Heat Treatment on Fly and Bottom Ash Based Geopolymers: Effect on the Immobilization of Lead and Cadmium

K. Krausova, T. W. Cheng, L. Gautron, Y. S. Dai, and S. Borenstajn

Abstract— **This study focuses on geopolymers produced from Municipal Solid Waste Incineration ashes, in order to transform ultimate and hazardous waste containing heavy metals into a chemically stable and economically competitive construction product. The main objective of the study is to evaluate the efficiency of the toxic elements immobilization after heat treatment. Samples were prepared with different proportions of fly ash, bottom ash and waste glass by activation with an alkaline solution. Waste glass was used to improve certain physical properties and decrease possible leaching. Incinerator waste-based geopolymers were observed and analyzed by X-Ray Diffraction and by Scanning Electron Microscopy coupled with Energy Dispersive X-ray microanalysis. The sustainability of these waste-bearing geopolymer materials has been constrained through leaching experiments (TCLP), density, porosity and water absorption measurements. The important result is that heat treatment appears to decrease both porosity and water absorption of geopolymers, thus resulting in a strengthening of waste-bearing matrices. The effect of heat treatment on leaching behavior was more difficult to identify, as discussed below. Furthermore, we observe that replacing a portion of FA and BA by waste glass significantly increases both physical and chemical resistance of geopolymers, probably due to pore filling by melted waste glass.**

Index Terms—**Cadmium, geopolymers, heat treatment, lead, municipal solid waste.**

I. Introduction

One of the main problems in the world is the increasing amount of waste generated which is related to the fast growing world population and development. Today, the main means of treating ordinary waste are incineration and landfilling. None of this is good for the environment. During incineration two types of ashes BA (Bottom Ash) and FA (Fly Ash) are generated which is highly dangerous for the environment and for human health and it is stored in a special landfill for hazardous waste. Besides these two MSWI (Municipal Solid Waste Incineration) ashes, dangerous gases and particles are also released and even in industrialized countries cleaning air systems are used for removal of the particles containing heavy metals, they are finally landfilled. Waste disposal causes possible danger of penetration of harmful substance into the air, the water or the soil. Many studies have focused on treatment of MSWI ashes with the aim of preventing any landfilling. One of the solutions for this could be a recycling of these MSWI ashes by their incorporation into glass, glass ceramic matrix or concrete materials. Geopolymer matrices have also been proposed for a sustainable immobilization of toxic elements. Geopolymers, considered as inorganic polymers with a three-dimensional polymeric structure, have been selected as possible matrices for hosting toxic elements like lead and cadmium.

The first concept, on basis of geopolymers, has been made in the Soviet Union in the 1950's by G.V. Glukhovsky [1] and its name was given by J. Davidovits in 1979 [2]. Typically the geopolymers are constituted by aluminosilicate powder activated by an alkaline solution. In nature they can be compared to zeolites and feldspars which are supposed to be efficient in the immobilization of toxic ions [3]. At the beginning of waste incorporation into geopolymers, radioactive waste was used [4]. The studies have treated the incorporation of FA into geopolymers by different methods performed by research teams of J. Davidovits [5,6]; Palomo [7] and Swanepoel [8].

The objective of the present study is to determine the effect of various heat treatment on the geopolymer structure. Such effect is poorly known even if it is expected to imporve the efficiency of the immobilization of lead and cadmium into these mineral matrices. This study is achieved by combining precise physical and mineralogical characterization and leaching experiments on these waste-bearing geopolymer matrices.

II. Material and Methods

A. Materials

The samples were synthesized from MSWI fly ash and bottom ash by adding waste glass powder in different proportions (Tab.1.). Heavy metals are mainly present in FA, and BA. Waste glass powder was added with the purpose of filling in the pores during heating up to 700°C and 800°C and therefore improving the mechanical resistance of the samples. The objective was to produce new, chemically stable and less dangerous materials.

Three types of samples were synthetised, each in six exemplars with various waste proportions (G10, G20, G30 respectively with 10, 20 and 30 wt% of waste glass). All these samples were brought to high temperatures during 1 hour at 700°C (G10/700, G20/700, G30/700) or at 800°C (G10/800, G20/800, G30/800) .

The samples were dried at ambient temperature to simplify the synthesis. Moreover geopolymers dried at room

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temperature display insignificant differences in physical properties compared to samples at 100°C in a stove [9].

The alkaline solution plays an important role in the polymerization process and in this study we used sodium silicate solution (Na_2SiO_3) with the chemical composition by mass: N_2O=9,5%; SiO_2=29%; H_2O=61,5% and sodium hydroxide solution (NaOH=45%). Molar ratio of the sodium silicate solution was SiO_2/N_2O=3. The proportions and parameters of the alkaline activation solution are presented in Table I.

