



Characterization and hazard evaluation of bottom ash produced from incinerated hospital waste

Evangelos Gidarakos^{a,*}, Maria Petrantonaki^a, Kalliopi Anastasiadou^a, Karl-Werner Schramm^{b,c}

^a Laboratory of Toxic and Hazardous Waste Management, Department of Environmental Engineering, Technical University of Crete, Chania, P.C. 73100, Greece

^b Helmholtz Zentrum München, Institute of Ecological Chemistry, Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany

^c TUM – Technische Universität München, Department für Biowissenschaftliche Grundlagen, Weihenstephaner Steig 23, 85350 Freising, Germany

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ABSTRACT

The uncontrolled disposal of bottom ash from incineration units of hazardous and infected wastes in many countries causes significant scale damage, since it contaminates the soil as well as surface and underground waters, putting both the environment and the public health at risk. In view of the above, a study of bottom ash produced at a hospital medical waste incinerator (HMWI) in Greece was conducted, in order to detect the presence of heavy metals and therefore assess its toxicity; this led to conclusions on the possible contamination of the soil as well as surface and underground waters as a result of its disposal in landfills. The study was conducted at a typical general hospital with 500-bed capacity. About 880 kg of infectious waste coming from a general hospital with all medical departments are pyrolytically incinerated at the HMWI every day. International literature contains many references to research that characterizes bottom ash as either dangerous, not dangerous, or inert, in an effort to diagnose its proper management and disposal. For this reason, this study focuses on the characterization of bottom ash. Samples were collected from a combustion chamber, over a period of 1 year, and a series of tests were conducted, including an analysis of particle size distribution, morphology, mineralogical and chemical composition, heavy metal leaching behavior and PCDD/F.

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1. Introduction

Hospital waste management by means of incineration processes generates solid residues, such as bottom and fly ash and air pollution control residues with high levels of heavy metals, inorganic salts and other organic compounds. Hospital medical waste incinerators (HMWI) can be operated as integrated waste management systems. They offer a reduction in both mass (around 70%) and volume (around 90%) of waste subjected to final disposal, as well as the possibility of energy recovery [1].

For infectious hospital wastes, another major objective of the incineration process is the destruction of infectious organisms that may exist in the waste. The permissible operational temperature range is between 1100 and 1200 °C [2]. Two additional objectives achievable through the proper operation of waste incinerators are the minimization of the organic content in the solid residue and the control of atmospheric emissions within acceptable levels [3].

International literature contains many references to research that characterizes bottom ash as either dangerous, not dangerous, or inert, in an effort to diagnose its proper management and dis-

posal. Reasons such as limited available land areas for the creation of specialized bottom ash burial grounds and, therefore, the necessity to reduce the quantities sent to landfills, channel research to finding ways of recycling bottom ash into products used in structural and construction materials. Thus, the impact on public health has once again become the focus of scientific research.

Bottom ash was only recently included (2003) on the list of dangerous waste materials according to the Council of the European Union, while fly ash and solid waste coming from the fluglas control system have already found their place on the list of dangerous waste materials with codes 19.01.13 and 19.01.07, respectively [4]. According to bibliography, fly ash possesses a high content of heavy metals, dioxins and furans. For this reason it requires special management [5]. Moreover, if the fluglas control system collects a high amount of gaseous waste, it must also be treated as hazardous waste [6]. Indeed, special waste management remains an issue of ongoing debate. Stabilization processes, mixing and its use as road construction material or as structural or ceramic material, provide some management solutions for bottom ash [7–9], though the disposal of bottom ash at special landfills still remains the most common practice.

Technologies for bottom ash treatment are placed under continuous scrutiny and control in order to minimize the potential for environmental pollution due to the following causes:

* Corresponding author. Tel.: +30 2821037789; fax: +30 2821037850.
E-mail address: gidarako@mred.tuc.gr (E. Gidarakos).

the presence of pollutants in bottom ash, non-existent or insufficient segregation of the waste produced at a health unit (that is subsequently incinerated).

Unfortunately, only a limited amount of research exists regarding the characteristics, particle size distribution, morphology and mineralogy of bottom ash. Further research is needed to investigate the characteristics and the toxicity of bottom ash in order to explore its potential use as construction material. Finally, the category of waste in which bottom ash belongs (hazardous, non-hazardous, or inactive) must be clarified, so that an appropriate management program can be applied before its disposal in a landfill.

The limited space and the high cost for land disposal led to the development of recycling technologies and the reuse of bottom ash as structural and constructional material [10].

In this case the bottom ash must be examined for its toxicity and all the necessary measures must be taken in order to minimize leaching of its hazardous components into the environment [11].

Bottom ash and fly ash, produced from incinerated hospital waste, are used for the production of concrete and bricks, after mixing (50–50) with the remainder materials [12]. In several European countries high quantities of ash are reused for the manufacture of pavements, bridges and structural stones but also as sublayer in the manufacture of motorways and as daily cover of landfills. On the contrary, in USA and Canada a general interest exists without constituting common practice to use ash as a construction material.

