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CHARACTERISATION OF GENERATED ASH FROM HAZARDOUS WASTE INCINERATION

EMANUELA ADINA COCIŞ[a], VASILE FILIP SOPORAN[a], PETRU ILEA[b], FLORICA IMRE-LUCACI[b], BIANCA MICHAELA SOPORAN[a], PAUL BERE[c], OVIDIU NEMEŞ[a, *]

ABSTRACT. Ash from hazardous waste incineration represents the most important residue of the total products resulted from the incineration process. International literature contains many references to research that characterize ash as 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 ash. Samples were collected from a typical hazardous waste incineration and a series of tests were conducted, including a particle size distribution analysis, humidity content, surface morphology, elemental composition, chemical composition and heavy metal content.

Keywords: *hazardous waste, incineration, ash, metals, elements.*

INTRODUCTION

Waste generation has increased considerably worldwide in the last few decades [1]. One of today's major concern and problem is represented by the increasing amount of waste and the decreasing available areas for landfilling. The harmful products of chemical processes produced from either industries or hospitals are called hazardous waste. Hazardous waste is also generated in recycling centers, where waste from industries is recycled. Hazardous waste can be explosive, oxidizing, highly flammable, corrosive, infectious, mutagenic, irritant, toxic, or carcinogenic. The common hazardous waste disposal methods are incineration, land disposal and new technologies like solar detoxification [2].

Incineration significantly reduces the volume of hazardous waste (by 95%) and has advantages such as pathogen inactivation and potential energy recuperation [3].The massive volume of hazardous waste in many countries

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[a] Technical University of Cluj-Napoca, Faculty of Materials Engineering and Environment, Muncii Bd., No. 103-105, RO-400641, Cluj-Napoca, Romania, * ovidiu.nemes@sim.utcluj.ro

[b] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Janos Arany Str., No.11, RO-400028, Cluj-Napoca, Romania

[c] Technical University of Cluj-Napoca, Faculty of Mechanical Engineering, Muncii Bd., No. 103-105, RO-400641, Cluj-Napoca, Romania

is mostly reduced through incineration that leads to the generation of ash as a new type of waste.

Ash is a grey to black granular, porous, glasslike material which can be intermingled with ferrous and nonferrous metals and other incombustible materials contained in the waste composition before the incineration process it consists of fine, powdery particles, spherical or angular in shape, solid or hollow [4].

International literature contains many references to researches that characterize the resulted ash as dangerous, not dangerous, or inert, in an effort to diagnose its proper management and disposal. 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 [5].

Unfortunately, only a limited amount of researches exists regarding the characteristics, particle size distribution, morphology and ash [6]. Further research is needed to investigate the characteristics and the toxicity of bottom ash in order to explore its potential use as construction material [7]. Limited space and high cost for landfilling, led to the development of recycling technologies and reuse bottom ash as an admixture material (in cement and concrete production) [8 - 11], in road pavement, embankment, soil stabilization, ceramics, glass and glass–ceramics [4].

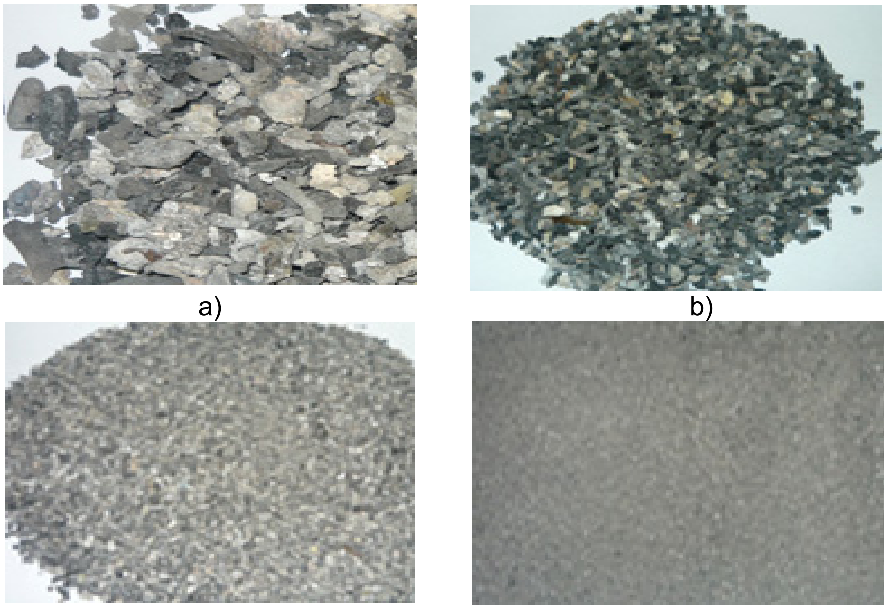
Bottom ash and fly ash, produced from incinerated hospital waste, are used for the production of concrete and bricks [5]. In several European countries high quantities of ash are reused for the manufacture of pavements, bridges and structural stones but also as sub layer in the manufacture of motorways 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 [5].

