

CHARACTERIZATION AND LEACHABILITY EVALUATION OF FLY AND BOTTOM ASHES GENERATED DURING INCINERATION OF MEDICAL WASTES

C. Tsakalou^{1,3}, P.E. Tsakiridis^{2,3}

¹*Association of Municipalities in the Attica Region-Waste management (EDSNA), Athens, Greece*

²*National Technical University of Athens, School of Mining and Metallurgical Engineering, Greece*

³*Hellenic Open University, School of Science and Technology, Waste Management, Patra, Greece*

Corresponding Author email: tsakalou@edsna.gr

Abstract

Incineration is one of the best choices, carried out in many developed countries worldwide for most of the health-care hazardous wastes, as it can eliminate all pathogens and also decreases the waste weight more than 70 wt% and reduces their volume accordingly. Nevertheless, significant amounts of combustion residues enriched in heavy metals are produced. The present investigation aims to the characterization and leachability evaluation of incineration ashes, produced during the combustion of medical wastes. Two types of ashes were examined: A fly ash derived from the incinerator waste gases de-dusting system (fabric filter dust collector), and a bottom ash produced from the heavier particles of the agglomerated remaining matter, which are precipitated and accumulated usually in the combustion chamber. The characterization of both ashes was carried out using particle size distribution analysis, chemical analysis, X-ray diffraction and thermogravimetric/differential thermal analyses. Fly ash microstructure and morphological characteristics were examined by scanning electron microscopy and transmission electron microscopy, whereas the corresponding of bottom ash was studied in polished section through scanning electron microscopy. Their behaviour during leaching was determined by the Toxicity Characteristic Leaching Procedure test and the EN 12457-2 compliance leaching test and according to the results both ashes should be treated as hazardous wastes and in case of landfilling they should be disposed of at appropriate, regulation-prescribed waste dumps.

Keywords: Medical Wastes, Fly ash, Bottom ash, Characterization, Leachability

1. Introduction

The ability of a health unit to improve the quality of the health services and also to provide a reliable level of medical care not only refers to the medical and hospital services, but also expands to activities parallel or subsequent to the main. One of these contiguous or resultant activities with significant impact on the environment and on human health is the management of medical waste produced by hospitalization. According to the World Health Organization (WHO) 80 wt% of the waste generated at health units presents similar properties with the corresponding of municipal solid wastes. The remaining 20% has been classified as hazardous, appearing properties such as infectivity, toxicity, carcinogenicity, radioactivity etc, thus requiring special treatment [1,2].

The term “Medical Waste” refers to all medical waste generated by Health Units, which have been mentioned in the waste catalogue of the Annex of the European Communities Decision [3]. In recent decades, the safe treatment and disposal of hazardous medical wastes is a major problem of the health sector worldwide and concerns not only the government mechanisms or the health unit’s administration, but the society as a whole. The problem has been aggravated by the emergence of new infectious diseases and the simultaneous lack of the appropriate infrastructure for the safe handling of hazardous medical waste. The risk, therefore, for the environment and human health degradation, due to the release of hazardous substances, arises from the inappropriate waste management practices. On the other hand, proper medical waste management requires significant funding, thereby administrations of health facilities do not give the necessary priority to address the problem [4,5].

The amount and the type of medical waste generation differs not only from country to country, but also among health units of a country and depends on many factors, such as the waste management methods, the type and size of the health unit, the type of services, the percentage of reusable materials, the number of patients hospitalized per day and the standard of living in the country [6,7]. Regarding Greece, there are about 320 hospitals with 53.700 beds, without including the number military hospitals. 140 of them are public hospitals, the majority of which is supervised by the Ministry of Health. Considering the annual medical waste generation in Greece, about 15.000 tons of medical waste is produced yearly, while the 53wt% of them is produced in Attica. Moreover, of the 350.000 tons of hazardous waste which are produced annually in Greece, about 4.5 wt% is produced in hospitals, the majority of which is considered infectious. In accordance with the European legislation, infectious is considered the waste that has been in contact with blood or body fluids [8-10].

In recent years there is an intense concern about the earlier practice of disposal in a landfill, which is the most common way of medical waste management today in developing countries, not only because of its low cost, but also due to the shortage of alternatives [10-12]. Selecting the appropriate hospital waste management method mainly depends on their quality and quantity, and according to the World Health Organization, the decision should be based on environmental and economical standards. The existing methods of disposal have been repelled due to ineffective inactivation of the contained pathogenic microorganisms, resulting in the risk of contagion of infectious diseases, either by direct contact through wounds, inhalation, ingestion or by indirect contact via the food chain or a host pathogen. The main acceptable alternatives available today are the methods of thermal treatment (incineration, pyrolysis, gasification) and the methods of sterilization (thermal, chemical disinfection), but mainly for the lower pathogen load wastes [13-16].

Incineration is one of the best choices, carried out in many developed countries worldwide for the most of the health-care hazardous wastes, as it can thermally eliminate all pathogens and also decrease the waste weight more than 70 wt% (90%, in terms of their original volume) [17-18]. Incineration is the process of waste dry oxidation at high temperatures, which converts them into ash and gaseous residues. It is suitable for all kinds of medicals wastes except specific types such as radioactive, batteries, etc. Among the proposed methods, incineration and disposal of the resulting ashes in landfills is considered, as the most technically and economically feasible solution for the hospital waste treatment. [19-21]. A typical example is Japan, where 82.3 wt% of hospital waste managed by means of this method [22].

The main advantages of the incineration process are the volume reduction of the wastes, their sterilization and the possibility of heat recovery or electricity. On the other hand, the risk of toxic gaseous emissions, the high operation and maintenance costs, as well as the demand for the management and the disposal of produced ashes may be considered as disadvantages. It should be also noticed that in case that incinerator is not working properly, large amounts of hazardous air pollutants, such as carbon monoxide (as a result of incomplete combustion), hydrochloric acid, heavy metals (mercury, arsenic, cadmium), dioxins and furans may be emitted [23-25].

Attica, mainly because of its metropolitan character, is facing the biggest problem relating to the management of hospital waste, which today has been addressed with the operation of a medical waste incineration facility of Association of Municipalities in the Attica Region (EDSNA) at Ano Liossia, near Athens with a treatment capacity of 30 tonnes/day, consisting of two parallel production lines capacity of 15 tonnes/day each (Figure 1). According to the followed process, the hospital wastes entering the plant site via trucks refrigerators. After their weighing and inspecting for presence of radioactive elements, they are driven, through a receiving hopper in a rotary kiln, where they are incinerated at temperatures in the range of 1100-1200 °C, with about 70wt% excess of air, by using natural gas and oil as energy sources. The solid residue of the combustion process (bottom ash) is mechanically removed from the combustion chamber and it is cooled through water-quenching. The exhaust gases from the rotary kiln are directed to the secondary chamber with an afterburner, operated at 1000 °C, where they stay for about 2-5 seconds in order to be achieved the completion of the combustion process and the destruction of dioxins and furans [8,18].