In Germany 50% of the ash produced from incinerated waste is used for the manufacturing of sound insulation walls at national roads, as well as, sublayers on the streets. In The Netherlands 60% of the bottom ash is used for the construction of asphalt and as a sublayer of roads. Aim is the reuse of 80% of bottom ash. In Denmark above 72% of ash is reused for the manufacture of parking spaces, cycling tracks and other roads [13].

In the present work, the nature of bottom ash has been examined through chemical analysis of several samples of bottom ash produced at a hospital incineration plant. The main aim was the determination of heavy metals, dioxins and furans, particle size distribution, morphology and mineralogy, in order to evaluate the toxicity of the bottom ash and to categorize it accordingly on the European list of hazardous waste materials.

2. Methods and materials

Bottom ash was sampled from a HMWI. About 880 kg of hospital waste coming from a general hospital with all medical departments and a capacity of 500 beds are pyrolytically incinerated at the HMWI every day. Hospital medical waste (HMW) include about 80% general refuse waste (i.e. paper, food, plastic cups), 15% infectious waste (human blood and blood products, tissues and body parts, cultures, etc.), 1% contaminated sharp instruments (needles, syringes, etc.), 3% laboratory and pharmaceutical chemicals, and finally less than 1% radiotoxic and genotoxic waste. The composition of the HMW in this study is in accordance with previous literature [14].

A total amount of 12 samples were collected in a period of 1 year (4 samples per month, 1 month per season) from the combustion chamber. It employs a rotary kiln system with a capacity of 180 kg/h. The samples were cooled at room temperature. The operational temperature of the combustion chamber was recorded between 650 and 800 °C. The samples were collected from a pile of bottom ash according to ASTM D6009 Standard Guide for sampling waste piles [15].

The weight of each sample was approximately 20 kg. These samples were mixed per season (winter, spring, summer and autumn) for the creation of four representative samples (S1, S2, S3 and S4).

This sampling method was chosen in order to determine the composition of bottom ash and the possible change in its composition according to different quality of HMW incinerated per season.

According to European Legislation 1999/31/EC [16] “composition, leachability and other general characteristics of wastes must be examined before the final disposal”. In the present research, according to the European Directive and in order to determine the nature of the waste, the following investigations were carried out:

1. Particle size distribution.
2. Chemical composition—XRF.
3. Morphology and mineralogical determination—XRD.
4. Leaching test of heavy metals.
5. Determination of dioxins and furans (PCDD/F)—HRGC/HRMS.

2.1. Particle size distribution

Four random samples S1, S2, S3 and S4 were collected from the combustion chamber. The samples were cooled at room temperature. The weight of each sample was approximately 20 kg.

Visible and comparably large parts, such as metals, glass or incombustible plastic materials, were separated from the bottom ash using a 9.5 mm mesh. For each sample, the remaining material was separated into two equal parts using the Jones separator device. The first part was prepared for chemical and mineralogical analyses by being crushed, using a cone crusher, down to the particle size class <1 mm.

The second part was used to determine particle size distribution. The bottom ash particles were segregated into different fractions using a shaker fitted with standard meshes of different sizes. After drying the bottom ash for 24 h at 105 °C, the four samples were sieved into particle size classes 4.75, 1, 0.5 and 0.25 mm, respectively. Last but not least, the particles of each sample were crushed down to particle size class <1 mm and then underwent chemical analyses and the leaching test for heavy metals.

2.2. Chemical composition X-ray fluorescence spectrometer

Atoms fluoresce at specific energies when excited by X-rays. The X-rays emitted are characteristic of the atom, and provide a qualitative identification of the element. Comparing the intensities of the X-rays from an unknown sample to the measured/tabulated values of known elements provides the basis for quantitative analysis of the element.

The samples were prepared by grinding the bottom ash down to particle size class <60 μm and then pressing it into a cake. An S2 Ranger EDS (Bruker Ltd.) was then used to qualitatively analyze the chemical composition of the bottom ash.

2.3. Morphology and mineralogical determination—X-ray diffraction

X-ray diffraction was utilized to determine the mineralogical properties of the bottom ash. The bottom ash cake (the test sample) was placed in a holder which was then placed in a Rigaku XRD machine with a copper target ($\lambda = 15.406$ nm). A diffraction angle of between 10° and 80° (2θ), and a scanning rate of 4°/min was utilized to analyze the crystal phases of the bottom ash for each sample (S1–S4). Diffraction patterns were manually analyzed utilizing the joint committee on powder diffraction standards.

2.4. Leaching test for heavy metals

Land disposal of solid waste can lead to environmental impacts associated to the leaching of pollutants to surface and ground water.

Table 1
GC/MS parameter for the isomer specific detection of PCDD/Fs and PCBs.

