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Characterisation and management of ash produced in the hospital waste incinerator of Athens, Greece

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ABSTRACT

Bottom and fly ash samples (BASH and FASH) from the APOTEFROTIRAS S.A. medical waste incinerator (Athens, Greece) were investigated. Powder-XRD data and geochemical diagrams showed BASH to be an amorphous material, analogous to basaltic glass, and FASH consisting of crystalline compounds (mainly CaClOH). Bulk analyses by ICP-MS and point analyses by SEM-EDS indicated a high content of heavy metals, such as Fe, Cu and Cr, in both samples. However, BASH was highly enriched in Ni while FASH was additionally enriched in Zn and Pb. Gamma-ray measurements showed that the radioactivity of both ash samples, due to natural and artificial radionuclides (^{137}Cs, ^{57}Co), was within the permissible levels recommended by IAEA. According to EN-type leaching tests, BASH was practically inert with regard to the mobility of the hazardous elements in aqueous media. FASH, however, showed a relatively high EN (and TCLP) leachability with regard to Pb and Zn. Finally, the stabilisation method, suggested for the treatment of FASH, included compression of the powder into briquettes using an appropriate machine and embedding the briquettes into pozzolanic cement blocks. After this treatment, TCLP and EN-type tests showed minimal release of Pb and Zn, thereby demonstrating a reliable management of ash waste.

1. Introduction

Hazardous medical waste originates from the operation of any sanitary unit, such as public and private infirmaries, municipal surgeries, military hospitals, blood donation centres, diagnostic laboratories, microbiological laboratories, veterinary clinics and veterinary diagnostic laboratories. These wastes need proper collection, transportation and management. As such, Greek law article 37591/2031/2003, entitled "Measures and Terms on the Management of Medical Waste from Sanitary Units", determines the measures, terms and processes for the handling of medical waste so that public health and the environment are protected.

Every year, 14,000 tons of medical waste is produced, with 53% of that waste produced in the greater Athens area (Attica, Greece), which is populated by about 4 million people. Therefore, the necessity of managing that waste constitutes a leading force in the area of collection, transportation and treatment of this medical waste. To meet this need, APOTEFROTIRAS S.A. has been made responsible for the operation and maintenance of the Medical Waste Incineration Plant of ACMAR (Association of Communities and Municipalities in the Attica Region) at Ano Liossia, near Athens. It also owns the largest medical waste transportation network in Attica. The main activity of the company is the implementation of a public contract with ACMAR for the operation and maintenance of the Incineration Plant of Athens, as well as the collection and transportation of medical waste to the incineration plant.

APOTEFROTIRAS S.A. possesses an internal protocol for the collection and transportation of medical waste, as well as an ISO 14001:2004 Environmental Management Certification, signifying compliance with safety regulations and environmental protection. In the waste handling process, medical waste is first weighed at a weighbridge and unloaded into the facility's refrigeration chambers for storage. They remain in storage for a maximum of 2–3 days and are then unloaded on a first-in, first-out basis. Next, there are two independent lines for incineration at high temperature (>1100 °C). The waste produced from incineration is of two kinds: (a) wastew-

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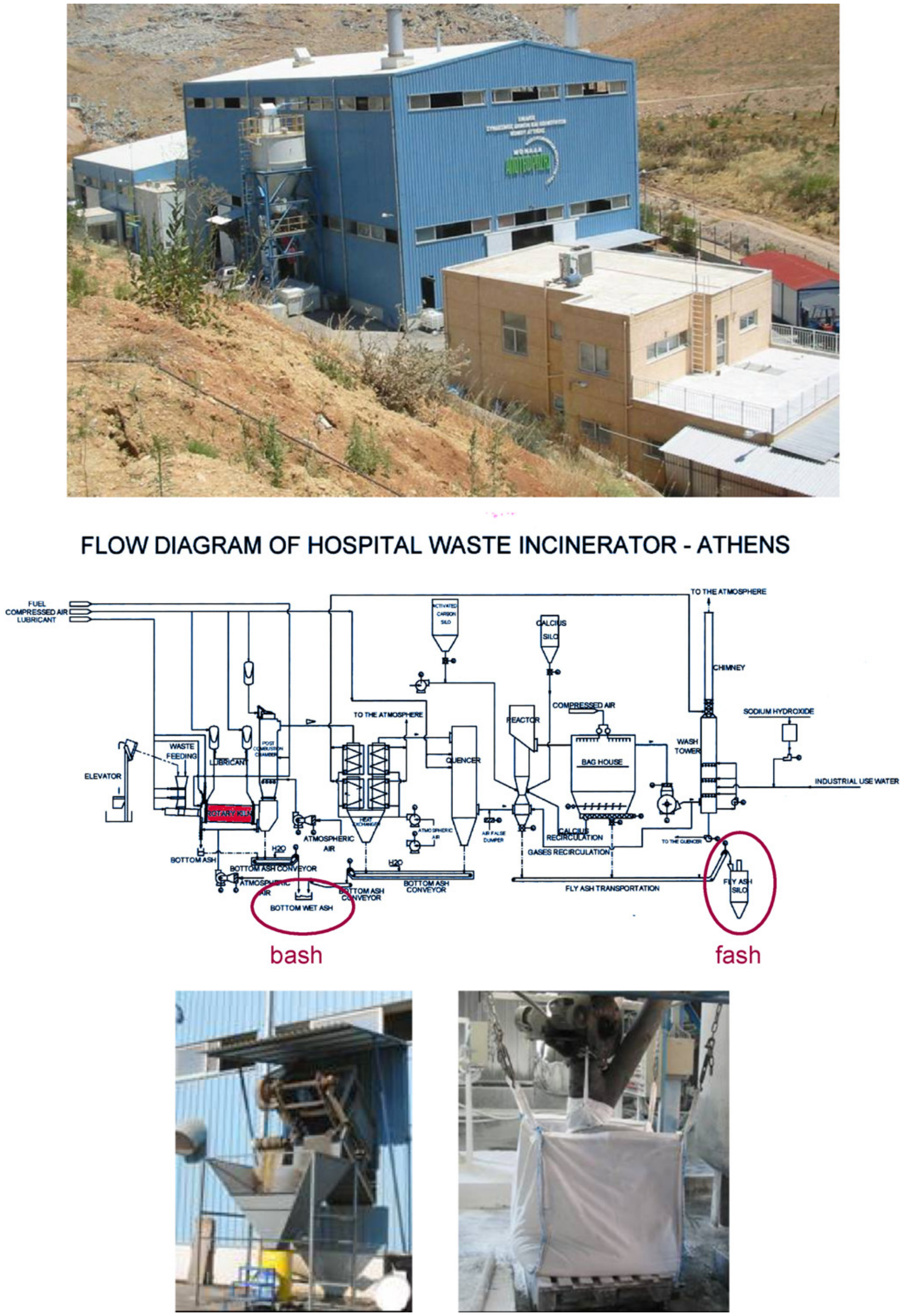

Fig. 1. The ACMAR/APOTEFROTIRAS S.A. hospital waste incinerator plant located in Ano Liossia area, near Athens, Greece.

ater which is evaporated for the production of distilled water; and (b) ash (fly ash is collected in large bags and sent abroad for storage and bottom ash, which is collected in barrels and temporarily stored at the plant). The fact that the incinerator is near the mega city of Athens and very close to the inhabited municipality of Ano Liossia necessitates the constant analysis of the by-products that are produced from the incineration. The necessity for the characterisation and management of these by-products led to this study. Therefore, our purpose was not only to characterise this ash by means of microscopic and spectroscopic techniques, but also, for the first time, to suggest a stabilisation model for the management of these potentially hazardous wastes.