Figure 1: Medical waste incineration facility at Ano Liossia, Attica

The next stage is the exhaust gas de-dusting system. The gas stream is entered into the reactor, wherein hydrated lime and dry activated carbon are provided, in order to eliminate the acid gases (HCl, HF), simultaneously with the retention of heavy metals. The exhaust gas from the reactor passes through bag filters, where the major part of the particles is collected as fly ash. The final purification stage is the washing tower. An aqueous sodium hydroxide solution is used not only to reduce certain pollutants, but also to maintain the exhausts pH to basic values, before their release to the atmosphere.

As it was mentioned above, one of the main drawbacks of the incineration process is the production of significant amounts of incineration ashes (bottom and fly), which usually are enriched with toxic substances. The organic compounds are destroyed and the corresponding organic percentage in the

ashes represents normally less than 1wt% of the mass, with PCDD's and PCDF's concentrations often undetectable. Their compositions it can be either siliceous or calcareous origin, and also contain oxides of aluminium and iron. However, the heavy metals usually remain in the ashes, as they cannot escape along with the gases, with the exception of mercury, which remains in vapour state. It has been found that the rates of most of the other heavy metals which are retained mainly in the fly ash are high, provided that the incinerator is equipped with an efficient de-dusting and cleaning system. Considering that a significant reduction of solids during combustion can be achieved, the heavy metals concentrations in ashes are usually higher than the corresponding in the initial wastes [17,26].

Fly ash has been classified as hazardous waste and it is usually handled separately from the ashes of the combustion chamber, in dry phase, mainly through cement or thermal solidification before its final disposal. The amount of fly ash generated corresponds to 2-3 wt% of the original weight of the wastes, while most of the ash produced is bottom ash (10-15 wt%), which has been also classified as hazardous wastes [27]. After removing from the main combustion chamber it is cooled by quenching. It can be handled in a dry or liquid state and is transferred to closed drums or containers for storing.

The aim of the present research work is to present the results on the complete characterization and the leachability examination of bottom and fly ashes, generated during the incineration process of medical wastes. Chemical analysis, X-ray diffraction, thermal analysis, scanning electron microscopy and transmission electron microscopy were used in order to characterize both ashes, whereas their leachability evaluation was carried out by the Toxicity Characteristic Leaching Procedure test [28] and the EN 12457-2 compliance leaching test [29].

2. Experimental

2.1. Bottom and Fly Ashes Characterization

The ashes under investigation were generated by a medical waste incineration plant in Greece and typically consist of the coarser bottom ash, collected from the bottom of the combustion chamber, and the finer fly ash that has been captured by the fabric filters. The coarser bottom ash appeared black, opaque and glassy, while the finer fly ash, grey in colour (Figure 2). Fly ash particle size distribution was determined by a laser scattering particle size distribution analyzer (Mastersizer 2000, Malvern) after dispersion treatment with ultrasonic. Chemical analyses were carried out with X-ray Fluorescence (Spectro-Xepos), Atomic Absorption, Spectrophotometry (Perkin Elmer 4100) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS X Series II, Thermo Scientific).



Figure 2: Incineration ashes, produced during the combustion of medical wastes

The mineralogical phases were determined by XRD analysis, using a Bruker D8-Focus diffractometer with nickel-filtered CuK α radiation ($\lambda=1.5406$ Å), at 40 kV and 40 mA. TG/DTA analysis was conducted with a Setaram-Labsys thermal analyzer. Samples were placed in ceramic crucibles and

heated from room temperature to 1000°C at a heating rate of 10°C/min using N₂ as a medium under static condition. The morphology of both dusts was examined by scanning electron microscopy (SEM) using a Jeol 6380LV Scanning Electron Microscope. Furthermore, bottom ash was examined in polished sections, which were produced by vacuum impregnation in a low viscosity epoxy resin. After removing a small surface by cutting in micro-saw, the sample was grinded and polished with 1µm diamond paste, on a lapping disk. Spot chemical analysis of samples particles was carried out by an Oxford INCA Energy Dispersive Spectrometer (EDS) connected to the SEM. Finally, TEM measurement was conducted with a high resolution JEOL JEM-2100, operating at 200 kV, equipped with an Oxford X-Max 100 EDS detector.

2.2 Leachability Tests

Both dusts were subjected to the Toxicity Characterization Leaching Procedures (TCLP) test, in order to determine the heavy metals leachability, simulating the scenario of a common landfill under laboratory conditions [28]. The extraction solution was prepared using glacial acetic acid to obtain a pH value of 2.88. The ashes samples and acetic acid solution were placed into beakers with liquid/solid ratio of 20:1 and extracted for 18 hours.

Furthermore, the batch test EN 12457-2 leaching procedure, which is performed on materials with particle size below 4 mm, was also carried out, in order to assess what type of landfill site (for inert, non hazardous or hazardous wastes) is suitable for the examined ashes disposal. The test was conducted in a batch reactor, by mixing the waste with deionized water with continuous stirring (10 rpm) for 24 h at a controlled temperature value equal to 20±5 °C in a solid/liquid ratio of 1:10, followed by filtration and determination of dissolved elements [29]. The results of the applied test were compared with the regulatory limits issued by the European Council (2003) [30].

3. Results and Discussion

3.1. Bottom and Fly Ashes Characterization

Bottom ash appeared black-grey and glassy, with a density of 0.95 kg/ m³, mainly due to its high rate cooling, through the quenching process, after its removal from the bottom of the furnace chamber. According to its particle size distribution, which was determined by sieve analysis using a shaker fitted with standard sieves of different sizes (Figure 3), it presented a size fraction of <9.5 mm, whereas the over 250 µm size fractions comprise about the 85wt% of the bottom ash. At the temperature of 1100-1200 °C and because of the presence of silicate or aluminosilicate compounds, bottom ash is melted and then, because of the sudden cooling at room temperature, is transformed to slag. Although the process results in the destruction of the hazardous organic compounds, the heavy metals are still remained in the solidified slagged ash with the form of solid solution.