	PCDD/F	PCB
GC:	Type: Agilent 6890; column: Rtx-Dioxin2, 60 m, 0.25 mm ID, 0.25 μ m film thickness (Restek); temperature program: 130 °C, 1.5 min, 45 °C min ⁻¹ , 205 °C, 5 min, 9 °C min ⁻¹ , 305 °C, 20 °C min ⁻¹ , 310 °C, 15 min; carrier gas: helium, constant flow: 1.5 mL/min; injector: cold injection system CIS 4 (Gerstel); temperature program injector: 120 °C, 12 °C s ⁻¹ , 280 °C, 5 min; temperature transferline: 300 °C; autosampler: A200S (CTC); injection volume: 1 μ L pulsed splitless	Type: Agilent 5890 Series II; column: Rtx-CLPesticides2, 30 m, 0.25 mm ID, 0.2 μ m film thickness (Restek); temperature program: 100 °C, 1.5 min, 3 °C min ⁻¹ , 270 °C, 15 °C min ⁻¹ , 300 °C, 10 min; carrier gas: helium, head pressure: 16 psi; injector: cold injection system CIS 3 (Gerstel); temperature program injector: 120 °C, 12 °C s ⁻¹ , 280 °C, 5 min; temperature transferline: 300 °C; autosampler: MPS2 (Gerstel); injection volume: 1 μ L splitless
MS:	Type: MAT 95S (Thermo); ionisation mode: EI, 50 eV, 260 °C; resolution: >9000; detection: SIM mode	Type: MAT 95 (Thermo); ionisation mode: EI, 47 eV, 260 °C; resolution: >8000; detection: SIM mode

Therefore, leaching tests play a major role to assess the possibility of use and treatment within regulatory limits [14,17].

In the leaching test for heavy metals the standard test DIN 38414 was applied. Powdered bottom ash was agitated with distilled deionised water for 24 h, maintaining a 10:1 liquid-to-solid ratio. The leachate (about 100 mL) was filtered through a 0.45 μ m membrane filter and was analyzed by atomic absorption spectrometry (AAS). The same procedure was applied for each particle size class of the bottom ash samples.

The quality and precision of heavy metal analysis were controlled using atomic absorption spectrometry standard solutions for each element analyzed. Laboratory quality control procedures included sample triplicates. Averages of the triplicates as well as the detection limit for each element are presented.

2.5. PCDD/F and PCB analysis

2.5.1. Extraction and clean-up of samples

Extraction of PCB and PCDD/F was carried out with 20 g of sample, previously treated with hydrochloric acid to liberate the carbonized fraction of the analytes using an Accelerated Solvent Extractor (ASE 200) device (Dionex, Sunnyvale CA, USA) according to Roots et al. [18].

After spiking with the ¹³C-labelled standard mixture for quantification the extraction was performed by using a mixture of n-hexane:acetone (75:25, V/V) at a temperature of 120 °C and a pressure of 12 MPa. Two static cycles of 10 min were applied for a complete extraction. To remove interferences, the concentrated crude extracts (ca. 1 mL) were cleaned-up by several sequential liquid chromatography steps as follows: A multilayer chromatography column was filled with 5 g anhydrous Na₂SO₄, 2 g activated silica gel, 4 g silica gel treated with 10% AgNO₃, 2 g silica gel, 2 g silica gel treated with 30% NaOH, 2 g silica gel, 10 g of silica gel treated with 44% H₂SO₄, 2 g silica gel and 5 g anhydrous Na₂SO₄ (top) and washed with 50 mL n-hexane.

A reversible carbon column (100 mg Carboxen 1016, Supelco) was rinsed with 25 mL toluene and 25 mL n-hexane, respectively and directly connected to the outlet of the multilayer column. The concentrated extract was added onto the top of the multilayer column and eluted with 200 mL n-hexane. The PCDD/F and coplanar PCB congeners passed both columns, whereas all other PCB congeners passed both columns. After disconnection the carbon column is further eluted with 30 mL of n-hexane/dichloromethane (9:1, V/V). Both eluates were combined, concentrated and further cleaned on a C₁₈-modified silica column (1 g Isolute C18, Biotage). The column was eluted with 4 mL acetonitrile and the eluate was reduced to a final volume of 20 μ L for GC/MS analysis.

The PCDD/F and coplanar PCB were back-washed from the carbon column with 100 mL toluene. This fraction was further cleaned on a chromatography column filled with 5 g aluminium oxide (Alumina B super I, ICN) [19]. The first fraction with 35 mL n-hexane/chloroform (88:12, V/V) was discarded; the second fraction

with 50 mL dichloromethane was reduced to a final volume of 10 μ L and analyzed by GC/MS.

2.5.2. Determination

PCDD/F and PCB analysis was performed by gas chromatography–high resolution mass spectrometry; the instrumental parameters are listed in Table 1. The MS was operated in SIM mode and the two most intense ions of the molecular ion cluster were monitored for the unlabelled and labelled isomers [20,21].