In the present work, nature of the ash has been examined through chemical analysis of samples collected from a hazardous waste incinerator. The main goal was to determine particle size distribution, humidity, heavy metals, morphology and elemental composition of ashes.

RESULTS AND DISCUSSION

The obtained grain sizes after particle size distribution were 1000 µm, 500 µm, 250 µm, < 250 µm (Figure 1).

The humidity content was between 5.86 - 9.84%.



a) b) c) d)

Figure 1. Granulometric sizes: a) 1000 μm; b) 500 μm; c) 250 μm; d) <250 μm

The metal elements determined were Pb, Zn, Cu, Cr, Ni, Ag, Sn and Mn. Figure 2 shows the metal concentrations in ash obtained by inductively coupled plasma mass spectroscopy (ICP-MS). The method used for the elementary analysis is based on SR EN ISO 17294-2/2005.

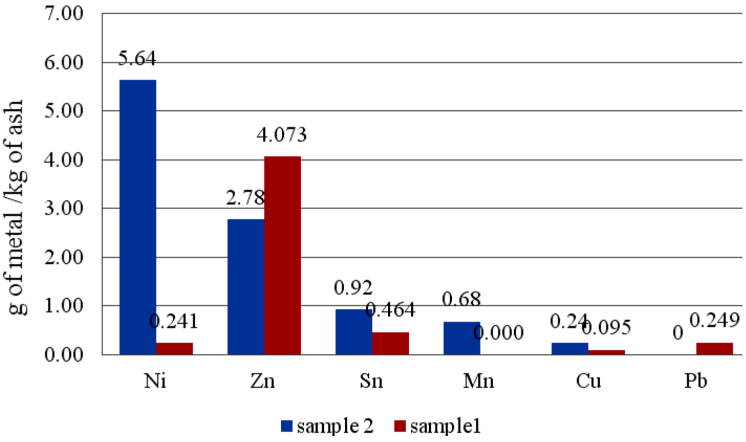


Figure 2. Metal concentrations in ash determined by ICP-MS

The obtained results were compared to the values indicated by the international literature in Table 1.

Table 1. Metal composition of ash

Element [g/kg]	Sample 1 [g/kg]	Sample 2 [g/kg]	Metal concentrations [g/kg]	Reference	Medium concentration according to literature [g/kg] [12]
Pb	0.249	0.00	4.76	[13]	0.098 - 0.137
Zn	4.073	2.78	6.08	[13]	0.613 - 7.77
Cu	0.095	0.24	0.97	[13]	0.290 - 8.240
Ni	0.241	5.64	0.185	[13]	0.007 - 4.28
Sn	0.464	0.92	5.87	[13]	0.002 - 0.38
Mn	0.000	0.68	2.03	[13]	1
Se	-	-	0.00005	[15]	0.0003
Co	-	-	0.03	[14]	0.008
Ag	-	-	0.004	[14]	0.000005
As	-	-	0.001	[15]	0.005
Cd	-	-	0.001	[15]	0.00006
Hg	-	-	0.00007	[15]	0.000003
Cr	-	-	0.00006	[15]	0.1

As seen, the metal concentrations from or samples do not exceed the literature indicated limits. The difference between these results is due to the composition of waste before incineration. Another cause may be the ineffectiveness of incineration process.

