Mn (1158mg/kg). All heavy metal values measured in present samples were within the range of those reported in literature for similar waste materials, as illustrated in Table 4 and below the upper limit for disposal in landfills, according to EU directives (32). Their potential environmental hazards, as derived from the leaching experiments through the soil, are discussed below.

#### *Leachability of fly ash species through the soil*

The cumulative concentrations of the elements leached through the soil/fly ash mixtures, according to the column leaching tests previously described, are summarized in Tables 5 and 6. From major elements, those which presented a higher mobility were Na and Mg, the former due to partial solubility of hydroxides and sulphates from OS ash (dawsonite) and OS/MSW (aphthitalite), while the latter due to magnesium hydroxide formed and partial solubility of magnesium sulphate (epsonite) from OS/MSW fly ash. Ca was released in lower amounts from all ashes, mainly from partial dissolution of carbonates (calcite, fairchildite) and sulphates (anhydrite). The lowest extractability of these elements occurred from the leaching of OS/SS mixture through the soil.

**Table 5.** Cumulative major element concentrations (mg/kg) in the leachates and relative mass leached (%)

Sample	Major element concentration (mg/kg)								
	Na	Mg	Al	K	Ca	Fe	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>
Soil	77.8 (45.7)*	18.1 (0.9)	9.7 (0.05)	119.8 (9.0)	16.2 (0.22)	4.7 (0.02)	-	-	-
Soil/OS	512.6 (24.5)	180.2 (5.6)	6.7 (0.04)	24.7 (0.45)	324.9 (2.2)	4.8 (0.02)	76.1	521.4	47.6
Soil/OS-SS	148.5 (8.4)	56.2 (1.6)	31.7 (0.19)	14.5 (0.33)	146.8 (1.5)	13.4 (0.06)	52.0	416.4	9.8
Soil/OS-MSW	491.6 (19.9)	150.5 (4.2)	9.7 (0.06)	23.8 (1.1)	341.9 (2.2)	5.3 (0.02)	63.4	515.3	21.0

\*Values in parenthesis represent cumulative mass leached (%)

**Table 6.** Cumulative trace element concentrations (µg/kg) in the leachates and relative mass leached (%)

Sample	Trace element concentration (µg/kg)						
	Cr	Ni	Cu	Zn	Sr	As	Mn
Soil	264.7 (0.51)*	80.6 (0.44)	79.5 (0.27)	32.5 (0.06)	31.4 (0.19)	24.3 (0.36)	44.8 (0.004)
Soil/OS	11290.3 (15.9)	6.9 (0.02)	87.3 (0.22)	27.3 (0.03)	1420.9 (3.1)	20.0 (0.31)	3.5 (0.0002)
Soil/OS-SS	705.4 (1.3)	6.7 (0.03)	-	113.6 (0.12)	513.9 (1.1)	-	30.3 (0.002)
Soil/OS-MSW	12541.0 (20.3)	1.8 (0.008)	15.9 (0.05)	3.2 (0.004)	1341.6 (3.8)	-	9.0 (0.0008)