3. Results

3.1. Particle size distribution

The incombustible materials, with particle size >9.5 mm, accounted for approximately 52.55% (w/w) of total bottom ash. These materials were not examined in the process of determining the nature of bottom ash. It must be pointed out that the incombustible materials were disposed of, together with the bottom ash.

Fig. 1 shows the incombustible materials found in the samples of bottom ash which were collected from the combustion chamber of a HMWI. Large objects are visible, even entire glass bottles polluted with blood, plastic bottles, incombustible gauzes as well as a large amount of hypodermic needles. None of these materials have been burned, maintaining their original form.

Unfortunately, the high proportion of incombustible materials (>50%, w/w) indicates the ineffectiveness of the incineration process. Likely causes are: insufficient incineration time; insufficient air quantity in the primary combustion chamber; the waste was not properly mixed during incineration; the increased humidity levels of waste led to temperatures in the combustion chamber that were

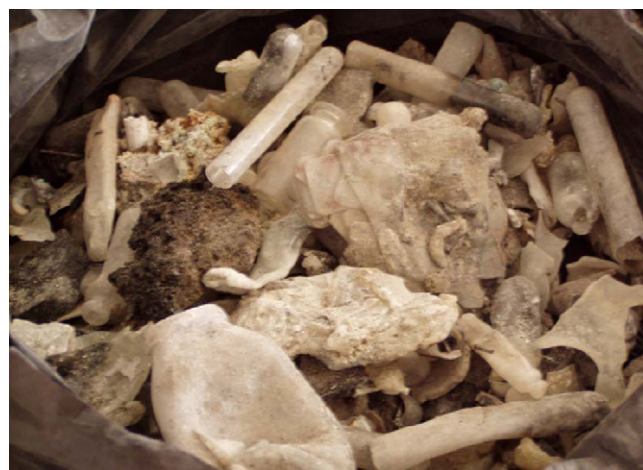


Fig. 1. Incombustible materials separated from the bottom ash.

Table 2

Percentages of incombustible materials found in each sample of bottom ash collected from the combustion chamber of a HMWI.

Percentage weight (%)	Sample 1	Sample 2	Sample 3	Sample 4
Incombustible materials	55.7	45.5	54.2	52.55
Bottom ash	44.3	54.5	45.8	47.45

lower than those required for a successful incineration operation. According to official documents [22] the operating temperature of the combustion chamber oscillates between 650 and 800 °C.

Table 2 shows the high percentages of incombustible materials found in each sample of bottom ash which were collected from the combustion chamber of a HMWI. The same table also states the percentages of bottom ash used for further analysis.

The mass percentages of the particle size distribution of the bottom ash samples are shown in Fig. 2. The majority of particles in the bottom ash exist in the range +1.00–4.75 mm. These particles constitute 32.7% (w/w) of the total particles while, together with the larger particle size materials, they constitute 52.16% (w/w), respectively. The percentage of the particle size class 0.50–1.00 mm considerably reduced, constituting a mere 11.05% (w/w). The bottom ash contained a high proportion of large particles (with 78.63% of the total weight larger than 250 μm).

It must be also pointed out that the results of particle size distribution of the bottom ash are in close agreement with previous studies [23] regarding the grain size of bottom ash coming from municipal solid waste incinerators (MSWIs).

Table 3

Qualitative analysis of the bottom ash using the X-ray fluorescence spectrometer.

Chemical composition (wt%)	Sample 1 (1.1–1.4)	Sample 2 (2.1–2.4)	Sample 3 (3.1–3.4)	Sample 4 (4.1–4.4)
SiO ₂	42.78–47.28	42.58–47.06	40.97–45.29	37.58–41.54
CaO	25.18–27.56	28.51–31.19	27.79–30.41	29.67–32.47
Al ₂ O ₃	12.81–13.61	12.90–13.70	11.98–12.72	10.21–10.85
Na ₂ O	6.89–7.69	4.39–4.91	7.42–8.28	10.96–12.24
TiO ₂	3.80–3.62	3.88–4.08	3.70–3.88	3.60–3.78
Other	4.10–4.66	3.18–3.62	3.53–4.03	3.33–3.79

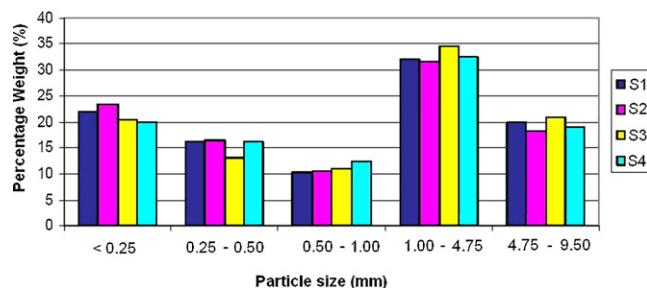


Fig. 2. Mass percentages of the particle size distribution of the bottom ashes.