On the other hand, regarding fly ash, a finer particle size was observed and its density was determined at 0.74 kg/m³. Its particle size distribution ranged from 0.15 to 88µm, with 90 wt% of the powder under 56.23 µm, whereas 50 wt% of it was below 16.57 µm. The generation of the larger particles should be attributed to the injection of hydrated lime for the flue gas neutralization, thus controlling the HCl emissions, and to the fragmentation phenomena due to the agglomeration of the finer particles on the lime seed-particles. The above particle size distribution could be also observed in the micrograph from SEM analysis, shown in Figure 7.

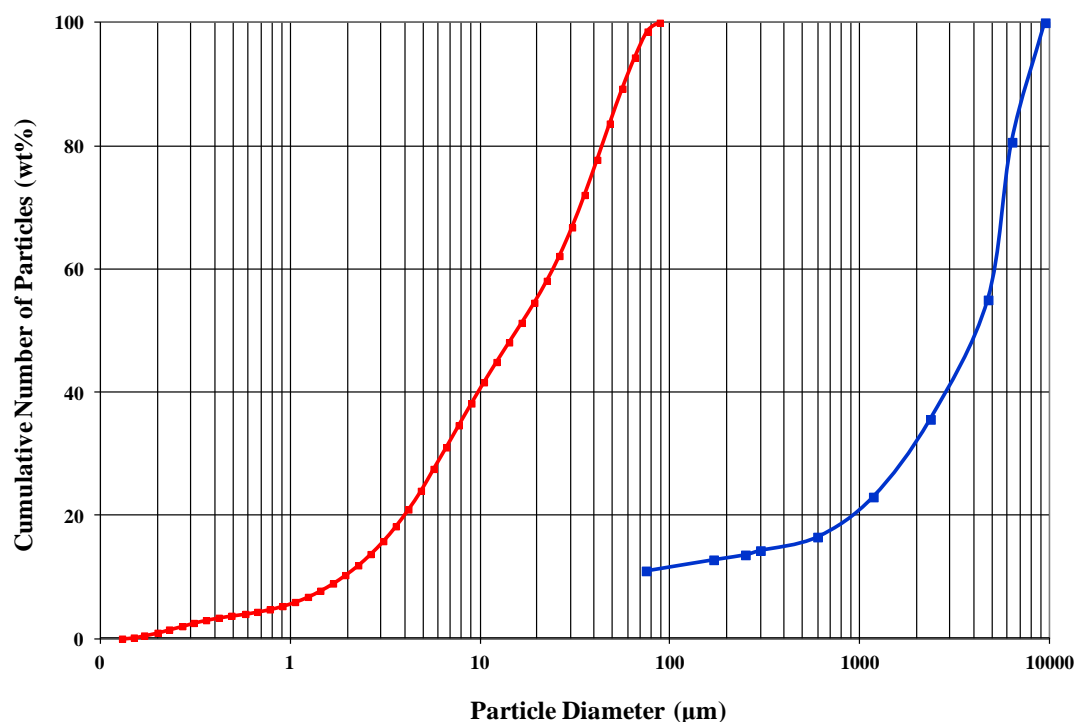


Figure 3: Particle size distribution of fly and bottom ashes

As it was mentioned above, the chemical and mineralogical composition of the produced ashes depends not only on the type of the original medical wastes, but also on the incineration process (rotary kiln, temperature, excess of air, flow rate, etc) and the configuration of the subsequent flue gas cleaning installation (cyclones/ filters bags, hydrated lime, active carbon, etc). Chemical analyses of bottom and fly ashes are shown in Table 1, whereas their trace elements analyses results are presented in Tables 2 and 3.

Table 1: Bottom and fly ashes major elements chemical analyses

<i>Oxides</i>	<i>Bottom Ash (wt%)</i>	<i>Fly Ash (wt%)</i>
SiO₂	57.52	1.30
Al₂O₃	7.32	0.91
Fe₂O₃	1.18	0.23
CaO	19.34	62.02
MgO	1.83	1.80
K₂O	0.92	0.82
Na₂O	6.50	4.47
SO₃	0.03	-
Cr₂O₃	0.42	0.02
ZrO₂	0.92	1.04
MnO	0.04	0.01
TiO₂	0.61	-
Cl⁻	0.38	4.87

Bottom ash is mainly composed of silicon (SiO₂: 57.52 wt%). The relatively low calcium content (CaO: 19.34 wt%) together with the corresponding of SO₃ (≈0.03 wt%) is typical for its rank in the “Class F”, indicating pozzolanic properties, as more glass and aluminosilicate amorphous phases (Al₂O₃: 7.32 wt%) are expected after its cooling through quenching. Other components, such as Fe₂O₃

and MgO were also found in lower quantities, while the presence of alkalis (Na₂O and K₂O) reached 7.50 wt%. On the other hand, fly ash chemical composition is significantly misquoted, mainly due to the flue gas cleaning installation, where hydrated lime and/or NaOH solution are used in order to neutralize acidic gases. Consequently, calcium was its main constituent and accounted for 62.02 wt% (as oxide) of the ash mass, while the presence of alkalis was relatively low and similar with the corresponding of bottom ash, as small amounts of Na₂O (4.47 wt%) and K₂O (0.82 wt%) were detected.

Table 2

Trace elements analysis of bottom ash

BA	<i>Trace Elements (mg/Kg)</i>								
	As	Cd	Hg	Ag	Mo	Ni	Zn	Sb	Ba
	11	3.2	1.3	0.8	12.3	124	52.7	4.7	3840
BA	Ga	Ge	Co	La	Ce	Cu	Pb	Y	Nb
	2.7	0.8	34	44	81	1287	18	7.3	0.2

Table 3

Trace elements analysis of fly ash

FA	<i>Trace Elements (mg/Kg)</i>								
	As	Cd	Hg	Ag	Mo	Ni	Zn	Sb	Ba
	12.7	3.3	1.8	4.2	27	22.4	1103	13.6	102
FA	Ga	Ge	Co	La	Ce	Cu	Pb	Y	Nb
	0.8	-	28	43	53	138.2	135.5	9.8	-

Regarding trace elements, it is known that the incinerator operating parameters, such as temperature, flue gas compositions, waste incineration time and presence of active substances during incineration (Cl, S, Al, Si, etc) determine the kind and the concentration of heavy metals [31,32]. The trace elements analysis showed that their concentrations were relatively high in both ashes. However, according to the results there were detected some variations that were mainly attributed to the volatility of some metallic compounds, which after evaporation are gathered in the flue gases and consequently in the fly ash. Heavy metals concentrations in case of bottom ash were the following in decreasing order: Ba>Cu>Ni>Ce>Zn>La>Co>Pb>Mo>As>Y>Cd>Hg>Ag. On the other hand, the corresponding order of heavy metals concentrations in case of fly ash was: Zn>Cu>Pb>Ba>Ce>La>Ni>Co>Mo>As>Y>Ag>Cd>Hg. The above heavy metals are usually contained in medicines, in photographic materials and medical tools [17]. The presence of As and Ag should be attributed to ingredients used in some medicines and to radiographic plates. The presence of Ni, Cr, Co and Mo is mainly derived from stainless steel medical tools [17,33]. The presence of Ba should be attributed to the consumption of medical materials such as contrast agents used in radiology and to its use as additive in plastics [8,34]. On the other hand, the high Zn content is coming from various sources, such as plastics and rubber, adhesive bandages, medicines and medical tools (together with Cu and Pb). Finally rare earths are usually found in alkali-resistant glass, ceramics, semiconductors, electrodes, camera lenses, etc.