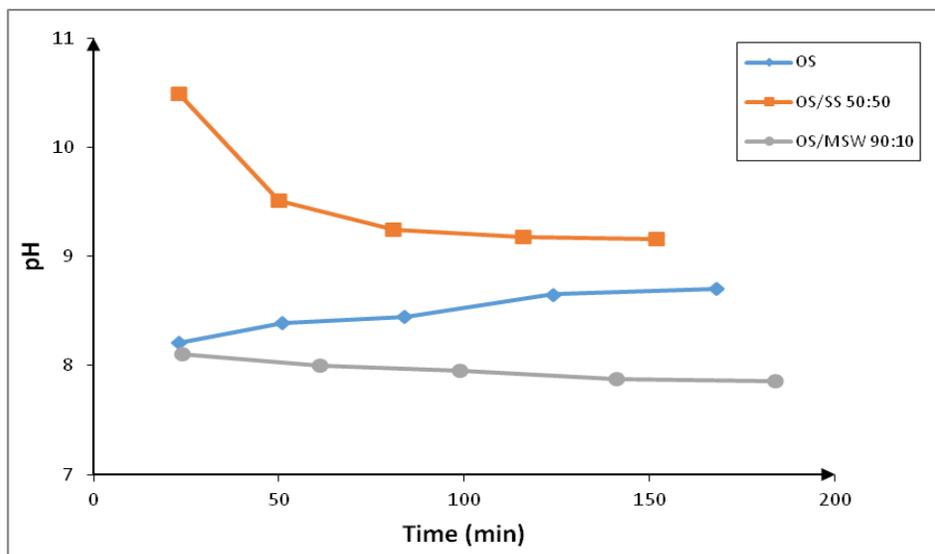
\*Values in parenthesis represent cumulative mass leached (%)

The chlorine ions detected in all leachates were very low and were attributed to highly water extractable sylvite in OS fly ash. Also, phosphate ions in the leachates were extremely low, being strongly correlated to the mineral phases of ashes whitlockite magnesian (insoluble) in OS/SS and OS/MSW mixtures and hydroxyapatite in OS (Table 3). In contrast, the concentration of sulphate ions measured in the leachates was significant, due to the sulphate phases present in all ash materials arcanite, anhydrite, as well as apthitalite and epsomite in the case of OS/MSW blend.

A direct comparison of present values with those of other investigations is not possible, due to the lack of data, different raw materials and experimental equipment and conditions used. Nevertheless, chlorine ions and sulphate ions measured in the leachates of forest residues and coal/sewage sludge/meat and bone meal fly ashes (16,23) were 900-1280mg/kg and 14308mg/kg, respectively, i.e. much higher than those of present study.

As concerns trace elements Cd, Hg, Pb and Co, these were not quantified in the extracts, because their concentration was below the instrument's detection limit (0.004-0.035ppb) in all leachate samples. Furthermore, Table 6 shows that Mn, Ni and As were leached in levels not exceeding 30, 6.9 and 20µg/kg, respectively, from all ashes, while Cu and Zn were extracted in moderate amounts from OS and OS/SS samples, but still the percentage relative mass leached

was very low (0.22 and 0.12%, respectively). On the other hand, Cr presented the highest mobility among heavy metals (up to 20.4%), especially from OS/MSW ash, reaching leachable levels up to 12.5mg/kg, followed by Sr, the cumulative mass leached of which varied between 1.1 and 3.8%. When OS was mixed with SS, all heavy metal levels in the extracts were remarkably decreased. More importantly, none of the values of measured elements reported in the table exceeded the allowable limits stipulated by the European Union Community Directives for soil disposal (29,33).



**Figure 5.** Variation of leachates pH of fly ashes as a function of time

The above behaviour of ash elements leaching through the soil is complex, as it is influenced by several factors, among which the mineralogical and chemical composition of the solid materials involved, various reaction kinetics, the pH of solid and liquid phases, the permeability and cation exchange capacity of soil, etc. (14,29,34). As previously indicated (Table 2), the cation exchange capacity of the soil was very low for adsorbing toxic species, whereas all fly ashes were alkaline. Thus, as Figure 5 shows, addition of fly ashes to the soil increased the pH values of the water extracts initially up to 8.2, due to basic Na, Mg and Ca-bearing minerals, such as hydroxides (dawsonite, hydroxyapatite, portlandite, magnesium hydroxide) and carbonates (calcite, fairchildite), (Table 3), which were partly dissolved in water. The small drop of pH with time, in the leachates of urban waste mixtures, was most probably a result of decreased concentrations of hydroxides and carbonates of alkali species and the increased concentration of sulphate ions in the extracts of OS/MSW fly ash mixture. The low migration of trace elements through the soil (apart from Cr and Sr), indicates that these were partly adsorbed on stable oxide surfaces, such as quartz and hematite, or bound in aluminosilicates, such as microcline, as also found in other studies (25). Furthermore, dissolution and precipitation of hydroxides/oxides have been reported as the major mechanisms, controlling leaching of some trace elements under alkaline conditions (25). The practically null leachability