Literature on the characterisation and management of ashes produced in hospital waste incinerators around the world, despite the social and scientific interest of the issue, is relatively shallow. The majority of existing literature concerns materials from Asian countries (i.e., China, Pakistan, Taiwan, Malaysia and Japan) and S. America [1–11]. Meanwhile, previous work in Greece concerned investigation of samples collected from a medical waste incinerator [12] and analyses of certain metals (e.g., Fe, Cu, Zn), PAHs and PCBs

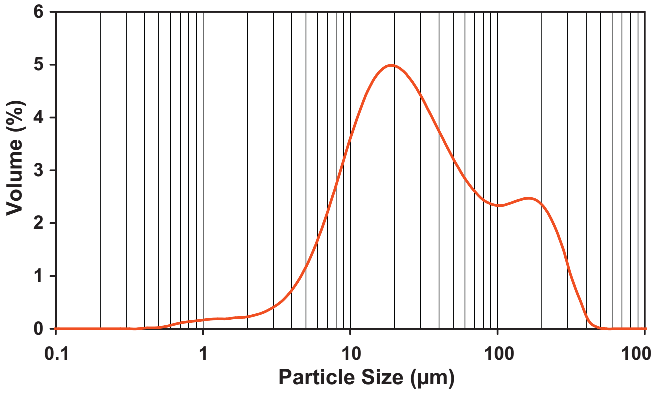

Fig. 2. Particle size distribution of FASH according to LALLS measurements.

in ashes from the ACMAR plant operated by APOTEFROTIRAS S.A. [13]. In addition, it should be noted that there are no studies about all of the elements contained in APOTEFROTIRAS S.A. ash (such as REE and actinides related to radioactivity applications), as suggested in relevant papers on incinerator ash from other countries [9].

The methodology followed in the present paper included the study of particle size distribution, particularly of fly ash using low-angle laser light scattering (LALLS), phase determination by means of powder-XRD, morphology investigation and point analyses using a scanning electron microscope (SEM) equipped with an EDS, bulk chemical analysis performed by ICP-MS, high-resolution gamma-ray spectroscopic measurements and US EPA toxicity characteristic leaching procedure (TCLP) together with European norm (EN-type) leaching tests for the mobility of heavy metals in aqueous media. Moreover, though leaching tests have already been reported by Valavanidis et al. [13], there were no further studies suggesting how to immobilise ash that contains hazardous elements or how to stabilise these materials. For this study, samples were pulverised and shaped into briquettes, then embedded into pozzolanic cement (e.g., [2]). Based on the results, the above methodology can be proposed for the final management of ACMAR/APOTEFROTIRAS S.A. ashes exhibiting TCLP and/or EN-toxicity.

2. Materials and methods

Bottom ash (BASH) and fly ash (FASH) samples were collected from the ACMAR/APOTEFROTIRAS S.A. hospital waste incinerator plant located in Ano Liossia, near the greater Athens urban waste disposal site (Fig. 1). The BASH was selected from the combustion chamber and was a brownish-black and compact glassy, inhomogeneous material containing visible and comparably large pieces of metal that were separated by hand. The FASH sample collected from the electrostatic filters was a greyish-coloured, fine-grained material. The two ash samples used in the present study concerned in fact composite materials which were created by taking the appropriate number of specimens in different seasons and using standard mixing procedures and sample splitters. FASH was subjected to particle size analysis by means of LALLS, in dry, using a MALVERN Scirocco 2000 instrument. BASH was initially crushed down to a particle size <1 mm using a cone crusher. Then both materials were dried at 105 °C and pulverised using an industrial mill. Homogeneous specimens were separated into two equal parts using a separator device. The first part was prepared for chemical and phase analyses and the second one for leaching (TCLP and EN) tests to investigate the mobility of heavy metals.

The phase characterisation of the two types of ash (BASH and FASH) was performed by means of powder-XRD using a SIEMENS D5005 (currently BRUKER AXS) diffractometer with CuK_α radiation

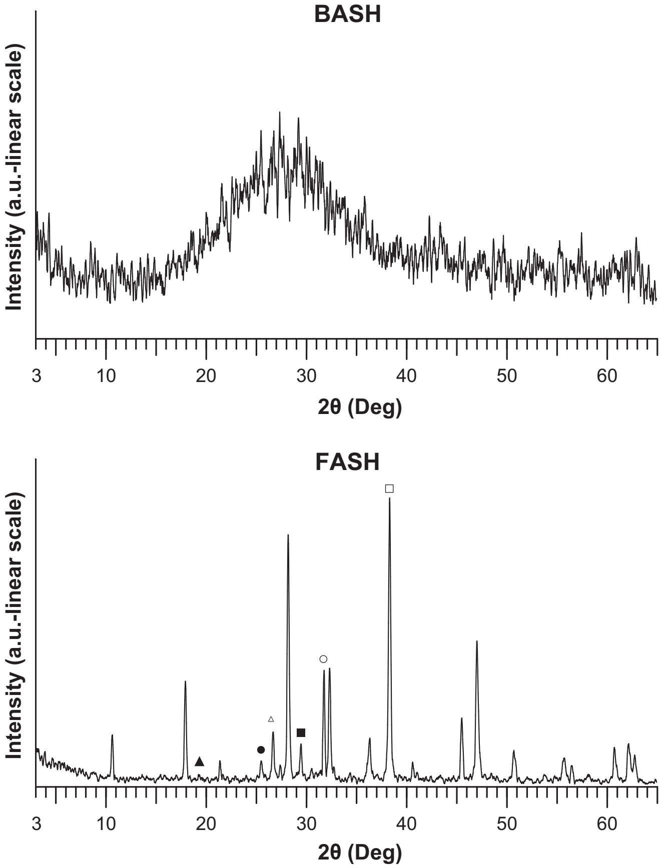

Fig. 3. Powder-XRD patterns of BASH (upper) and FASH (lower; the strongest reflections of calcium chloride hydroxide, calcite, halite, anhydrite, quartz and kaolinite clay are indicated by □, ■, ○, ●, △, ▲ symbols, respectively).

($\lambda = 1.54$ Å) at an accelerating voltage of 40 kV. The identification of crystalline phases was obtained with data from ICDD (International Centre for Diffraction Data) and the evaluation was performed with EVA software from SIEMENS (currently BRUKER AXS) for semi-quantitative analysis.

Subsequent morphology investigation and point analyses were performed, on both free surfaces of the materials and polished-sections in epoxy resin, using a JEOL JSM-5600 SEM equipped with an EDS type Link Pentafet from Oxford Instruments. The observations were made with an accelerating voltage of 20 kV, a working distance of 20 mm, a current beam of 1.5 nA, an active time of 20–100 s and a magnification from ×35 to ×3500. Pure metallic materials and minerals were used as standards.

Bulk analyses for major and trace elements were performed using a Perkin Elmer ICP-OES and a Perkin Elmer Sciex Elan 9000 ICP-MS following a $LiBO_2/LiB_4O_7$ fusion and HNO_3 digestion of a 0.2 g sample. In addition, a separate 0.5 g split was digested in a HNO_3:HCl mixture (1:3) and analysed by ICP-MS for precious and base metals. The chemical composition of BASH and FASH composite samples, were achieved using strict QA/QC procedures including, of course, three analytical replicates. Blanks (analytical and method), duplicates and standard geological and synthetic reference materials provided a measure of background noise, accuracy and precision. QA/QC protocol incorporates a granite or quartz sample-prep blank(s) carried through all stages of preparation and analysis as the first sample(s) in the job, a pulp replicate (REP) to monitor analytical precision, a −10 mesh reject duplicate (DUP) to monitor sub-sampling variation, a reagent blank (BLK) to measure background and an aliquot of In-house Reference Materials and Certified Reference Materials (CRM) to monitor accuracy. In-house