3.2. Chemical composition X-ray fluorescence spectrometer

EDS analyses of bottom ash revealed that the major elements were SiO₂, CaO and Al₂O₃, accounting for 81.16% of the total amount. The qualitative analysis of the bottom ash samples, according to the X-ray fluorescence spectrometer, is shown in Table 3.

Comparing the present results with previous studies, regarding the content of bottom ash produced at a HMWI in Italy [24], Malaysia [25] and China [26], a complete agreement was observed concerning the type of oxides that were present in the bottom ash of HMWI. Moreover, the results regarding the percentages of various oxides present in bottom ash are in close agreement with the previous studies. The percentage of CaO was higher in the bottom ash of this research, while the percentage of SiO₂ was substantially less.

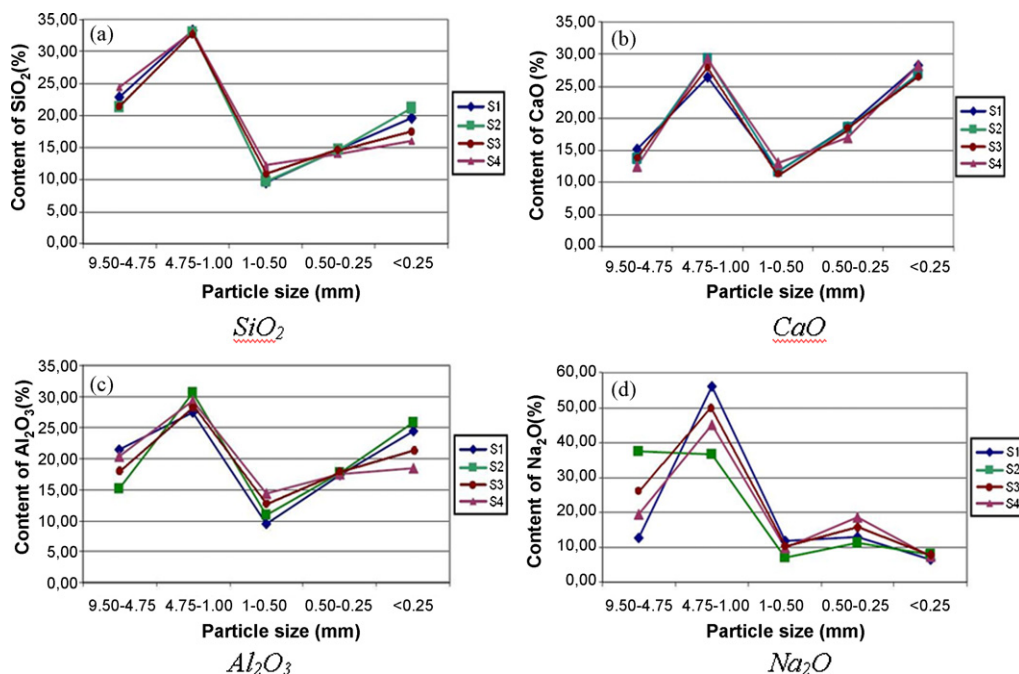


Fig. 3. Percentages of oxides in the different particle size classes.