of Pb from all samples, suggests that this element, which is known to have a carbonate/organic affinity (29), was converted during the tests to insoluble oxide, or could be associated to insoluble phosphates. On the other hand, the higher extractability of Sr reveals its potential association with organic matter or carbonates, as found in a previous investigation by the authors (35), however that of Cr is principally owned to the contamination of fly ashes during the fluidized bed experiments, as previously discussed. Therefore, if the system is carefully managed, especially in larger units, the concentration of Cr in fly ashes of the waste materials studied could be much lower. As stated above, a direct comparison of the results herein with literature data is not possible. As a general observation, the concentrations of As, Pb, Cu and Zn detected in the leachates of mixtures of coal, peat, industrial and urban wastes were higher than those of this study, while the concentration of Cr was lower (As=<0.03-3.7mg/kg, Pb=<0.4-5000mg/kg, Cu=<0.1-1000mg/kg, Zn=<0.13-100mg/kg, Cr=0.2-3mg/kg) (23,25,36).

Concerning the potential utilization of present ashes produced by blends of SS and MSW with OS burned in a fluid bed unit, the results showed that these, despite their elevated SiO<sub>2</sub> content, are not suitable as received for the cement industry, due to their minor amounts in aluminosilicate minerals. Fly ashes (containing ~20% of SiO<sub>2</sub>) and bottom residues (containing ~95% of SiO<sub>2</sub>) could be used as secondary building materials. Nevertheless, the alkaline nature of these ashes, along with the fulfilment for land disposal, could allow their use for soil liming. Furthermore, due to the low leachability of plant nutrients such as Ca, P, K and Mg, these fly ashes could be blended with compost or other organic and inorganic by-products, in order to increase the capacity of the soils to retain nutrients and reduce their leaching to surface or groundwaters. However, long term leaching tests are required to verify these observations. Generally, the valorization of such ash materials demands their proper management in thermal units, according to their physical and chemical characteristics.

## Conclusions

Fly and bottom ashes, produced from combustion of mixtures of sewage sludge (SS) and MSW with olive stone (OS) in a fluid bed unit, were enriched in Ca, Si, P and K. The principal mineral phases associated with these elements were calcite, quartz, fairchildite and hydroxyapatite. When OS was mixed with SS, a new phase whitlockite magnesian appeared in the ash, whereas when mixed with MSW three new phases apthitalite, monticelite and eponite were identified. The trace elements, which dominated in fly ashes, were Zn, Sr, Mn and Cr. Their contents in OS/MSW fly ash were much lower. All ash materials were alkaline, with low electrical conductivity and cation exchange capacity. When leached through a soil of quartzitic nature and low cation exchange capacity, through continuous column leaching experiments, the elements with higher mobility were found to be Na, Mg, Cr and Sr. For OS/SS mixture, all heavy metal levels in the extracts were remarkably decreased. None of the measured values exceeded allowable limits for disposal in landfills. The concentrations of chlorine and phosphate ions detected in all leachates were very low, however that of sulphate ions was significant. Fly and bottom residues could be used as secondary building materials, or for soil liming. Fly ashes blended with other byproducts could also be used for soil amelioration. Field trials are recommended to verify these findings.

### Author Contributions

SA and VP conducted the experiments and DV evaluated the results and wrote the paper.

### Conflicts of Interest

Authors declare no conflict of interest

### Acknowledgements

The authors kindly thank the laboratories of Hydrogeochemical Engineering and Soil Remediation, Geochemistry, Management of mining/metallurgical wastes, Applied Mineralogy and Ore Processing and Beneficiation, of the Technical University of Crete, for the ICP-MS, UV-VIS, XRD and PSD measurements.