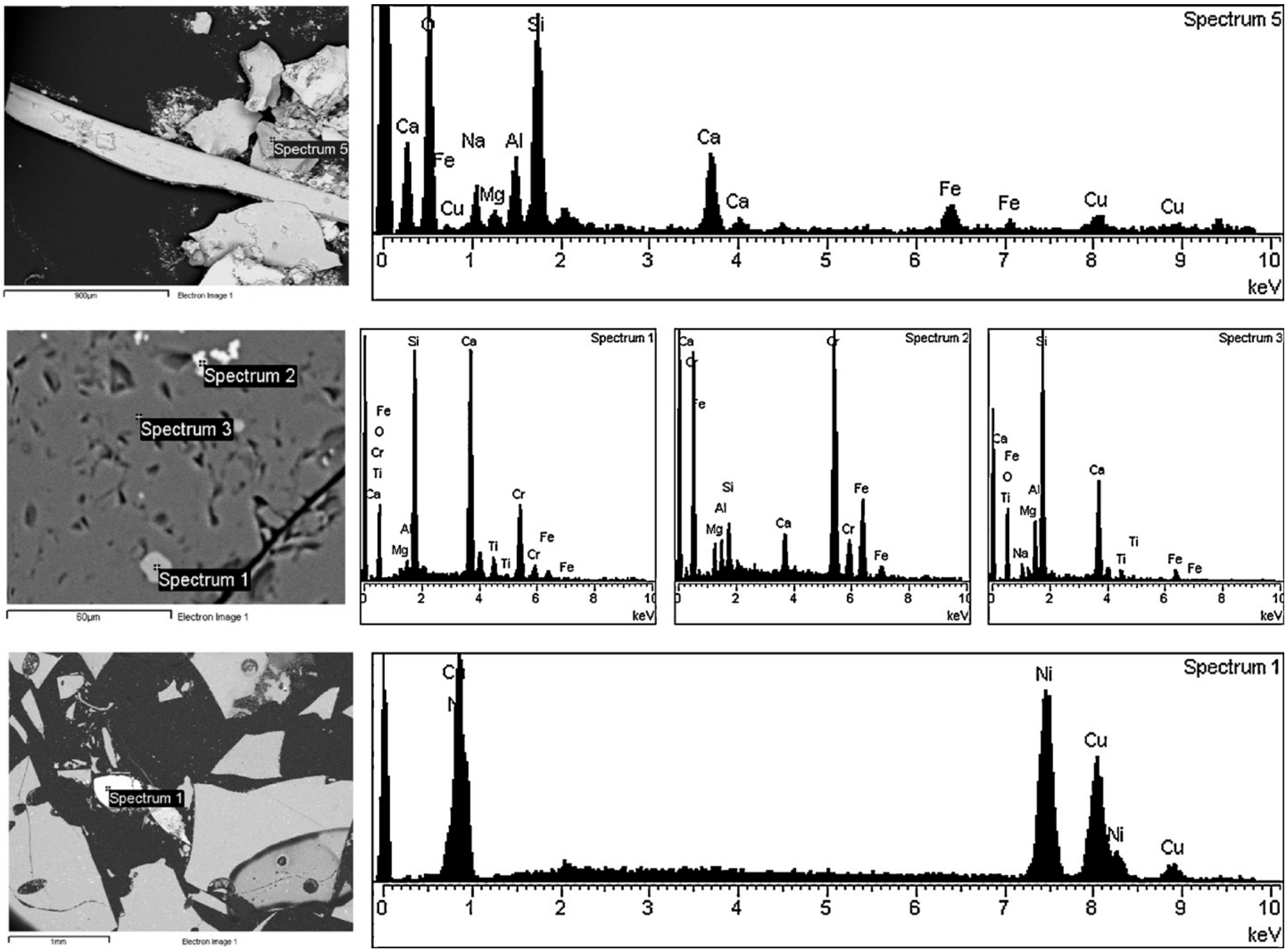

Fig. 4. SEM-EDS data for the BASH sample (free surfaces of glassy fragments and polished material embedded in epoxy resin).

Reference Materials were prepared and certified against internationally Certified Reference Materials (CRM), such as CANMET and USGS standards where possible, and they were externally verified at a minimum of three commercial laboratories. The QA/QC data, using four different Reference Materials (STD1, In-house Reference Material based on soil samples; STD2, In-house Reference Material, matrix of geological samples with additional elements spiked into the material; SDT3, In-house Reference Material, based on geological samples; STD4, CRM from Ore Research & Exploration PTY Ltd. Australia for carbon and sulphur analyses), and appropriate blanks (BLK), are summarized in Table 1. Concentrations exceeding 5% of the lowest sample concentration or 5 times the detection limit for that element, (whichever is higher) the blank reporting > DL were confirmed by re-analysis of the same solution. Elements whose concentration exceeded 5 times the detection limit and did not repeat values within 10% were flagged and investigated. In that case, solutions were rerun and if confirmed the pulp material was retrieved for the sample to inspect the material for homogeneity and fineness. The process for evaluating reject reruns is the same as for pulp reruns except 30% is the acceptable tolerance. If reported concentrations are higher than expected values, contamination may have occurred. Preparation blanks were used to monitor contamination only. Concentration of preparation blanks greater than 50 times the sample concentration should be rechecked by first re-analysis of a group of samples followed by re-weighing, if the contamination is confirmed.

The measurement of radioactivity was obtained with a high-purity Ge detector (HPGe). Natural and artificial radionuclides in the samples were analysed using a 50% (nominal relative efficiency) HPGe (Canberra) GEM-FX 8530 P4. A lead shield surrounding the detector to reduce the ambient gamma-ray background was also used. Analyses of gamma-ray spectra for each sample were conducted with the software SPECTRG.

The energy and efficiency calibrations were performed using a ^{152}Eu(93%) + ^{154}Eu(7%) reference source that had been prepared and calibrated at NCSR “Demokritos” (Athens, Greece) in the following way: a small quantity of ^{152}Eu + ^{154}Eu diluted liquid source (obtained originally from Amersham, Co.) was taken up in a 0.5 ml syringe, placed at a distance of 25 cm from the face of the HPGe detector and its activity measured. Then the contents of the syringe were injected into an inert material (talcum powder) that had been placed inside a plastic container (diameter 6.9 cm) identical to the ones used for the subsequently measured samples. The self-absorption of the inert material then approximated that of the samples. The residual activity remaining in the syringe was then measured to determine the final activity actually injected into the inert material. Finally, this newly prepared source was placed in contact with the front of the detector. The source was rotated so that the back face was in contact with the detector’s front and a second spectrum was recorded. The difference in the counting rate of the gamma-ray peaks for the two spectra was less than 3%, thus ensuring that the distribution of radioactivity in the inert material

Table 1
QA/QC data concerning bulk chemical analysis of BASH and FASH composite samples by ICP-MS.

Analyte	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Sc	Ba	Co
Unit	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm
MDL	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	1	1	0.2
STD1	58.25	14.08	7.58	3.33	6.34	3.68	2.13	0.69	0.82	0.39	0.545	25	499	26.2
STD1	58.12	14.09	7.62	3.34	6.36	3.68	2.15	0.69	0.83	0.39	0.546	25	497	26.7
STD1 expected	58.47	14.23	7.67	3.35	6.42	3.71	2.17	0.69	0.83	0.39	0.55	25	514	26.2
BLK (blank)	<0.01	<0.01	<0.04	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.002	<1	<1	<0.2

Analyte	Cs	Ga	Hf	Nb	Rb	Sn	Sr	Ta	Th	U	V	W	Zr	Y
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MDL	0.1	0.5	0.1	0.1	0.1	1	0.5	0.1	0.2	0.1	8	0.5	0.1	0.1
STD1	6.7	17.1	9.3	20.5	27.8	15	398.4	6.8	9.9	16	200	14.5	278.3	30.5
STD1	6.5	17	9.5	20.4	27.5	14	398.7	6.8	9.7	16	200	14.6	278.1	30.5
STD1 expected	7.1	17.6	9.8	21.3	28.7	15	407.4	7.4	9.9	16.4	200	14.8	280	31
BLK (blank)	<0.1	<0.5	<0.1	<0.1	<0.1	<1	<0.5	<0.1	<0.2	<0.1	<8	<0.5	<0.1	<0.1

Analyte	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
MDL	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01
STD1	11.7	27.1	3.3	13.5	2.89	0.85	2.82	0.5	2.86	0.59	1.72	0.27	1.72	0.27
STD1	12	27.4	3.3	13.5	2.82	0.85	2.82	0.49	2.83	0.6	1.71	0.24	1.68	0.26
STD1 expected	12.3	27.1	3.45	14	3	0.89	2.93	0.53	3	0.62	1.84	0.27	1.79	0.27
BLK (blank)	<0.1	<0.1	<0.02	<0.3	<0.05	<0.02	<0.05	<0.01	<0.05	<0.02	<0.03	<0.01	<0.05	<0.01

Analyte	Mo	Cu	Pb	Zn	Ni	As	Cd	Sb	Bi	Ag	Au	Hg	Tl	Se
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppm	ppm	ppm
MDL	0.1	0.1	0.1	1	0.1	0.5	0.1	0.1	0.1	0.1	0.5	0.01	0.1	0.5
STD2	20.8	105.5	72.6	407	58.5	54.2	6.4	5	5	0.9	63.4	0.18	4.3	4
STD2 expected	20.5	109	70.6	411	56	48.2	6.4	4.6	4.5	0.9	70	0.2	4.2	3.5
STD3	1.1	607.1	18.9	123	295.1	3.6	0.1	0.2	0.2	0.3	41.2	0.02	<0.1	0.6
SDT3 expected	0.9	600	19	119	281	4.2	0.09	0.13	0.18	0.3	43	0.03	0.07	0.54
BLK (blank)	<0.1	<0.1	<0.1	<1	<0.1	<0.5	<0.1	<0.1	<0.1	<0.1	<0.5	<0.01	<0.1	<0.5