The oxide composition of the ash was determined through alkaline decomposition, based on STAS 9163/7. The obtained data are presented in Figure 3. The loss on ignition was 31.71%, based on STAS 9163/3 – 73.

The obtained results were compared to the values indicated by the international literature in Table 2.

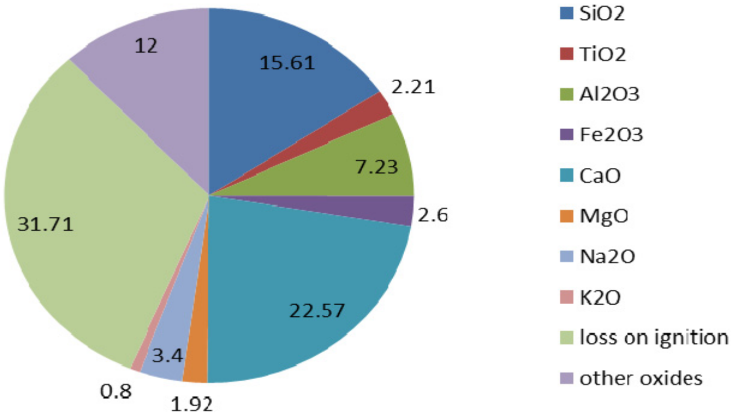


Figure 3. Oxide composition of the ash [%]

Table 2. Oxides identified in ash

Al_2O_3 [%]	SiO_2 [%]	CaO [%]	K_2O [%]	Na_2O [%]	MgO [%]	Fe_2O_3 [%]	Other oxides [%]	Reference
8.18	23.64	22.78	5.6o	5.28	-	-	5%	[13]
10.0	26.1	30.5	-	-	-	-	21%	[14]
17.83	0.18	22.90	-	3.68	1.04	11.39	-	[16]
14.34	0.39	33.18	0.6	3.64	2.81	4.64		[7]

As seen, the ash is mainly comprised from CaO, SiO_2 and Al_2O_3.

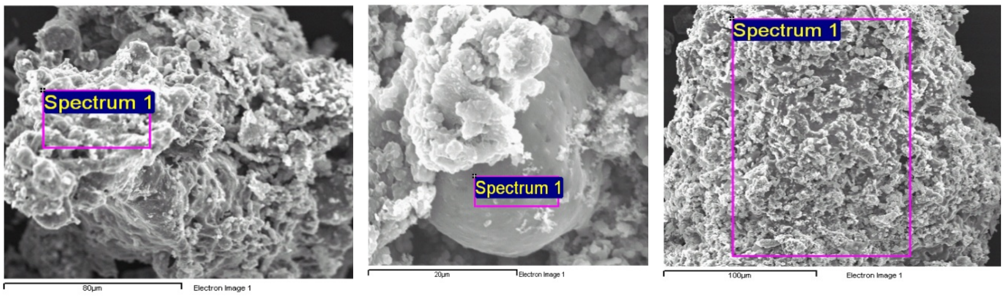
A morphology analysis by SEM is conducted to clearly understand how incineration process affects the ash surface structure [17].

The morphology of an ash particle is controlled by combustion temperature. The sizes of the observed particles are ranged from 9 μm to 1000 μm.