The X-ray diffraction patterns of both ashes are presented in Figure 4. The complex mineralogy of bottom ash could be ascribed to several high temperature processes such as melting, crystallization, and vitrification and also to sudden cooling. Its amorphous/semi-crystalline nature was confirmed by the presence of a diffuse wide band derived from the glassy phase in the range of 20-40°, as the ash has been vitrified (forms a glassy phase), during rapid cooling. On the other hand the presence of crystalline phases correlated with chemical composition of the melt and its cooling rate. The main crystalline phases detected were monocalcium silicate (CaSiO₃) and corundum (Al₂O₃).

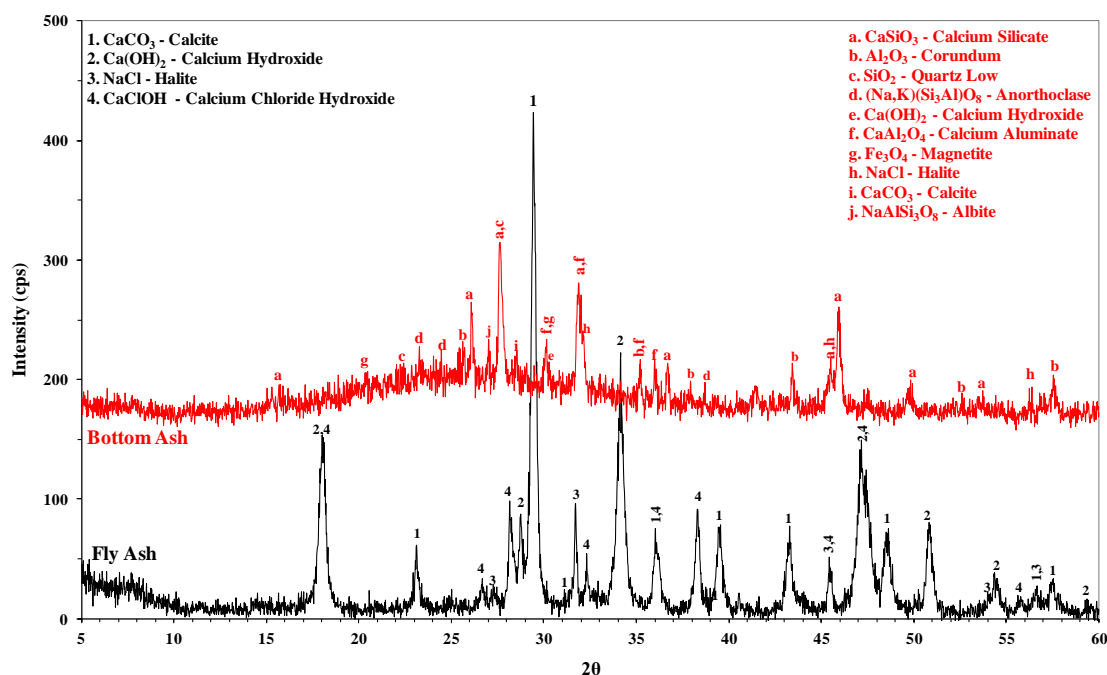


Figure 4: Bottom and fly ashes mineralogical phases

Other phases such as quartz, magnetite, halite, calcium aluminate and feldspars were also present in lower percentages. CaSiO_3 , a high temperature mineral compound, which was detected as the main crystalline phase, has been formed through a diffusion reaction of CaO and SiO_2 , in the range of 1200°C , which is indicative of the final sintering temperature. Quartz contained in bottom ash results from the raw materials (primary quartz), or formed during the incineration (secondary quartz). The presence of corundum derived from the reaction of the atmospheric oxygen with metallic or other constituent of aluminium at high temperatures, while the detection of CaAl_2O_4 is also an indication of temperatures in the range of 1200°C . The presence of halite should be attributed either to medical disinfectants in the original medical wastes or to the plastic decomposition. In case of fly ash, the abundance of Ca(OH)_2 , is due to the injection of hydrated lime for the flue gas neutralization (HCl emissions control), while the CaCO_3 has been generated during the lime partial carbonization. The elimination of acid gases resulted to the formation of calcium chloride-hydroxide phases and halite.

The results of the thermal analysis (TG) and the differential thermal analysis (DTA) of both ashes are presented in Figure 5. Regarding bottom ash, it was confirmed its sintered, fully transformed-fused nature. The total weight loss until 1000°C was very low and did not exceed 3.5 wt%, partially corresponding to the evaporation of physically adsorbed water at in the range of 120°C and to the carbonation decomposition at 800°C . On the other hand, fly ash presented mass loss at about 80, 440, 518 and 764°C . The first one corresponds to the evaporation of physically adsorbed water. The decomposition of crystalline hydrated lime was evident by the presence of second main mass loss, which can be observed at around 440°C , whereas the third endothermic peaks at 518°C should be attributed to the calcium chloride hydroxide decomposition. Finally, the loss at 765°C should be attributed to the CO_2 release, during the carbonates decomposition.

According the SEM examination of bottom ash in polished section a glassy colourless matrix, chemically heterogeneous, as it was formed mostly by silicon, calcium, sodium, aluminium and magnesium, was the dominated phase, mainly due to the fast cooling during water quenching (Figure 6). Within the glass matrix, monocalcium silicate (CaSiO_3) and corundum were the most abundant phases, while some calcium aluminate crystalline phases are less common. Calcium silicate appeared with the form of elongated prismatic plates and it has been formed during the solid state reaction of CaO (produced after the decomposition of carbonates at $800\text{--}900^\circ\text{C}$) with reactive silica in the range of $1100\text{--}1200^\circ\text{C}$. It was found to contain small amounts of iron and magnesium.