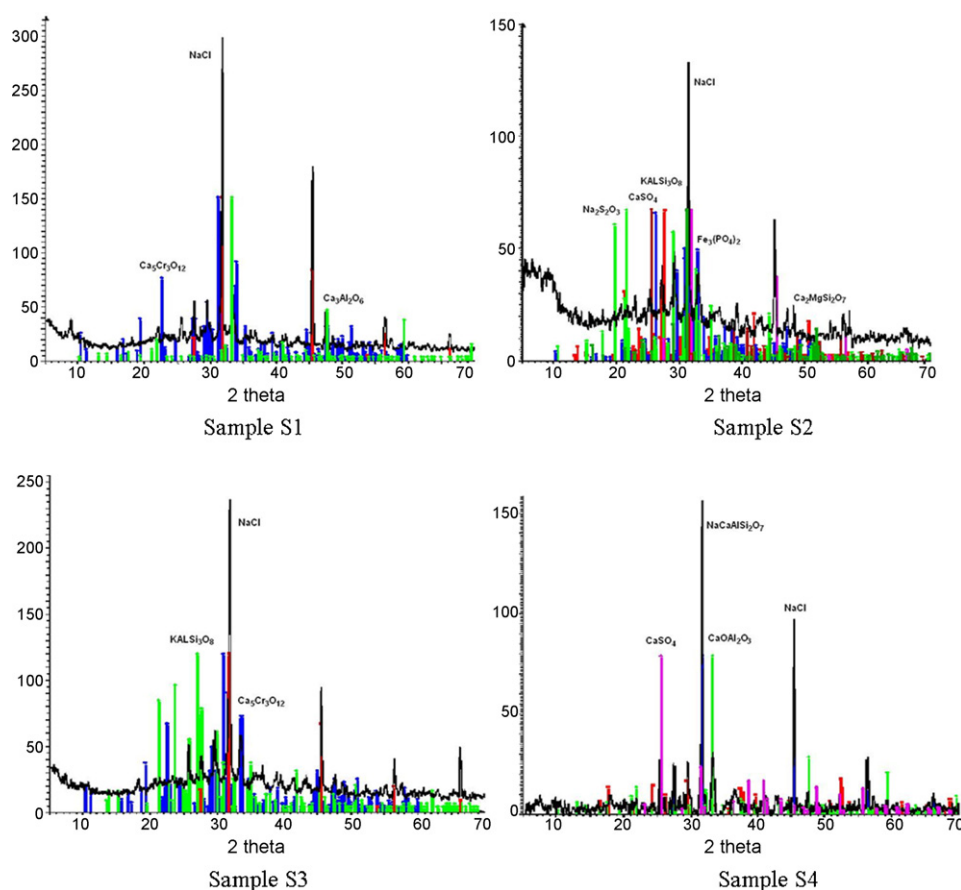


Fig. 4. XRD patterns of bottom ash samples (S1–S4).

The graphs (a–d) of Fig. 3 show how the oxide content varied with bottom ash of different particle sizes. Studying the behavior of each oxide separately, it was observed that larger particles ($-9.50+1.00$ mm) consisted of a high percentage of Na_2O (64.31–74.06%), while the percentage of SiO_2 found in each sample was between 54.37% and 57.55%, that of Al_2O_3 was between 45.62% and 49.74%, that of CaO was between 41.51% and 42.98% and finally, that of TiO_2 was between 24.39% and 41.05%.

As a result, chemical analysis identified an increase of Na_2O and SiO_2 in the larger particle size class of bottom ash. Minimal proportions of oxides were present in the particle size class $-1.00+0.50$ mm, with almost equal percentages: SiO_2 23.31%, CaO 27.64%, Al_2O_3 25.08%, Na_2O 22.09% and TiO_2 25.74%, respectively. Overall, Na_2O and SiO_2 accounted for the largest percentages of oxides found in the particle size class $-9.50+0.50$ mm of 3 samples, 80.99–74.15% and 64.09–69.85%, respectively. The presence of Al_2O_3 covered 56.52–64.1%, CaO 53.16–54.78% and TiO_2 48.96–51.84%. As a result, a strong presence of TiO_2 and CaO was observed in the fine particles of bottom ash.

3.3. Morphology and mineralogical determination—X-ray diffraction

According to X-ray diffraction, the bottom ash contained a considerable percentage of amorphous mass. As a result, a high background signal was present in all samples. Moreover, the results of the X-ray diffraction analysis of the 4 samples were not in agreement with each other. Different components were found in the 4 samples. This is evidence of the fact that different kinds of waste were sent for incineration.

The main components in this category, according to the diffraction pattern obtained by XRD, were halite (NaCl), different kinds of silicon oxides, such as $\text{Ca}_5\text{Cr}_2\text{SiO}_{12}$, KAlSi_3O_8 , $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermenite) and $\text{NaCaAlSi}_2\text{O}_7$. In addition, the presence of several oxides or oxide mixtures, such as $\text{Ca}_3\text{Al}_2\text{O}_6$, $\text{Ca}_5\text{Cr}_3\text{O}_{12}$ and CaOAl_2O_3 , was verified. Samples 2 and 3 consisted of anhydrite (CaSO_4), while sulphurous sodium ($\text{Na}_2\text{S}_2\text{O}_3$) and phosphoric iron ($\text{Fe}_3(\text{PO}_4)_2$) were also found in sample 2. Previous studies have demonstrated that the main minerals present in bottom ash are quartz, halite, anhydrite, anorthite, calcite, and hematite [23,27]. In conclusion, these results are in agreement with previous studies.

The XRD patterns for each sample of the bottom ash shown in Fig. 4.

3.4. Leaching test of heavy metals

Table 4 shows the heavy metal concentrations which were determined in the leachates of the 4 bottom ash samples, as well as the permissible limits for leachate disposal with a 10:1 liquid-to-solid ratio for drinking water.

During the application of DIN 38414, no leaching of lead (Pb) was detected in the leachates of the bottom ash (the detection limit of the instrument used was 0.1 ppm). This is probably due to the absence of lead in the bottom ash or to the null leaching phenomenon experienced when distilled water is used. Finally, in accordance with previous research into the presence of heavy metals in the bottom ash of HMWI in Thailand, the lead found in the bottom ash in the particle size class above 9.50 mm was excluded from the study [28].

Zinc (Zn) was seen to have small concentrations in the leachates of bottom ash. Its measured concentration did not exceed any of the

Table 4
Cumulative leaching amount of heavy metals from the bottom ash (ppm).