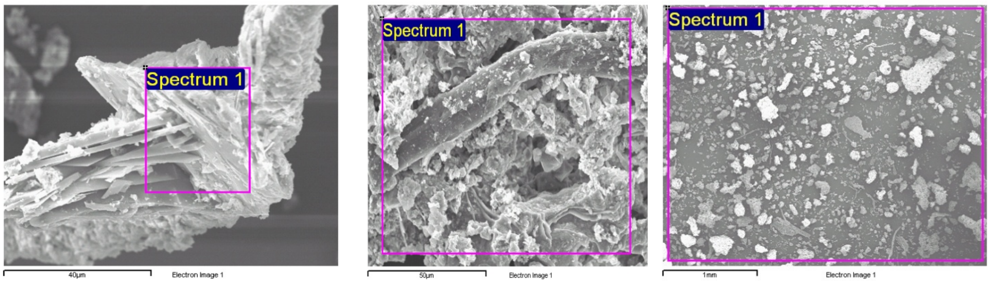
The micrographs showed agglomerated and irregularly shaped particles. This phenomenon occurs because of wastes containing impurities and complex components that may cause the particles to agglomerate at high temperature.

There were analyzed 20 areas (Z 1 ÷ Z 20) chose randomly, and depending on analyzed spectrum, we can observe smoother agglomerations and different shapes of ash particles (Figure 4).

The elemental composition of ash was determined by energy dispersive spectroscopy (EDS). The identified elements in the ash samples were C, O, Mg, Na, Al, Si, S, Cl, K, Ca, Ti, I, Zn, Ir, Zr, Fe (Table 3).



a) 80 µm b) 20 µm c) 100 µm



d) 40 µm e) 50 µm f) 1 mm

Figure 4. SEM images of ash

Based on the data given in the table we can observe that aluminum, silicon, calcium, chlorine and oxygen were identified in bigger percentage than other elements. We can also observe that the distribution of elements is heterogeneous and depends on the observed area (Figure 5).