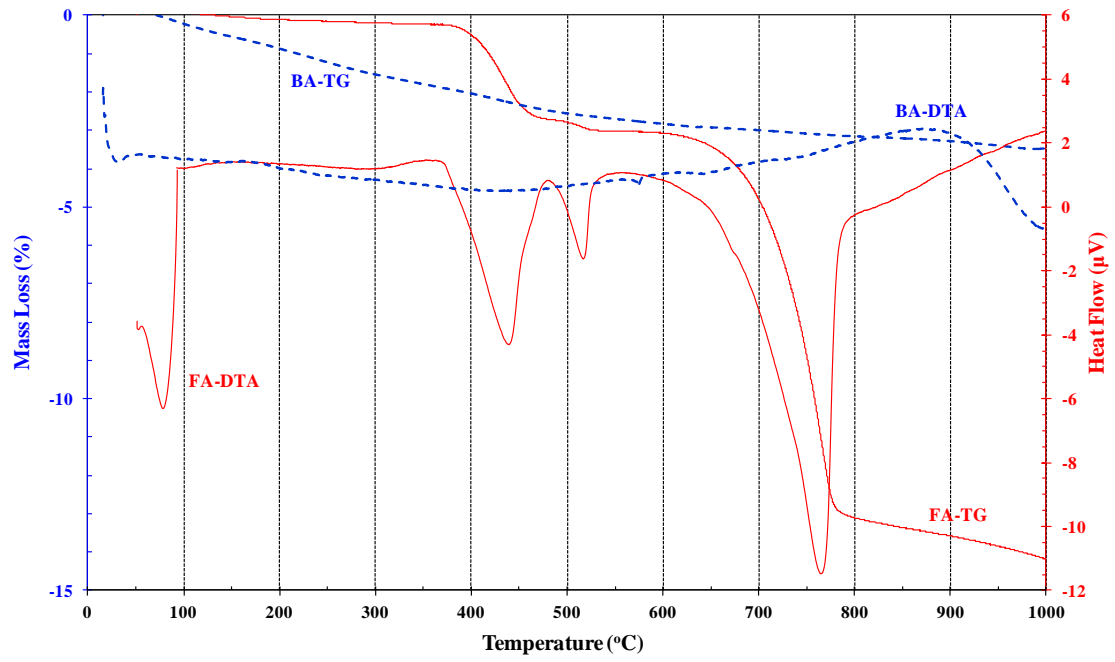


Figure 5: TG-DTA curves of bottom and fly ashes

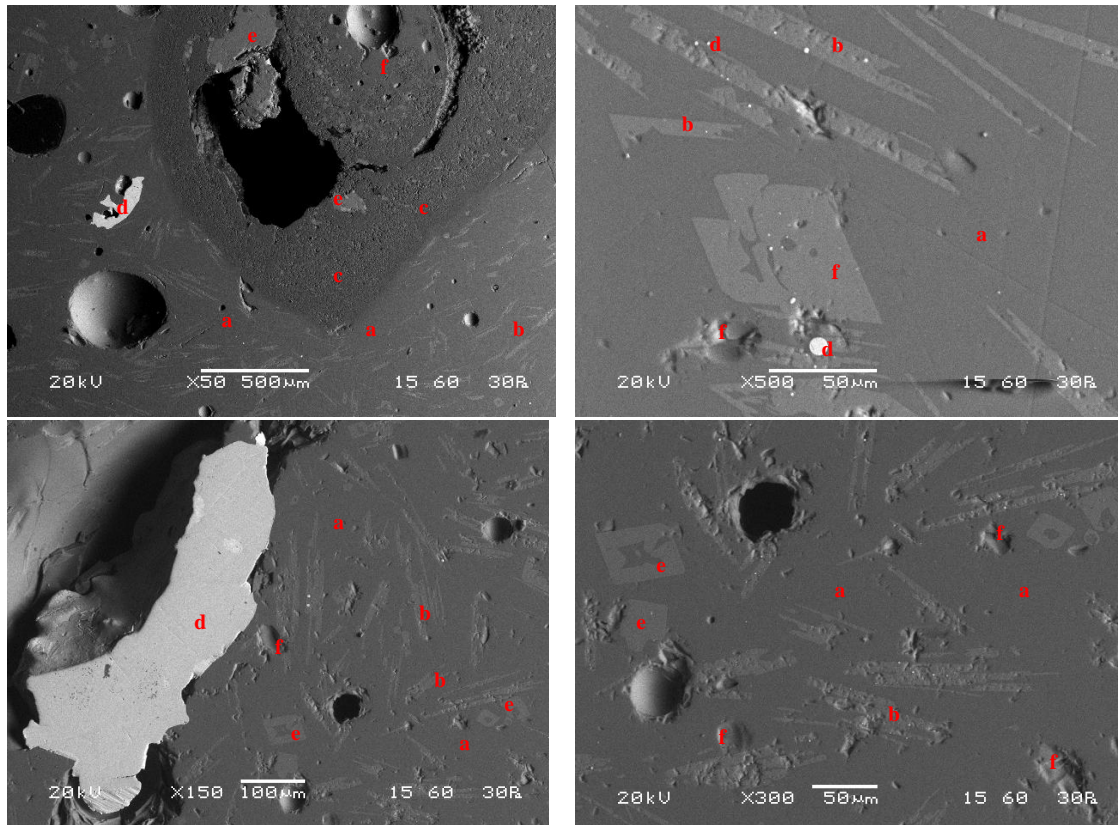


Figure 6: Backscattered electron micrographs of bottom ash polished sections. a: Amorphous Glass b: Mono-Calcium Silicate (CaSiO_3), c: Corundum (Al_2O_3), d: metallic particles, e: plagioclases, f: Calcium Aluminates

On the other hand the formation of corundum should be attributed either to the partial oxidation of metallic Al, or to the calcinations of aluminium hydroxide phases in the initial medical wastes. At temperatures up to 1200 °C, where there is still no melting, a small amount of intermediate calcium aluminates were also formed. Furthermore, plagioclases were also observed with the form of glassy brittle plates, which consisted of a solid solution between albite (rich in Na) and anorthite (rich in Ca). The formation of some rich aluminium silicate phases was also detected due to the presence of aluminium in the quenched ash. They were detected with the form of dendritic growths, which were found to be embedded in vitreous matrix. Finally, the metal alloys were easy to distinguish as they exhibited higher reflectance. Austenitic non magnetic stainless steel, with high nickel concentration, was the most abundant, but also aluminium and copper alloys (mainly brasses) were also detected with the form of drop-like and oval metallic particles.