Sample	Metal							
	Ni	Pb	Zn	Cu	Cd	Cr	As	Σ (metals)
S1	3.16	<0.02	0.50	6.11	1.18	1.13	<0.01	12.11
S2	3.13	<0.02	0.60	2.68	1.24	2.45	<0.01	10.04
S3	1.09	<0.02	0.30	1.62	0.45	0.98	<0.01	6.47
S4	3.13	<0.02	0.70	4.05	1.19	1.79	<0.01	10.89
Detection limit	0.01	0.02	0.02	0.02	0.001	0.01	0.01	
Permissible limit of heavy metals (ppm) for the leachates of solid wastes with a w/s ratio of 10 L/kg								
Inert wastes	0.4	0.5	4	2	0.04	0.5	0.5	
Non-hazardous	10	10	50	50	1	10	2	
Hazardous	40	50	200	100	5	70	25	
Permissible limit of heavy metals (ppm) for drinking water								
	0.02	0.1	3	2	0.003	0.05	0.01	

environmental permissible limits. The concentration of nickel measured was a class higher than the concentration of zinc, exceeding the permissible limits for drinking water as well as the leachate disposal limit for inactive solid waste.

Copper (Cu) was found in higher concentrations in the leachates mainly because of the surface clashes-symplokes that copper creates with hydroxides of other metals. Generally speaking, copper is a heavy metal that creates an abundance of clashes, such as sulphides, sulphic salts, carbonic, etc. Its measured concentration mainly exceeded the permissible limits for drinking water and also the leachate disposal limit for inactive solid waste.

Cadmium (Cd) was found in higher concentrations than are currently permissible for drinking water. This may be due to the presence of chloride ions in the samples (cadmium frequently creates soluble clashes-symplokes with the chloride ions). Also, cadmium competes strongly with other heavy metals, which deters its adsorption onto the surface of solid waste. Its measured concentration exceeded the permissible limit for non-hazardous waste.

Finally, chromium (Cr) was also found in higher concentrations than are currently permissible for drinking water. The results of DIN-38414 leaching of HMWI bottom ash are in close agreement with previous studies as far as the heavy metals concentration coming from HMWI in Spain is concerned [14]. It must be pointed out that the concentrations Ni, Cu and Cd found in the leachates of this study are about 10 times higher than those found in previous studies [14]. This is due to the different composition of the HMW.

The particle size classes of the four bottom ash samples (9.50–4.75, 4.75–1.00, 1.00–0.50 and 0.5–0.25 mm) were also separately examined for heavy metal content using method DIN 38414. Combining the content in each sieve with the weight of material, the mass balances and the metal units were calculated to derive the distributions of heavy metals for various sizes of particles.

Regarding the distribution of heavy metals in the individual sieves, it was observed that the particles exhibited the behavior of particle size distribution, with the presence of heavy metals being minimal in the –1.00 + 0.50 mm sieve. Particles of metals were distributed in sizes –9.50 + 1.00 mm or smaller than 0.50 mm. There were small differences between the size range –9.50 + 1.00 mm, that contained the biggest particles, and sizes under 0.50 mm containing the finer particles, with Zn oscillating in each sample between 43.48% and 43.45%, respectively. Ni was more likely to be found in the finer ash, with a percentage 44.68%, than in the ash with larger particles (40.97%). Cd was present with corresponding percentages of 44.50% and 41.19%, and finally Cu was found more in the larger particles of bottom ash (47.32%) than in the finer particle samples (42.80%). In the –1.00 + 0.50 mm sieve where the minimal percentage of heavy metals was observed, the above-mentioned metals dominated with almost the same percentages. In total, the highest percentages of heavy metals were measured

in the leachates of the particle size class –9.50 + 0.50 mm, with Cu 57.21%, Zn 56.46%, Cd 55.49% and Ni 55.31%.

Finally, it must be pointed out that the quantity of bottom ash that had particle size above 1 mm was suitable for disposal or recycling as secondary construction material since it did not contain a high percentage of heavy metals. In the present study, the percentage of bottom ash with particle size above 1 mm was 52.16% while, in agreement with the aforementioned assertion, the heavy metals were present in higher percentages in the thin sieves. In the particle size classes of less than 1 mm in each sample, Zn had an average concentration of 56.42%, Ni 59.03%, Cu 52.68% and Cd 58.8%.

Comparing the present results with previous studies, using US EPA TCLP Method 1131 regarding the content of heavy metals of fly and bottom ashes of a medical waste incineration facility in Greece [29], a relative correlation between these studies was observed concerning the concentrations of several metals that were present in the bottom ash leachates.

3.5. PCDD/F

Only few records exist in the national bibliography regarding the content of dioxins and furans in bottom ash, because of the existing legislative gap [30,31]. Theoretical and inquiring studies proved that more than 97% of dioxins is present in the ash and not in the flugas of incineration [31–33]. In the flying ash the levels of dioxins oscillate between ppt and ppb. In the bottom ash the levels are usually about ppt [34].