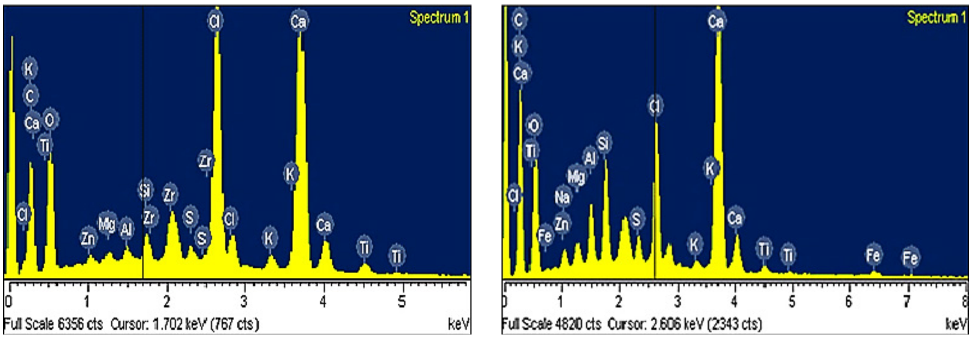


Figure 5. Elemental distribution determined by EDS

Table 3. Elemental composition of ash determined by EDS

Element [%] / Sample	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Zr	Ir	Zn
Z1	6.00	41.79	2.16	1.83	3.90	15.41	0.43	2.42	0.36	14.79	0.97	1.62	6.56	1.76	-
Z2	30.86	28.64	-	0.35	0.38	0.88	0.67	13.53	0.91	17.54	1.12	-	4.32	-	0.79
Z3	35.84	27.34	0.51	0.72	1.81	3.44	1.16	7.12	0.48	18.92	0.81	1.01	-	-	0.83
Z4	12.66	36.70	-	0.37	0.74	1.96	1.35	7.22	0.40	37.24	0.47	-	-	-	0.89
Z5	5.16	35.35	2.21	1.50	1.91	6.78	1.66	13.80	0.62	19.83	1.60	5.62	-	2.22	1.75
Z6	8.17	36.27	-	0.32	0.92	1.31	0.40	17.00	0.52	33.42	1.66	-	-	-	-
Z7	8.81	40.65	0.86	0.41	1.08	1.65	1.43	14.29	0.43	28.82	1.56	-	-	-	-
Z8	4.06	25.78	-	-	0.79	0.72	-	7.63	-	61.02	-	-	-	-	-
Z9	8.64	37.16	2.06	1.04	3.80	4.75	0.62	15.38	0.32	24.42	1.33	0.49	-	-	-
Z10	51.97	22.59	-	0.33	0.87	1.20	1.03	8.11	1.12	8.51	1.37	0.55	-	-	2.36
Z11	3.42	49.03	0.84	1.51	12.16	15.33	0.47	4.29	1.41	11.18	0.36	-	-	-	-
Z12	39.64	28.10	1.70	0.26	0.95	1.28	0.64	3.40	8.36	14.80	0.86	-	-	-	-
Z13	83.63	15.23	0.12	-	-	0.11	0.17	0.40	-	0.33	-	-	-	-	-
Z14	32.25	27.63	0.20	0.55	2.98	4.18	0.74	7.22	0.49	20.13	2.01	-	-	-	0.36
Z15	68.33	14.50	0.46	0.26	0.17	0.58	0.86	4.18	0.85	4.21	2.63	-	-	-	-
Z16	62.66	16.27	-	0.30	0.27	0.44	1.67	7.26	1.18	3.10	-	2.49	-	-	4.37
Z17	4.19	41.73	1.81	0.74	4.08	6.44	-	1.52	-	21.67	13.16	0.69	-	-	-
Z18	42.41	14.38	5.37	0.84	1.72	3.02	-	15.92	0.36	6.00	4.06	-	5.10	-	0.83
Z19	83.82	10.24	0.98	0.18	0.36	0.62	0.29	2.04	-	1.46	-	-	-	-	-
Z20	56.69	23.81	1.06	0.46	1.47	1.99	0.72	4.02	0.20	8.33	1.24	-	-	-	-

Studies showed that the EDS spectra of the surface and the interior of ash particles are similar, both having calcium and silicon as major elements, which is a typical elemental composition of combustion residues. Potassium, chlorine, sulfur, aluminum, iron, chromium, magnesium, phosphorus, titanium and zinc were also found at all points [18].

Other research showed that the elemental composition of ash was the following listed in Table 4.

Table 4. Elemental composition of ash

Element	Concentration sample 1 [%]	Concentration sample 2 [%]	Reference
C	41.6	38.7	[19]
O	27.5	29.0	
Na	0.5	1.0	
Mg	2.0	2.5	
Al	5.3	3.6	
Si	8.8	6.9	
S	0.6	0.9	
Cl	1.9	3	
K	3.7	2.2	
Ca	8.1	12.1	

Comparing these results with the ones from our sample (listed in Table 3), we can say that the elemental composition of ash is similar, because the same major elements can be observed.

CONCLUSIONS

Based on the information and data presented in this paper we can formulate the following conclusions:

The generated ash from hazardous waste incineration process represents the most important residue from the total resulted products.

Ash from waste incineration is a granular, porous, glasslike material which can be intermingled with ferrous and nonferrous metals and other incombustible.

Chemical analysis showed that the major components identified in ash were CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2, Na_2O, K_2O. Metallic elements, such as Pb, Zn, Cu, Ni, Ag, Sn, Mn were determined.

The SEM images showed that particles are agglomerated and irregularly shaped.

As determined by EDS, the identified elements in the ash samples were C, O, Mg, Na, Al, Si, S, Cl, K, Ca, Ti, I, Zn, Ir, Zr, Fe .Distribution of elements is heterogeneous and depends on observed areas.

Aluminum, silicon and calcium were found in large quantities, being typical constituents of combustion residues.

EXPERIMENTAL SECTION

Two ash samples were collected from a typical hazardous waste incinerator functioning in Cluj-Napoca.

The samples were sieved by an auto sieve fitted with standard meshes of different sizes. The separated granulometric fractions were: 1000 μm, 500 μm, 250 μm, < 250 μm (figure 6).There were also two fractions, one containing oxidized needles, blades and other metal parts and one containing pieces of glass and unburned materials which were removed.

The humidity content was determined for each fraction using the gravimetric method in which the ash samples were dried in an oven (VO 500 oven) at 105 °C for 24 hours.