Analyte	C	S
Unit	%	%
MDL	0.02	0.02
STD4	0.17	18.85
SDT4 expected	0.16	18
BLK (blank)	<0.02	<0.02

was almost homogenous. After adding the two spectra and using the most intense gamma-ray peaks from the source, the absolute detection efficiency was determined as a function of the energy. The empirical function used for the fit was:

$$y = \frac{Ax^b}{C} + x^d \tag{1}$$

where y is the absolute efficiency, x is the gamma-ray energy and A, b, C and d are free parameters. The same geometry was used for all samples. In most cases, the measuring time was 24 h, but in cases of very low specific activity, 48-h spectra were recorded. Next, the activity was calculated according to the following equation (2):

$$A = \frac{\text{counts}}{TmI_\gamma\varepsilon} \tag{2}$$

where, A is the activity in units of Bq/kg, counts is the net area calculation, T is the measuring period in seconds, m is the mass of the samples in kilograms (kg), I_γ is the intensity of each gamma-ray peak and ε is the efficiency for the specific geometry.

The net area calculation (counts) was performed using the SPECTRG software package. The intensities of each radionuclide were taken from the literature and the efficiency was calculated as described in the previous paragraph (Eq. (1)) [14].

To investigate potential immobilisation methods, BASH and FASH samples were pulverised in an industrial mill and the powder was used for briquettes that were later embedded into pozzolanic cement blocks. Ash samples were wetted with 12–14% (w/w) water before agglomeration. To achieve homogenous dispersion of the added water to the ash mass, an industrial mixing device was used. During water addition and mixing, heat was produced due to the exothermal hydration reaction of the ash components. This observation was evidence that ash could act as a pozzolanic binder. In this way, the pozzolanic activity of the ash could be used for the development of hydraulic bonds to develop agglomerates without the addition of any other binder during briquetting. After 10 min of mixing, the ash was then shaped into briquettes by means of a laboratory scale briquetting machine. Conditions that produced the most stable briquettes was a pressure of 800 psi and a drum rotation speed of 10 briquettes/min. The size of the produced agglomerates was 15 × 5 mm. After production, fresh briquettes were cured for a period of 15 days in plastic bags under constant temperature (20 °C) and high relative humidity (>90%) in order for the hydraulic bonds to be developed. The creation of cement models required a co-mixture of 1920 g sand, 400 g pozzolanic cement, 240 g water and 5.6 g liquator, then stirring for 10 min. The cement mash was then poured into blocks, in the centre of which the briquettes were placed. The blocks were left in the cement maturation chamber (T: 20 ± 1 °C, RH: 90%) for 28 days under controlled conditions according to EN 196. The models of cement were prisms 40 × 40 × 160 mm in dimension [15].

Leaching tests were performed on raw BASH and raw FASH, as well as on both ashes embedded into cement in the form of briquettes, using TCLP (TCLP Method 1311, SW846, U.S. EPA 1996) and EN 12457-01 procedures [16,17]. The metal concentrations in

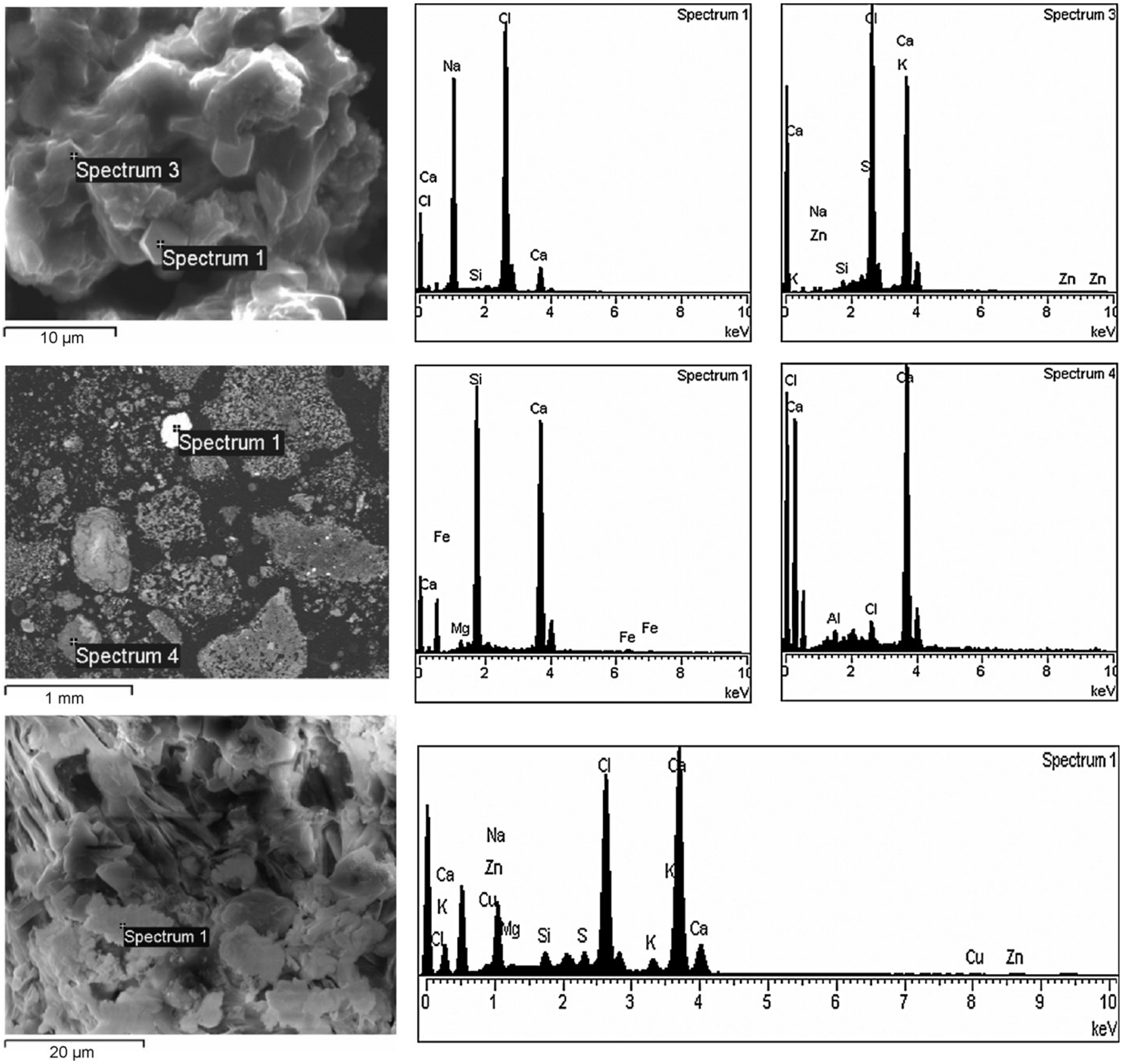

Fig. 5. SEM-EDS data for the FASH sample (free surfaces of aggregates and polished material embedded in epoxy resin).

the extraction solutions were determined by fast sequential atomic absorption spectrometry (AAS) using a Varian AA280FS instrument.

3. Results and discussion

According to particle size analysis, BASH could be considered a compact material (almost massive black glass) without visible grains at any scale. On the other hand, FASH was an aggregate of μm-sized grey particles having the distribution presented in Fig. 2. It is obvious that 90% of the FASH particles possess a spherical equivalent diameter below ca. 182 μm whereas 50% below ca. 30 μm and 10% below ca. 8 μm. However, most of the flakes, constituting the aggregates (see also Fig. 5 below), have dimensions in the region ca. 8–80 μm. The surface-weighted mean for the material is 15.5 μm, the volume-weighted mean is 63.3 μm and the geometric specific surface area is 0.4 m^2/g.

The characterisation by means of powder-XRD showed that BASH was practically amorphous, while FASH consisted of crystalline compounds. The main crystalline compound detected was CaClOH, but the material also contained minor amounts of calcite ($CaCO_3$), halite (NaCl), anhydrite ($CaSO_4$), quartz (SiO_2) and kaolinite clay ($Al_2Si_2O_5(OH)_4$) (Fig. 3).