As it was mentioned above, fly ash captured by the fabric filters was enriched in calcium hydroxide as hydrated lime had been used for the acidic gases neutralization and because of its composition has been ranked in “Class F”. Fine particles forming aggregates or covering larger particles were observed presenting an agglomerated morphology (Figure 7). Calcite spherical particles, mainly due to the Ca(OH)_2 carbonation, were dispersed among hexagonal plates of hydrated lime, or they have formed fragile aggregates of irregular shape, with a relatively homogeneous size of about 30-50 μm . A significant amount of the smaller particles has been enriched with chlorides ions, which had been entrapped during their contact with hydrated lime. They appear with the form of needle like crystallites and also form aggregates usually on larger plates of lime. And in this case, metallic inclusions are easily distinguishable, as they present higher reflectance.

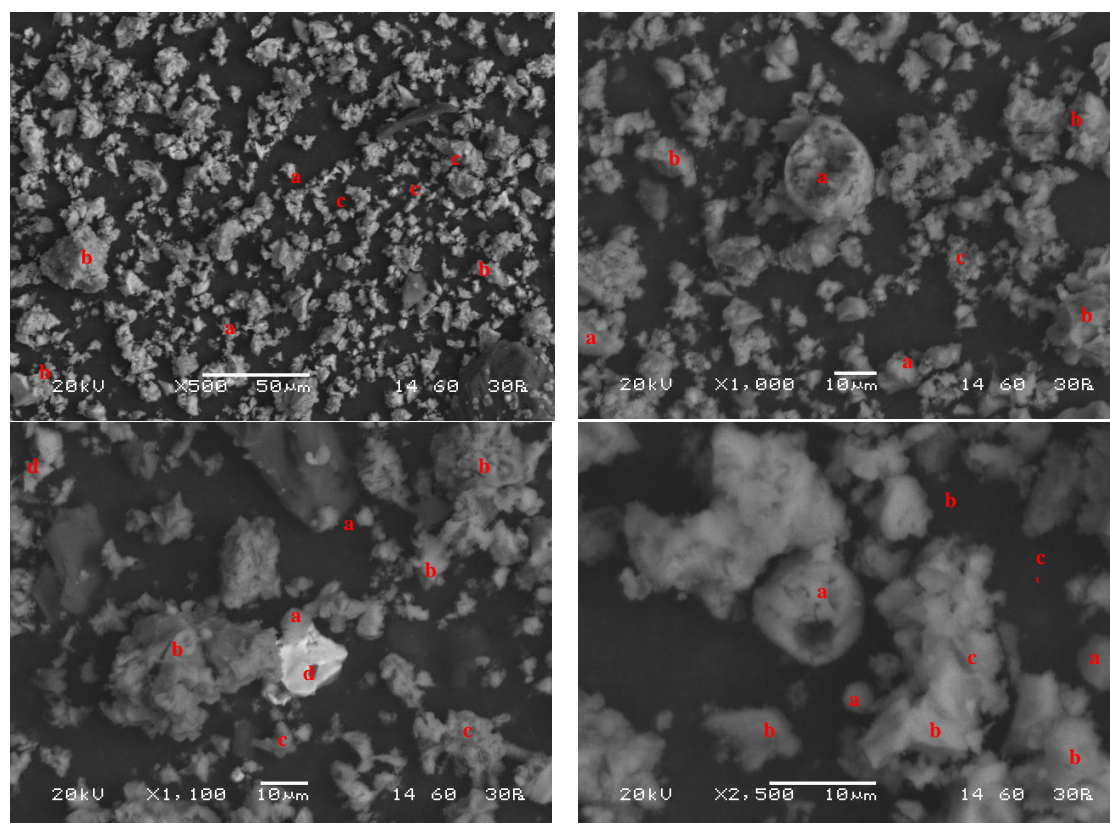


Figure 7: Backscattered electron micrographs of fly ash. a: Calcite, b: Hydrated Lime, c: CaClOH , d: metallic inclusions

The above results were also confirmed by the fly ash transmission electron microscopy analysis (Figure 8). More specifically, most of its finer part consist of calcite spherical particles with a size in the range of 50-200nm. Hydrated lime particles presented a round to subrounded morphology, very often consisting of a wide size distribution, ranging from 20 nm to 200nm. Most of the lime bigger particles

consisted of smaller hexagonal plates-grains, which seem to have developed maintaining similar lattice orientations (parallel development of plates). Chlorides have been bound by the hydrated lime grains, developing a network of finer plates of calcium chloride hydroxides. Some of the bigger particles presented an external rim, rich in chlorides, probably due to the lime partial chlorination, whereas, some others presented a cubic structure, which is indicative of the halite.