The determination of chemical composition was conducted on ash samples collected from the ash disposal place and straight from the furnace, due to water content difference. Each sample was divided into granulometric fractions as mentioned before. A quantity of 2 g of each fraction was accurately weighed into a 100 ml beaker. Twenty milliliters of aqua regia (HNO_3:HCl = 1:3) were added to the beaker. Then, the beaker was placed on a water bath for 24 hours and after that cooled at room temperature. The solution was filtered and then diluted with deionized water into a 100 ml volumetric flask. The element concentrations in the solutions were determined by inductively coupled plasma mass spectrometry (ICP-TOF-MS Optimass 9500 GBC, Australia, 2007) according to SR EN ISO 17294-2/2005.

The oxide composition of ash was determined through alkaline decomposition, based on STAS 9163/73 and the loss on ignition based on STAS 9163/3 – 73.

The morphology and shape of ash particles were determined using scanning electron microscopy (JOEL JSM5510 LV). A representative portion of ash was sprinkled onto double-sided carbon tape mounted on a SEM tub and coated with a thin layer of gold before examined. Each fly ash sample was characterized by randomly selecting 1 - 2 fields of view and examining all the ash particles observed within the selected fields. The elemental composition and morphology were noted for each particle and compiled for each sample [20].

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REFERENCES

1. S.Javied, M. Tufail, Sofia Khalid, *Microchemical Journal*, **2008**, *90*, 77.
2. E. Emek, B. Kara, *Computers & Operations Research*, **2007**, *3*, 1424.
3. Y.C. Lin, J.H. Yen, S.K. Lateef, P.K.A. Hong, C.F. Lin, *Journal of Hazardous Materials*, **2010**, *182*, 337.
4. R. Siddique, *Resources, Conservation and Recycling*, **2010**, *55*, 84.
5. E. Gidarakos, Maria Petrantonaki, K. Anastasiadou, K.W. Schramm, *Journal of Hazardous Materials*, **2009**, *172*, 935.
6. J.D. Chou, M.Y. Wey, H.H. Liang, S.H. Chang, *Journal of Hazardous Materials*, **2009**, *168*, 198.
7. M. Ahmaruzzaman, *Progress in Energy and Combustion Science*, **2010**, *36*, 328.
8. C. Genazzini, G. Giaccio, A. Ronco, R. Zerbino, *Waste Management*, **2005**, *25*, 649.
9. J.E. Aubert, B. Husson, A. Vaquier, *Cement and Concrete Research*, **2004**, *34*, 958.
10. H.-S. Shi, L. Kan, *Construction and Building Materials*, **2009**, *23*, 2160.
11. A.Yilmaz, N. Degirmenci, *Waste Management*, **2009**, *29*, 1542.
12. IAWG, “Municipal Solid Waste Incinerator Residues”, *Elsevier Science*, **1997**, chapter 9.
13. X. Wan, W.Wang, T.Ye, Y. Guo, X. Gao, *Journal of Hazardous Materials*, **2006**, *B134*, 199.
14. L. Zhao, F.-S. Zhang, M. Chen, Z. Liu, D.B.J. Wu, *Journal of Hazardous Materials*, **2008**, *173*, 183.
15. R.D. Alorro, S. Mitani, N. Hiroyoshi, M. Ito, M. Tsunekawa, *Minerals Engineering*, **2008**, *21*, 1095.
16. F.Y. Chang, M.-Y. Wey, H, *Journal of Hazardous Materials*, **2006**, *B138*, 601.
17. B.G. Kutchko , Ann G. Kim, *Fuel*, **2006**, *85*, 2539.
18. A. Phongphiphat, C. Ryu, K.N. Finney, V.N. Sharifi, J. Swithenbank, *Journal of Hazardous Materials*, **2011**, *186*, 221.
19. R. Rajamma, R.J. Ball, L.A.C. Tarelho, G.C. Allen, J.A. Labrincha, V.M. Ferreira, *Journal of Hazardous Materials*, **2009**, *172*, 1054.
20. S.V. Vassilev, C.G Vassileva, *Energy Fuels*, **2005**, *19*, 1090.