Subsequent investigation of BASH using SEM-EDS revealed the presence of particles composed of Si–Ca–Al–Na–Fe–Mg–Ti–Cu as well as Cr–Fe, Cr–Fe–Ti and Ni–Cu phases (most likely alloys) enclosed into the glass matrix (mainly Si–Ca–Al–Fe–Na–Mg–Ti), which consisted of irregular fragments of different dimensions (Fig. 4). These alloys came from metallic instruments present in the initial medical wastes (i.e., needles, grippers, medical instruments, etc.). The FASH sample, on the other hand, consisted of fine particulate aggregates containing Ca, Cl, Na, Si, Al, K and S. Only traces of Fe, Cu and Zn were detected in the FASH sample with the SEM-EDS (Fig. 5). The high amounts of Ca and Cl, corresponding to CaClOH,

Table 2
Chemical composition of the BASH and FASH composite samples.

Component	Unit	BASH	FASH	Component	Unit	BASH	FASH	Component	Unit	BASH	FASH	Component	Unit	BASH	FASH
SiO_2	wt.%	50.82	1.36	Ba	ppm	13826.00	540.00	Gd	ppm	17.32	0.45	Er	ppm	0.85	0.07
CaO	wt.%	19.29	48.18	Ni	ppm	3948.20	41.10	Ag	ppm	15.10	26.60	Yb	ppm	0.84	0.05
Al_2O_3	wt.%	12.10	0.13	Zn	ppm	526.00	5137.00	Au	ppm	12.68	0.03	Eu	ppm	0.61	0.02
Fe_2O_3	wt.%	4.98	0.20	Ce	ppm	415.30	0.70	Ga	ppm	7.20	4.10	Cd	ppm	0.40	29.40
Na_2O	wt.%	4.53	4.34	Sr	ppm	408.30	140.70	Hf	ppm	6.80	0.10	Tb	ppm	0.24	0.02
MgO	wt.%	2.09	0.41	Zr	ppm	246.70	2.60	Y	ppm	6.30	1.00	Ho	ppm	0.23	0.02
CuO	wt.%	1.95	0.23	Pb	ppm	82.50	1559.60	Pr	ppm	5.91	0.14	Lu	ppm	0.11	0.01
TiO_2	wt.%	1.78	0.03	Mo	ppm	69.00	9.10	Rb	ppm	5.70	13.90	Cs	ppm	0.10	1.60
Cr_2O_3	wt.%	0.87	0.01	V	ppm	61.00	147.00	Th	ppm	5.70	0.20	Tm	ppm	0.10	0.01
P_2O_5	wt.%	0.59	0.04	Sn	ppm	53.00	303.00	Sc	ppm	4.00	1.00	Tl	ppm	0.10	0.10
K_2O	wt.%	0.37	0.77	W	ppm	52.40	185.50	Bi	ppm	2.20	72.80	Hg	ppm	0.01	0.32
MnO	wt.%	0.15	0.01	Sb	ppm	50.90	73.20	U	ppm	2.00	0.80				
LOI	wt.%	0.10	26.00	Co	ppm	30.40	0.60	Sm	ppm	1.99	0.12				
Total C	wt.%	0.04	1.09	Nd	ppm	24.90	0.30	Ta	ppm	1.70	0.90				
Total S	wt.%	0.02	0.61	As	ppm	23.90	16.90	Dy	ppm	1.55	0.16				
SUM	wt.%	99.68	83.42	Nb	ppm	21.70	0.40	Be	ppm	1.00	1.00				
Cletc	wt.%	0.32	16.58	La	ppm	17.90	0.70	Se	ppm	1.00	2.00				

were due to the treatment of the combustion gases with hydrated lime and activated carbon for the removal of acidic substances and the absorption of dioxins and heavy metals.

Bulk chemical analysis by ICP-MS (Table 2) showed that most of the major elements (Si, Al, Fe, Na, Mg, Cu, Ti, Cr, P and Mn) were preferably concentrated in the BASH sample, with the exception of Ca and K, which were concentrated in FASH (Fig. 6). It was notable that C and S were insignificant in BASH and very low in FASH samples. Thus, BASH contained significant amounts of potentially hazardous metals, such as Cu, Cr and Mn, which were not found in FASH. However, FASH contained higher amounts of trace elements like Zn, Pb, V, Sn, W, Sb, Bi, Se, Cd and Hg, while Ba, Ni and As were relatively concentrated in BASH. It is important to note that REE and actinides (U, Th), as well as other high-field strength elements (HFSE), were also contained in the BASH glass. Moreover, BASH surprisingly contained elevated concentrations of Au (12.68 ppm), most likely from metallic medical implements.

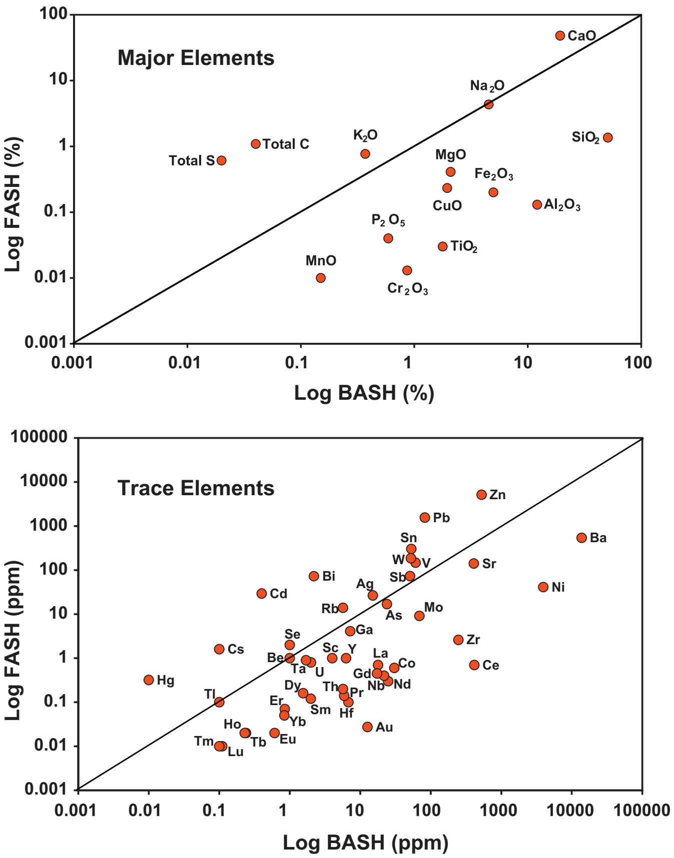

Fig. 6. Chemical composition of BASH and FASH (major elements and trace elements).

As illustrated in Fig. 7, using a total-alkalis vs. silica diagram (frequently used for classification of igneous rocks [e.g., [18]]), BASH material is a synthetic analogue of natural basalt. Since BASH was proven to be amorphous (see Fig. 3), it is actually analogous to natural basaltic glass (e.g., [19]). Basaltic glass is an uncrystallised product of rapidly cooling magma having high CaO and MgO and relatively low SiO_2 as well as alkali oxides ($Na_2O + K_2O$). It is a common amorphous igneous rock in volcanic islands like Hawaii and Iceland. In materials and environmental science basaltic glasses (either natural or synthetic) are greatly investigated because they are considered to be proper matrices for nuclear and conventional wastes long-term disposal (e.g., [20]). Thus, we herein demonstrate that in the bottom ash (BASH) from Athens medical waste incinerator all potentially hazardous elements are hosted in "basaltic glass" (basalt-type) matrix, which gave it the advantage of safe disposal in normal waste sites. The only difference between BASH and basalts was due to the much higher levels of Ca, Cu, Cr, P, Ni, Zr, Ba, REE (specially Ce and Gd), Zn, Pb, Th, As and Au. The potential availability of all the above toxic elements in BASH and FASH (including heavy metals) was subsequently checked by TCLP and EN.