### References

1. Van Caneghem J, Brems A, Lievens P, Block C, Billen P, Vermeulen I, Dewil R, Baeyens J, Vandecasteele C. Fluidized bed waste incinerators: Design, operational and environmental issues. *Prog. Energ. Combust. Sci.* 2012; 38: 551-582.
2. Bondarczuk K, Markowicz A, Piotrowska-Seget Z. The urgent need for risk assessment on the antibiotic resistance spread via sewage sludge land application. *Environ. Int.* 2016; 87: 49-55.
3. European Commission. Circular economy strategy. 2017.
4. Funari V, Braga R, Bokhari SNH, Dinelli E, Meisel T. Solid residues from Italian municipal solid waste incinerators: A source for critical raw materials. *Waste Manag.* 2014; 45: 206-216.
5. Vamvuka D, Alexandrakis S, Papagiannis I. Evaluation of municipal wastes as secondary fuels through co-combustion with woody biomass in a fluidized bed reactor. *J. Energy Inst.* 2019; in press.
6. Fedje KK, Rauch S, Cho P, Steenari BM. Element associations in ash from waste combustion in fluidized bed. *Waste Manag.* 2010; 30: 1273-1279.
7. Freire M, Lopes H, Tarelho LAC. Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F. *Waste Manag.* 2015; 46: 304-315.
8. Vamvuka D. Biomass, bioenergy and the environment. Salonica (Greece): Tziolas Publications; 2009.
9. Vamvuka D, Sfakiotakis S, Mpoumpouris A. Slagging and fouling propensities of ashes from urban and industrial wastes. *Rec. Innov. Chem. Eng.* 2018; 11(2): 145-158.
10. Vassilev SV, Vassileva CG, Baxter D. Trace element concentrations and associations in some biomass ashes. *Fuel* 2014; 129: 292-313.

11. Garcia-Maraver A, Mata-Sanchez J, Carpio M, Perez-Jimenez J. Critical review of predictive coefficients for biomass ash deposition tendency. *J. Energy Inst.* 2017; 90: 214-228.
12. Steenari BM, Lindqvist O. Stabilisation of biofuel ashes for recycling to forest soil. *Biomass Bioenerg.* 1997; 13(1): 39-50.
13. Adriano DC. Trace elements in terrestrial environments. Biogeochemistry, Bioavailability and Risks of Metals. New York (USA): Springer-Verlag; 2001.
14. Vamvuka D, Hahladakis J, Pentari D. Leaching of toxic elements from lignite and agroresidue ashes in cultivated soils of Crete. *Energy Fuels* 2005; 19: 807-812.
15. Magdziarz A, Dalai A, Kozinski J. Chemical composition, character and reactivity of renewable fuel ashes. *Fuel* 2016; 176: 135-145.
16. Tarelho LAC, Teixeira ER, Silva DFR, Modolo RCE, Labrincha JA, Rocha F. Characteristics of distinct ash flows in a biomass thermal power plant with bubbling fluidized bed combustor. *Energy* 2015; 90: 387-402.
17. Vamvuka D, Sfakiotakis S, Panopoulos K. An experimental study on the thermal valorization of municipal and animal wastes. *Int. J. Energy, Environ. Econ.* 2013; 4: 191-198.
18. Vamvuka D, Papas M, Alloimonos N, Kapenekaki M. Evaluation of meat and bone meal as a secondary fuel with olive byproducts in a fluidized bed unit. Performance and environmental impact of ashes. *Energy Fuels* 2017; 31: 7214-7222.
19. Sfakiotakis S, Vamvuka D, Kosmadaki M. Combustion characteristics and thermal behaviour of agricultural/urban waste blends as potential feedstocks for energy production. In *Proceedings of the 6th Int. Conference on Hazardous and Industrial Waste Management*; 2018; Chania-Crete.
20. Bogush AA, Stegemann JA, Williams R, Wood JG. Element speciation in UK biomass power plant residues based on composition, mineralogy, microstructure and leaching. *Fuel* 2018; 211: 712-725.
21. Long YY, Shen DS, Wang HT, Lu WJ, Zhao Y. Heavy metal source analysis in municipal solid waste (MSW): Case study on Cu and Zn. *J. Hazard. Mater.* 2011; 186: 1082-1087.
22. Tang P, Florea MVA, Spiesz P, Brouwers HJH. Characteristics and application potential of municipal solid waste incineration (MSWI) bottom ashes from two waste-to-energy plants. *Constr. Build. Mater.* 2015; 83: 77-94.
23. Barbosa R, Lapa N, Lopes H, Gulyurtlu I, Mendes B. Stabilization/solidification of fly ashes and concrete production from bottom and circulating ashes produced in a power plant working under mono and co-combustion conditions. *Waste Manag.* 2011; 31: 2009-2019.
24. Zhang G, Hai J, Cheng J, Cai Z, Ren M, Zhang S, Zhang J. Evaluation of PCDD/Fs and metals emission from a circulating fluidized bed incinerator co-combusting sewage sludge with coal. *J. Environ. Sci.* 2013; 25(1): 231-235.
25. Saqib N, Backstrom M. Distribution and leaching characteristics of trace elements in ashes as a function of different waste fuels and incineration technologies. *J. Environ. Sci.* 2015; 36: 9-21.