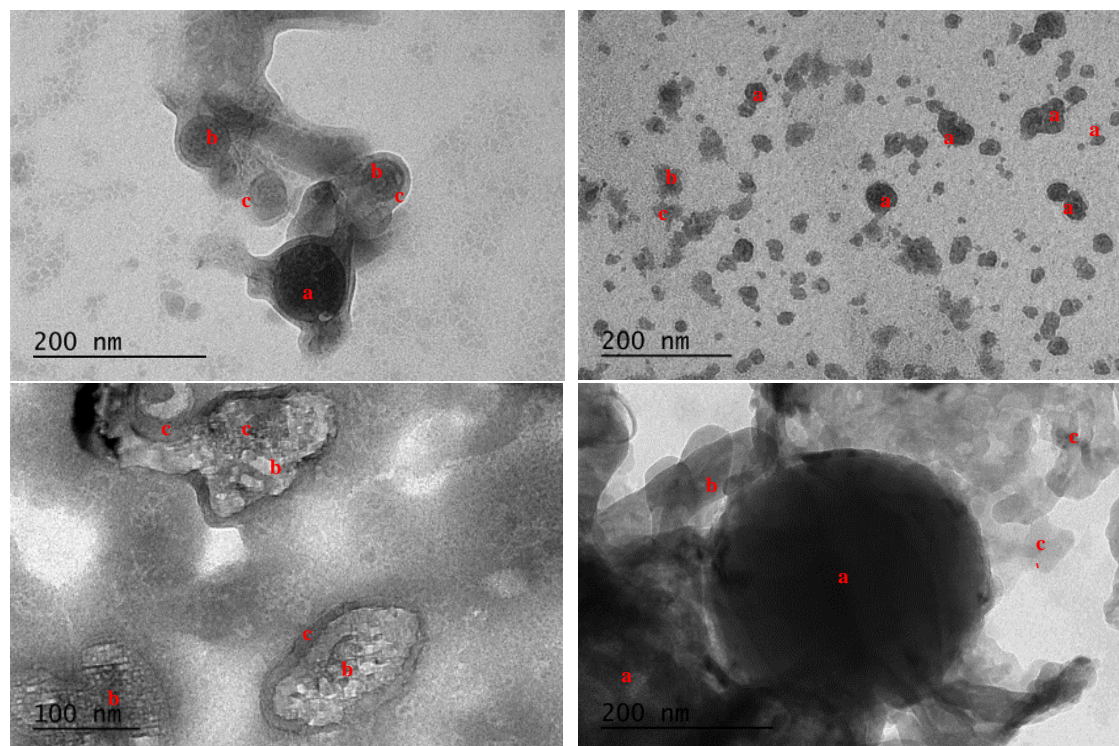


Figure 8: Fly ash transmission electron microscopy. a: Calcite, b: Hydrated Lime, c: CaClOH,

3.2 Bottom and Fly Ashes Leachability Tests

In order to simulate the bottom and fly ashes heavy metals leachability in case of disposal in sanitary landfills together with other municipal wastes, both ashes were subjected to the Toxicity Characteristics Leaching Procedure (TCLP) test. The leaching solution from both ashes was analyzed for cadmium, lead, barium, chromium, arsenic, zinc, aluminium, nickel, molybdenum and copper and the results are presented along with the corresponding limits in Table 4.

Table 4: TCLP results of bottom and fly ashes

Metals	Bottom Ash (mg/L)	Fly Ash (mg/L)	EPA TCLP Regulatory Limits (mg/L)
Cd	0.04	0.17	1.0
Pb	7.25	532.5	5.0
Ba	25.2	125.7	100
Cr	4.25	8.07	5.0
As	2.2	3.4	5.0
Zn	27.3	125.34	NRL
Ni	18.54	1.25	NRL
Mo	14.73	24.3	NRL
Cu	53.70	41.75	NRL

NRL: No regulatory limits are available

The heavy metals presence depended not only on the properties of each element, but also on their final form-phase (salt, oxide, etc.). Both ashes leach liquors presented high metals values, surpassing in cases the corresponding EPA regulatory limits. Lead and zinc presented the greatest affinity for the acetate ions. Together with cadmium presented higher mobility in fly ash, as they had been easier volatilized during the incineration process, being present in the flue gas with the form of vapours and subsequently condensed and trapped in fly ash with the form finer particles. Also, barium and chromium presented similar behaviour, as their final leaching values were higher in fly ash. Although nickel, molybdenum and copper do not contribute to the hazardous classification, they presented high values, especially in bottom ash, a fact that should be taken into account during the ashes management/disposal. Their presence has been mainly attributed to the metallic (stainless steel, or copper brass) medical equipment.

The leachability metals values according to EN12457-2 leaching test for both ashes are given in Table 5. The final pH after leaching procedure, in both cases, was measured in the range of 6.0-6.5, whereas no precipitates were observed. The heavy metals concentrations, as it was expected, were significantly lower in comparison with TCLP test, mainly because metals leaching values varied significantly due to the different leaching agent.

Table 5: Released metal concentration after EN 12457-2 leaching test at L/S = 10 l/kg

<i>Metals</i>	<i>Bottom Ash (mg/kg)</i>	<i>Fly Ash (mg/kg)</i>	<i>2003/33/CE</i>	
			<i>Inert (mg/kg)*</i>	<i>Hazardous (mg/kg)*</i>
Cd	0.01	0.02	0.04	5
Pb	0.83	123.5	0.5	50
Ba	4.32	38.53	20	300
Cr	0.15	4.05	0.5	70
As	0.02	0.01	0.5	25
Zn	0.12	42.53	4	200
Ni	0.10	0.05	0.4	40
Mo	0.13	7.28	0.5	30
Cu	0.12	23.05	2	100
Cl ⁻	1180	185270	800	25000

NRL: No regulatory limits are available

Regarding bottom ash, except Pb, whose concentration reached at 0.83 mg/L, the rest of heavy metals values in the leach liquor were below the regulatory limits for inert wastes, indicating a relatively stabilized material. However, the chloride anions dissolution value was about 1.5 times higher than the corresponding limit. Consequently, bottom ash cannot be ranked in the inert waste category and special treatment is required. On the other hand, fly ash exhibited much higher metals leaching values in all cases. The leaching values for Pb, Ba, Cr, Zn, Mo, Cu and Cl were found significantly higher than the accepted limits for inert wastes, according to the 2003/33/EC Directive [30]. Furthermore, the leaching value of Pb was about 2.5 times higher than the corresponding value for the hazardous waste category, indicating that in case of landfilling should be disposed of at appropriate, regulation-prescribed waste dumps, after treatment in order to remove the water soluble phases.

4. Conclusions

A characterization and leachability study of two different types of ashes (fly and bottom ash), derived from a medical wastes incineration plant, was carried out. Fly ash composition, captured by the fabric filters of the unit de-dusting system, was significantly misquoted, mainly due to the flue gas cleaning installation. It was mainly consist of hydrated lime, which is injected for the acidic gases neutralization and CaCO₃ which is generated during lime partial carbonization at high temperature. Its particle size distribution ranged from 0.15 to 88µm, with 90 wt% of the powder under 56.23 µm. On the other hand,

bottom ash was mainly consisted of amorphous aluminosilicate glass, due to its rapid cooling by quenching, monocalcium silicate (CaSiO_3) and corundum (Al_2O_3), whereas other phases such as quartz, magnetite, halite, calcium aluminate and feldspars were also present in lower percentages. It presented a size fraction of <9.5 μm , whereas the over 250 μm size fractions comprise about the 85wt%. According to TCLP leachability examination, both ashes presented high metals leaching values with lead and zinc to appear the greatest affinity for the acetate ions and together with barium and chromium presented higher mobility in case of fly ash. Bottom ash showed also high extraction values for nickel, molybdenum and copper, whose presence attributed to the metallic medical equipment. On the other hand, during the EN12457-2 leaching test, bottom ash due to its slaggy form exhibited more stabilized behaviour as except Pb, the rest of heavy metals values in the leach liquor were below regulatory limits. However, fly ash presented much higher metals leaching values as Pb, Ba, Cr, Zn, Mo, Cu and Cl were found significantly higher than the accepted limits for inert wastes, according to the 2003/33/EC Directive