In order to investigate the relative enrichment or depletion of elements in natural and synthetic glasses, we can "normalise" (e.g., [18]) the concentration of the each element to chondrites (particular meteorites thought to be relatively unfractionated samples of the solar system dating from the original nucleosynthesis) and/or to Upper Continental Crust/UCC (the surface of the Earth, i.e., the upper lithosphere, which is in contact to the biosphere and accessible to humans). As a consequence BASH is highly enriched in Ba and Ce compared to the solar system which is the fundamental non-anthropogenic source (Fig. 8). Of course BASH is also enriched in Ba and Ce compared to UCC which is the abiotic surface of the Earth providing industry and technology with raw materials. Thus, in addition to heavy metals that originated from medical tools, Ba and Ce enrichment was entirely anthropogenic due to excessive consumption of medical materials (contrast agents used in radiology and possibly glass ceramics). High levels of Ce enrichment in medical incinerator waste ashes have also been reported by Zhao et al. [9] using relevant normalised diagrams. In our case, there was

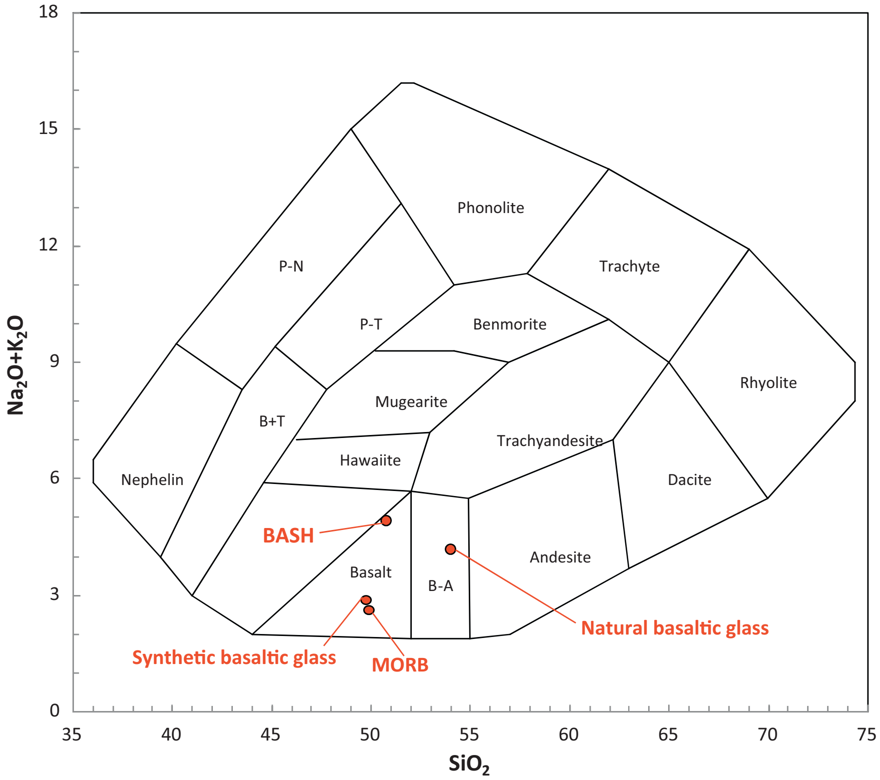

Fig. 7. Chemical composition of BASH in relation to natural and synthetic basaltic glasses and mid-ocean ridge basalt (MORB).

also a relative enrichment in Gd, the first demonstration in the literature (Fig. 9), probably due to the use of paramagnetic contrast materials.

According to high resolution gamma-ray spectra, the BASH and FASH materials contained both natural and artificial radionuclides. The activities, as calculated from Eq. (2), are given in Table 3 and depicted schematically in Fig. 10. A typical spectrum of FASH, normalised to 86,400 s, is also drawn. The radionuclides observed in BASH were both artificial (^{137}Cs and ^{57}Co) and natural radioactivity isotopes (^{214}Bi, ^{214}Pb, ^{212}Pb, ^{208}Tl, ^{40}K, ^{226}Ra and ^{235}U). The activity concentration for the ^{238}U decay series (progenies) varied from 577 Bq/kg (^{214}Bi) to 802 Bq/kg (^{214}Pb), while the ^{232}Th decay series (^{212}Pb and ^{208}Tl) was in equilibrium because their concentrations were 589 Bq/kg and 198 Bq/kg, respectively. Additionally, the activity concentration of ^{40}K was 1937 Bq/kg. Furthermore, ^{226}Ra

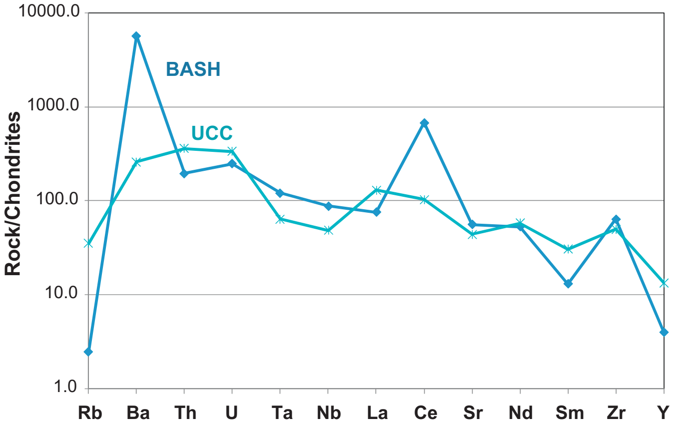

Fig. 8. Incompatible and compatible trace element diagrams of BASH and Upper Continental Crust (UCC) normalised to chondrites.

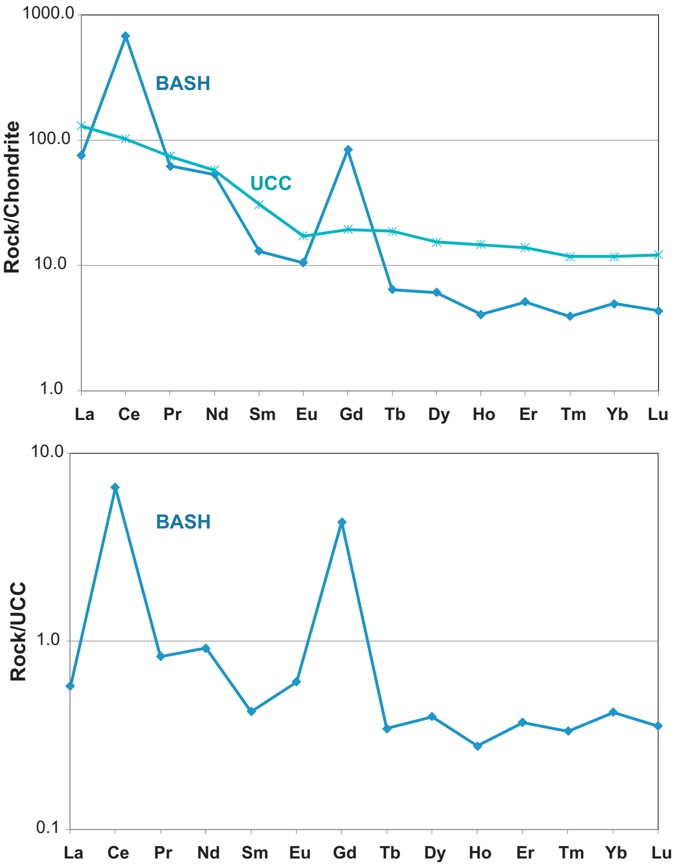

Fig. 9. REE diagram of BASH and UCC normalised to chondrite (upper line) and BASH normalised to UCC (lower line).