Tables 5 and 6 show the concentrations of dioxins and furans. In Germany compounds, formulations and products are not permitted to be marketed and distributed if the sum of the compounds indexed with 1 in Table 6 are exceeding 1000 pg/g or the sum indexed with 1 and 2 is exceeding 5000 pg/g or the sum of compounds indexed with 1, 2 and 3 is exceeding 1,00,000 pg/g [35]. Comparing the present results with a previous study, regarding the content of dioxins and furans produced at a HMWI in Japan [36], a complete agreement was observed concerning the concentrations of several types of dioxins and furans that were present in the bottom ash of HMWI.

Soil in residential areas should not contain more than 1000 pg/g TEQ (NATO/CCMS) and industrial soil must be remediated above concentrations of 10,000 pg/g TEQ (NATO/CCMS). Children's ingestion of material such as soil should not become more than an acceptable daily intake of 1 pg TEQ (WHO) per kilogram body weight and day (adults 10 pg TEQ (WHO) per kg and day).

According to Greek legislation [37], dioxins and furans emissions of incineration units must not exceed the permissible limit of 0.1 ng TEQ/m³. Unfortunately, no proportional limit exists for the concentration of dioxins and furans in the solid waste, such as bottom ash, which is led to landfills.

Table 5
Dioxin concentrations in the bottom ash samples (pg/g).

Dioxine type	S1	S2	S3	S4
2,3,7,8-Tetrachlorodibenzo-p-dioxin (pg/g)	56.7	672	43.6	132
Detection limit (pg/g) ¹	1.3			
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	418	5,940	289	1,539
Detection limit (pg/g) ¹	1.9			
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	250	3,889	186	1,264
Detection limit (pg/g) ²	1.5			
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	480	7,726	351	2,631
Detection limit (pg/g) ²	1.5			
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	336	5,807	230	1,802
Detection limit (pg/g) ²	1.5			
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	2502	41,953	1858	14,948
Detection limit (pg/g) ³	0.88			
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	3247	45,852	3250	20,525
Detection limit (pg/g) ³	1.4			

Table 6
Furans concentrations in the bottom ash samples (pg/g).

Furan type	S1	S2	S3	S4
2,3,7,8-Tetrachlorodibenzofuran	262	3,670	528	1,513
Detection limit (pg/g) ¹	1.2			
1,2,3,7,8-Pentachlorodibenzofuran	288	4,845	550	2,510
Detection limit (pg/g) ¹	0.6			
2,3,4,7,8-Pentachlorodibenzofuran	586	11,398	1191	5,976
Detection limit (pg/g) ²	0.7			
1,2,3,4,7,8-Hexachlorodibenzofuran	522	10,209	1186	7,823
Detection limit (pg/g) ²	0.87			
1,2,3,6,7,8-Hexachlorodibenzofuran	561	11,444	1208	8,314
Detection limit (pg/g) ²	0.93			
1,2,3,7,8,9-Hexachlorodibenzofuran	53.4	894	129	960
Detection limit (pg/g) ²	1.5			
2,3,4,6,7,8-Hexachlorodibenzofuran	827	18,079	1977	13,968
Detection limit (pg/g) ²	0.97			
1,2,3,4,6,7,8-Heptachlorodibenzofuran	2175	53,364	6617	53,775
Detection limit (pg/g) ³	0.57			
1,2,3,4,7,8,9-Heptachlorodibenzofuran	171	2,654	405	3,078
Detection limit (pg/g) ³	0.93			
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	733	9,392	2389	14,173
Detection limit (pg/g) ³	0.93			
TEQ (NATO/CCMS)	954	16,790	1485	8,595
TEQ (WHO 1988, Humans)	1160	19,710	1624	9,333

4. Conclusions

Despite the fact that medical wastes are considered as hazardous, due to their infectious and/or toxic characteristics, attention is given to their proper management and disposal of bottom ash. Based on the characteristics of a particular type of bottom ash it is concluded that bottom ash constitutes a danger to drinking water and soil and therefore must be managed as hazardous waste. In particular, the leachates of the samples of bottom ash examined after disposal were hazardous to drinking water. Despite the low quantities of nickel and copper, they still exceeded the permissible limits for the disposal of bottom ash as hazardous waste. Consequently, there is a danger of soil pollution since the permissible limits for the disposal of inactive solid waste are also being exceeded. The overshooting of cadmium limits for the extracts of non-hazardous solid waste were also observed. The concentrations of dioxins and furans in the samples of bottom ash are increased, wherefore the bottom ash must be disposed at special landfill or properly treated before it can or not be reused.

With respect to PCDD/F the materials S2 and S4 are exceeding the limits or TRGS 557 and are not even suitable as material for industrial settings.

Of course, the results of this research concern bottom ash from a particular incinerator and in no way attempt to characterize the bottom ash of HMWI for the whole of Greece. For this reason, a more

systematic and long-term study of the characteristics of bottom ash produced in Greece is required. Such a study must include a larger number of HMWIs and various types of incinerator chamber, in order to validate the above conclusions on the level of hazard that bottom ash presents and so lead to a more comprehensive management policy.

However, this study indicated the importance of the examination and monitoring of hospital bottom ash.

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