26. Pettersson A, Amand LE, Steenari BM. Leaching of ashes from co-combustion of sewage sludge and wood-Part II: The mobility of metals during phosphorous extraction. *Biomass Bioenerg.* 2008; 32: 236-244.
27. Schollenberger CJ, Simon RH. Determination of exchange capacity and exchangeable bases in soil-ammonium acetate method. *Soil Sci.* 1945; 59: 13-24.
28. Standard specification for fly ash and raw calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. ASTM C618-94a. American Society for Testing and Materials. Philadelphia. 1995.
29. Pentari D, Typou J, Goodarzi F, Foscolos AE. Comparison of elements of environmental concern in regular and reclaimed soils, near abandoned coal mines Ptolemais-Amynteon, northern Greece: Impact on wheat crops. *Int. J. Coal Geol.* 2006; 65: 51-58.
30. Sfakiotakis S. Study on the exploitation of agricultural, urban and industrial wastes of Crete for power production-Thermal and kinetic analyses. [PhD dissertation]. Chania (Greece): Technical University of Crete; 2016.
31. Chang FY, Wey MY. Comparison of the characteristics of bottom and flyashes generated from various incineration processes. *J. Hazard. Mater.* 2006; 138: 594-603.
32. EU Directive 86/278/EEC. Protection of the environment and in particular of the soil, when sewage sludge is used in agriculture. 1986.
33. European Community Council Directive 91/96/WC. Hazardous Wastes EWC Codes 1001 and 1901, CWC Codes 1001 and 1901. Council decision 22/12/94 (94/904/EC). 1994.
34. Vamvuka D, Sfakiotakis S, Pantelaki O. Evaluation of gaseous and solid products from the pyrolysis of waste biomass blends for energetic and environmental applications. *Fuel* 2019; 236: 574-582.
35. Vamvuka D, Trikouvertis M, Pentari D, Alevizos G, Stratakis A. Characterization and evaluation of fly and bottom ashes from combustion of residues from vineyards and processing industry. *J. Energy Inst.* 2017; 90: 574-587.
36. Pesonen J, Kuokkanen T, Rautio P, Lassi U. Bioavailability of nutrients and harmful elements in ash fertilizers: Effect of granulation. *Biomass Bioenerg.* 2017; 100: 92-97.