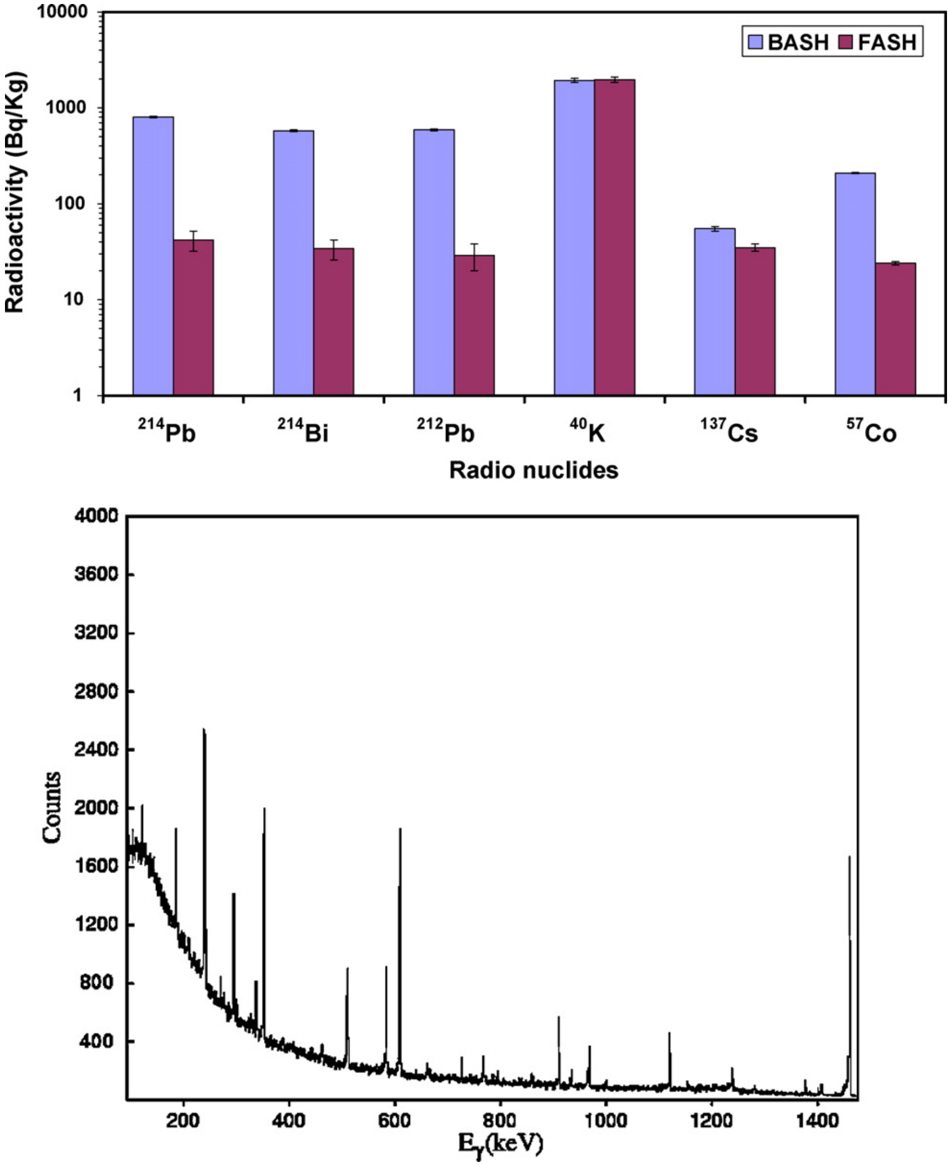

Fig. 10. Radioactivity measurements of BASH and FASH with the measured spectrum for FASH.

(641 Bq/kg) was in equilibrium with ^{214}Pb and ^{214}Bi, while ^{235}U was about 73 Bq/kg. However, the artificial radionuclides ^{57}Co and ^{137}Cs exhibited values of 209 and 55 Bq/kg, respectively. The spectrum for the FASH was then analysed for the same radionuclides. The activity concentration for the ^{238}U decay series (progenies) was in equilibrium with an average value of 38 Bq/kg (^{214}Bi and ^{214}Pb), while the ^{232}Th decay series (^{212}Pb) exhibited an activity concentration of about 29 Bq/kg. In addition, the contribution of ^{208}Tl was not observed due to its very low value (lower than the minimum detectable activity), while the activity concentration of ^{40}K was 1968 Bq/kg. However, the artificial radionuclides ^{57}Co and ^{137}Cs exhibited values of 24 and 35 Bq/kg, respectively. Taking into account the gamma-ray spectroscopic data, it was concluded that the radioactivity of both ash samples was within the permissible levels for solid waste disposal, as recommended by the International Atomic Energy Agency (IAEA), because the clearance levels for ^{137}Cs and ^{57}Co radionuclides in solid materials are 300 and 30,000 Bq/kg, respectively [21].

The investigation of briquettes, prior to stabilisation in pozzolanic cement by SEM-EDS indicated the presence of all the components observed in the initial materials, including high levels of halite, likely from serums and other medical waste. However, this phase was re-crystallised on the surface of the material or inside the cavities in the form of large well-shaped crystals during briquette fabrication.

The results of the TCLP and EN tests for raw BASH and FASH are shown in Figs. 11 and 12. Despite the fact that BASH is highly enriched in a variety of heavy metals, the TCLP tests indicated notable mobility of only Cu and Zn (10.56 and 5.24 ppm, respectively). However, as found from EN-type leaching tests, it was practically inert with regard to the mobility of all heavy metals in aqueous media. Thus, BASH could theoretically be considered acceptable for normal solid waste disposal sites without further special treatment according to European and Greek regulations. Potential seasonal variability in the heavy metal content could be practically surpassed by mixing with concrete, which provided TCLP and EN values at the level of background (Fig. 13).

On the other hand, though FASH itself was depleted of heavy metals, both leaching tests showed extensive mobility for Zn and, especially, Pb (19.75 and 96.92 ppm in TCLP leachates as well as 14.18 and 89.12 ppm in EN leachates), indicating that the material would need additional treatment before disposal in waste sites.

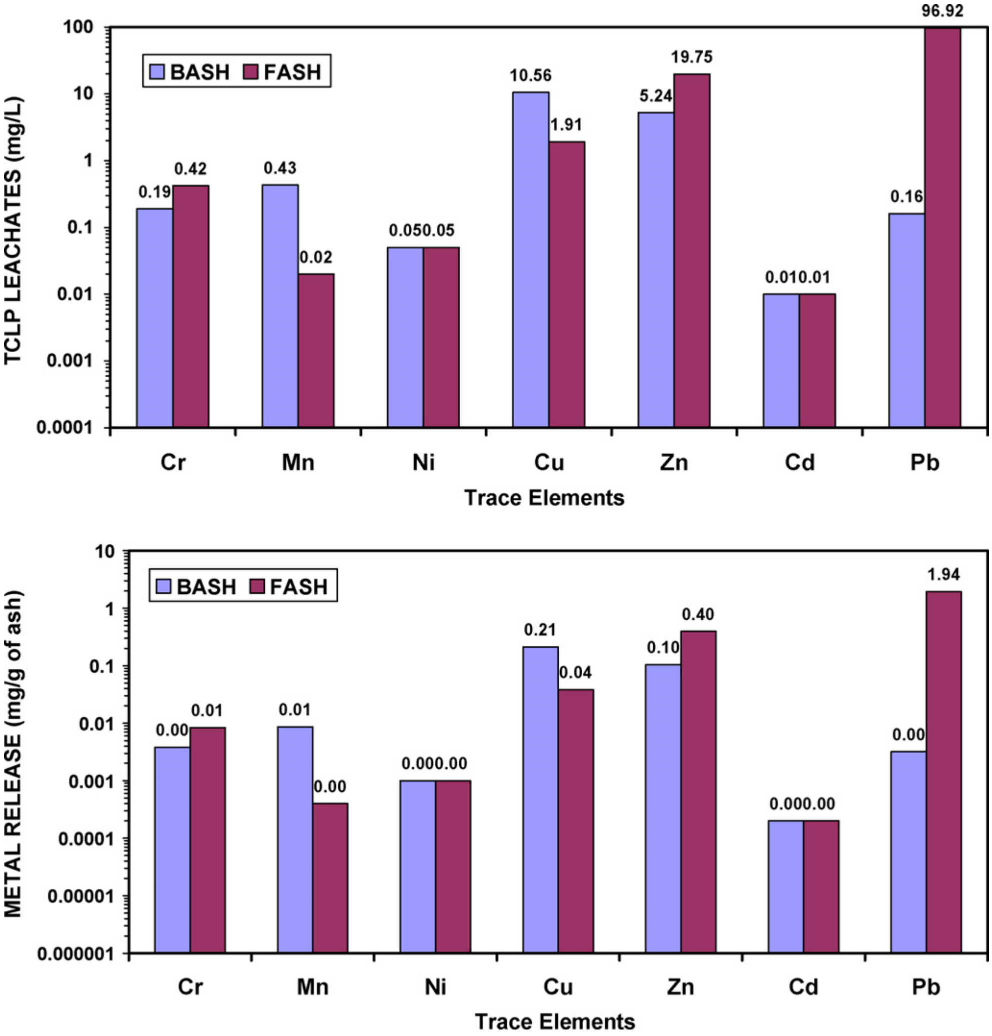

Fig. 11. Results from TCLP tests.

Table 3
Activities of the BASH (upper table) and FASH (lower table) samples.