5. References

1. W.H.O. (World Health Organization): Guidelines for the safe disposal of unwanted pharmaceuticals in and after emergencies, Report No. WHO/EDM/PAR/99.2. Geneva, World Health Organization (1999)
2. W.H.O. (World Health Organization): Health care waste management rapid assessment tool (RAT), 2nd ed. Geneva. World Health Organization (2010)
3. European Waste Catalogue and Hazardous Waste List: Environmental Protection Agency, Ireland (2002)
4. Hamoda H.M., El-Tomi H.N., Bahman Q.Y.: Variations in hospital waste quantities and generation rates. *Journal of Environmental Science and Health*, A40:467–476 (2005)
5. Tudor T.L.: Towards the development of a standardized measurement unit for health care waste generation. *Resources, Conservation and Recycling* 50:319–333 (2007)
6. Abdulla F., Qdais H.A., Rabi A.: Site investigation on medical waste management practices in northern Jordan. *Journal of Waste Management* 28: 450–8 (2008)
7. W.H.O. (World Health Organization): Laboratory biosafety manual, 3rd ed. Geneva, World Health Organization (2004)
8. Kougemitrou I., Godelitsas A., Tsabaris C., Stathopoulos V., Papandreou A., Gamaletsos P., Economou G., Papadopoulos D.: Characterisation and management of ash produced in the hospital waste incinerator of Athens, Greece. *Journal of Hazardous Materials* 187: 421–432 (2011)
9. Karagiannidis A., Papageorgiou A., Perkoulidis G., Sanida G., Samaras P., A.: multi-criteria assessment of scenarios on thermal processing of infectious hospital wastes: A case study for Central Macedonia. *Journal of Waste Management* 30: 251–262 (2010).
10. Komilis, D., Fouki, A., Papadopoulos, D.: Hazardous medical waste generation rates of different categories of health-care facilities. *Waste Management*, 32, 1434-1441 (2012)
11. Coker A., Sangodoyin A., Sridhar M., Booth C., Olomolaiye P., Hammond F.: Medical waste management in Ibadan, Nigeria: Obstacles and prospects. *Journal of Waste Management* 29: 804–811 (2009)
12. Sohrab H., Amutha S. Nik Norulaini N.A., Mohd Omar A.K.: Clinical solid waste management practices and its impact on human health and environment – A review. *Journal of Waste Management* 31: 754–766 (2011)
13. Blenkarn J.I.: A backward step: landfill disposal of clinical waste. *Journal of Hospital Infection* 63: 105–112 (2006)
14. Nema S.K., Ganeshprasad K.S.: Plasma pyrolysis of medical waste. *Journal of Current Science* 83: 271–278 (2002).

15. Park H., Lee H., Kim M., Lee J., Seong S.Y., Ko G.: Detection and hazard assessment of pathogenic microorganisms in medical waste. *Journal of Environmental Science and Health, Part A* 44: 995–1003 (2009).
16. Matsui M., Kashima Y., Kawano M.: Dioxin-like potencies and extractable organohalogenes (EOX) in medical, municipal and domestic waste incinerator ashes in Japan. *Chemosphere*, 53:971–980 (2003).
17. Zhao L.J. Zhang F.S., Hao Z.P., Wang H.L.: Levels of polycyclic aromatic hydrocarbons in different types of hospital waste incinerator ashes. *Journal of Science of the Total Environment* 397: 24–30 (2008)
18. Anastasiadou K., Christopoulos K., Mousios E., Gidarakos E.: Solidification/stabilization of fly and bottom ash from medical waste incineration facility. *Journal of Hazardous Materials* 207–208: 165–170 (2012)
19. Xie R., Li W., Li J., Wu B., Yi J.: Emissions investigation for a novel medical waste incinerator. *Journal of Hazardous Materials* 166, 365–371 (2009),
20. Shaaban A.F.: Process engineering design of pathological waste incinerator with an integrated combustion gases treatment unit. *Journal of Hazardous Materials* 145, 195–202 (2007)
21. Alvim-Ferraz M., Afonso S.A.V.: Incineration of healthcare wastes: management of atmospheric emissions through waste segregation. *Waste Management* 25, 638–648 (2005)
22. Sukandar S., Yasuda K., Tanaka M., Aoyama I.: Metals leachability from medical waste incinerator fly ash: A case study on particle size comparison. *Environmental Pollution* 144,726-735 (2006)
23. Jang Y., Lee C., Yoon C., Kim H.: Medical waste management in Korea. *Journal of Environmental Management* 80, 107–115 (2006)
24. Lee, B.K., Ellenbecker M.J., Moure-Eraso R.: Alternatives for treatment and disposal cost reduction of regulated medical waste. *Waste Management* 24, 143–151 (2004)
25. Ruoyan G., Lingzhong X., Huijuan L., Chengchao Z., Jiangjiang H., Yoshihisa S., Wei T., Chushi K.: Investigation of healthcare waste management in Binzhou District, China. *Waste Management* 30, 246–250 (2010)
26. Jung C.H., Matsuto T., Tanaka N., Okada, T.: Metal distribution in incineration residues of municipal solid waste (MSW) in Japan. *Waste Management* 24, 381-391 (2004).
27. Chang F.Y., Wey M.Y.: Comparison of the characteristics of bottom and fly ashes generated from various incineration processes. *Journal of Hazardous Materials* B138, 594-603 (2006)
28. EPA: Toxicity Characteristics Leaching Procedure (TCLP), Method 1311. U.S. Environmental Protection Agency, USA (1992)
29. EN-12457-2: Characterization of waste, Leaching–compliance test for leaching of granular waste materials and sludges, Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction) (2003)
30. European Council 33/2003: Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of an Annex II to Directive 1999/31/EC, Official Journal L 011, 16/01/2003 pp. 0027–0049 (2003)
31. Zhang, H., He, P.J., Shao, L.M.: Fate of heavy metals during municipal solid waste incineration. *Journal of Waste Management and Research* 20: 55-68 (2002).
32. Aho M., Silvennoinen J.: Preventing chlorine deposition on heat transfer surface with aluminium-silicon rich biomass residue and additive. *Journal of Fuel* 83: 1299-1305 (2004)
33. Kuo H.W., Shu S.L., Wu C.C., Lai J.S.: Characteristics of medical waste in Taiwan. *Journal of Water Air Soil Pollution* 114: 413–421 (1999).
34. Zhao, L., Zhang, F., Kaisheng, W., Jianxin, Z.: Chemical properties of heavy metals in typical hospital waste incinerator ashes in China. *Waste Management*, Issue 29, pp. 1114-1121 (2008).