Isotope	Energy	Net counts		Background	Final counts	Yield	Efficiency	Time (s)	Activity concentration (Bq/kg)	Uncertainty (Bq/kg)	Relative%
^{214}Pb	295	970	50	0	970	0.075	0.002995475	86400	945	49	5
^{214}Pb	352	3430	60	0	3430	0.371	0.002523396		802	14	2
^{214}Bi	609	1800	40	0	1800	0.461	0.001482046		577	13	2
^{212}Pb	238	4270	100	0	4270	0.43	0.003689665		589	14	2
^{208}Tl	583	1200	50	0	1200	0.86	0.001546169		198	8	4
^{40}K	1461	600	30	0	600	0.107	0.000633758		1937	97	5
^{226}Ra	186	450	40		450	0.0328	0.004687254		641		
^{235}U	185	844	60		844	0.54	0.004711846		73		
^{137}Cs	661	290	15	0	290	0.85	0.001368725		55	3	5
^{57}Co	121	5820	80	0	5820	0.857	0.007113849		209	3	1
Mass BASH	5.29E−02										

Isotope	Energy	Net counts		Background	Final counts	Yield	Efficiency	Time (s)	Activity concentration (Bq/kg)	Uncertainty (Bq/kg)
^{214}Pb	295	80	40	0	80	0.075	0.002995	86400	82	41
^{214}Pb	352	170	40	0	170	0.371	0.002523		42	10
^{214}Bi	609	100	25	0	100	0.461	0.001482		34	8
^{212}Pb	238	200	60	0	200	0.43	0.00369		29	9
^{208}Tl	583	0	10	0	0	0.86	0.001546			
^{40}K	1461	580	35	0	580	0.107	0.000634		1968	119
^{137}Cs	661	175	15	0	175	0.85	0.001369		35	3
^{57}Co	121	630	30	0	630	0.857	0.007114		24	1
Mass FASH	5.03E-02									

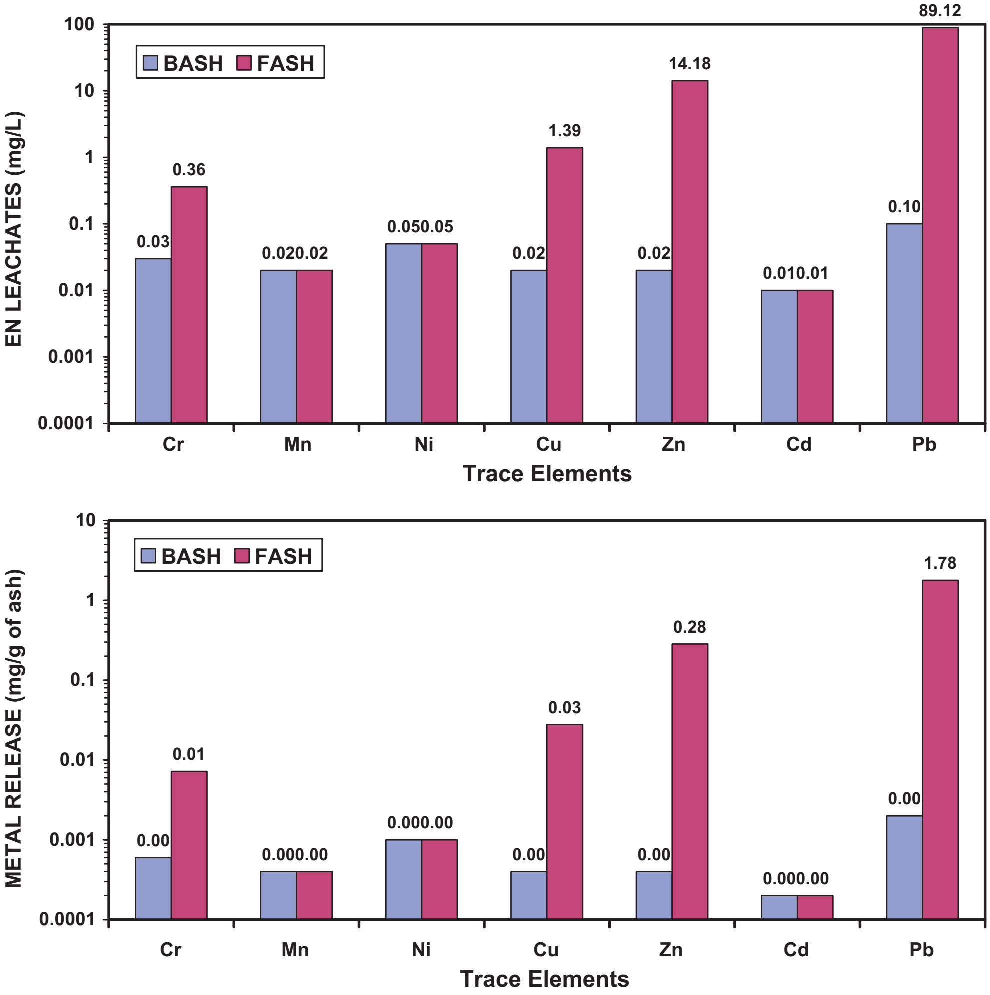

Fig. 12. Results from EN tests.

This potential release of Pb from FASH has also been mentioned by Valavanidis et al. [13]. Therefore, a stabilisation method, suggested within the framework of the present study, for treatment of ACMAR/APOTEFROTIRAS S.A. fly ash (FASH) produced in the hospital waste incinerator at Ano Liossia, included consolidation of the powder in the form of briquettes using an appropriate machine and then embedding of these briquettes into cement blocks. With this treatment, Zn and Pb concentrations in the TCLP leachates were adequately decreased to within environmentally acceptable levels (Fig. 13).

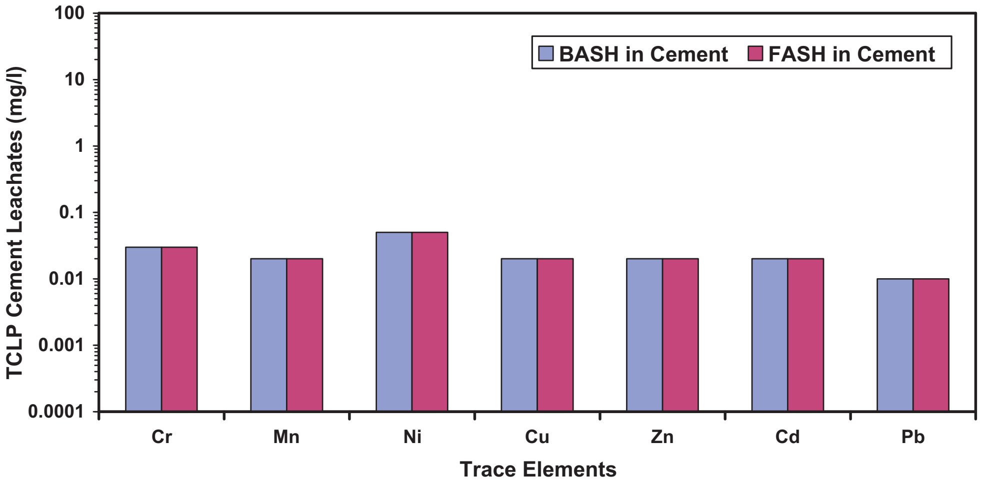

Fig. 13. Results from the TCLP test on the briquettes embedded in cement.

4. Conclusions

Bottom ash (BASH) and fly ash (FASH) samples from the Medical Waste Incineration Plant of ACMAR in Attica, Greece, operated by APOTEFROTIRAS S.A., were found to contain high concentrations of hazardous elements, such as Cu, Cr, Ni, Zn, Pb, Cd, Ni and As, derived from alloys and other medical materials. It was notable that BASH was also enriched in Ba, REE (Ce, Gd) and Au. Both waste materials, particularly BASH, contained actinides, giving them a slight, natural radioactivity due to ^{238}U and ^{232}Th series, together with ^{40}K. BASH also included artificial radionuclides from medical sources (^{57}Co) and nuclear accidents (^{137}Cs). According to EN tests, BASH, which corresponded to "basaltic glass", could be disposed in normal solid waste sites in Greece. FASH, on the other hand, because of high Zn and Pb availability, using both TCLP and EN, needed to be immobilised in proper solid matrices. Forming FASH into briquettes that were subsequently embedded in concrete blocks was found to be the most proper method of waste management, providing negligible release of heavy metals in aqueous media.

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