TABLE I: THE COMPOSITION OF SYNTHESIZED SAMPLES

	Fly ash (%Wt)	Bottom ash (%Wt)	Waste glass (%Wt)	Sodium Hydroxide Solution 45% (%Wt)	Sodium Silicate Solution (%Wt)	Added Water (%Wt)
G10 ; G10/700 ; G10/800	20,45	20,45	4,55	18,73	32	3,8
G20 ; G20/700 ; G20/800	18,18	18,18	9,1	18,73	32	3,8
G30 ; G30/700 ; G30/800	15,91	15,91	13,64	18,73	32	3,8

The positive point of such a synthesis is that the solid wastes are constitutive components of the geopolymer matrix.

After mixing, the polymerizing assemblage was transferred into plastic cubic molds of 45 x 10 x 10 mm blocks. Geopolymer samples were compacted on a vibration table to remove trapped air for preventing excessive evaporation and after that the samples were covered using a plastic film. The samples were removed from molds after 24 hours and maintained at ambient temperature with 0% humidity before heat treatment (performed maximum one week later).

A. Heat Treatment

The waste glass powder melting temperature is estimated to be around 900°C instead of about 1400°C for new glass production. Observations by optical microscopy revealed that even at 700°C the waste glass was melt or partially melted, as confirmed by the presence of round and shiny parts throughout the samples: the former liquid transformed into glass after quenching appear to have filled the pores of the material, then reducing the porosity and consequently strengthening the geopolymer both mechanically and against leaching.

The thermal treatment was performed at the rate of heating of 10°C/min up to 700°C and 800°C and the rate of cooling of 2°C/min down to room temperature. All samples were then kept at ambient temperature and relative humidity of 30% until the day of testing (performed maximum one week later).

III. CHARACTERISTICS AFFECTING IMMOBILIZATION EFFICIENCY

The efficiency of the immobilization of waste can be evaluated through measurements of physical properties, characterization of the microstructure, and through chemical resistance against heavy metal leaching. Porosity, water absorption and specific gravity were measured by the Archimedes method with an Electronic densitometer SD-200L. Microstructure was analyzed by optical microscopy, Scanning Electron Microscopy (SEM) using an ULTRA 55 by Zeiss, based on the GEMINI® Technology and by X-Ray Diffraction (XRD) with a Bruker D8 ADVANCE diffractometer using a copper anode. Toxicity Characteristic Leaching Procedure (TCLP) (published by Chinese environmental law with standards for hazardous industrial waste [10]) was used to determine the resistance of the geopolymers to heavy metal leaching. And leachates were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to detect the heavy metals released, with a ppm resolution.

A. Physical Properties

Specific gravity of all samples was found to display contrasted change with increasing temperature. Before heat treatment all three samples with different amounts of waste glass, displayed a similar specific gravity (see Fig.1.). It means that their starting composition does not have a major influence on specific gravity. But sample G20 presents a regular increase of specific gravity related to temperature whereas sample G30 displays a gravity decrease. Sample G10 gravity evolution with temperature is irregular, but we can note that G10 presents the highest specific gravity at any temperature.

As for specific gravity, all samples without heat treatment display the same values of water absorption (about 50%). As temperature increases, the water absorption decreases (see Fig. 2). The more waste glass powder is present in the sample, the more sharply the water absorption rate decreases. Between the sample G10/800 and G30/800 we observed a 29% difference, compared to 0.5% without heat treatment. This could be explained by a strenghtening of the whole structure and potential filling of the pores with waste glass when in a liquid state before quenching.

The total porosity of geopolymers with the addition of waste glass powder is presented in Fig.3. Observations by scanning electron microscopy reveal the presence of closed spherical-shaped pores, which were caused by dissolving particles of the MSWI, incorporating the air during preparation. As for porosity examination, the same effect was observed for water absorption – as water absorption like porosity decreases with increasing temperature. This phenomenon is expected since water absorption and porosity are strongly related. The porosity of samples without heat treatment is 46-47%. With heat treatment, the porosity of all samples decreases: this feature is expected to strengthen the geopolymer and could lead to a more efficient immobilization of heavy metals against leaching. As for water absorption, the porosity was influenced by chemical composition and preparation conditions (proportion of SiO_2/Na_2O, heat treatment, etc.). For samples containing waste glass powder, the porosity is observed to decrease with increasing temperature and increasing amount of waste glass. The greatest difference between samples was 26% which

proves the great influence of sample composition.

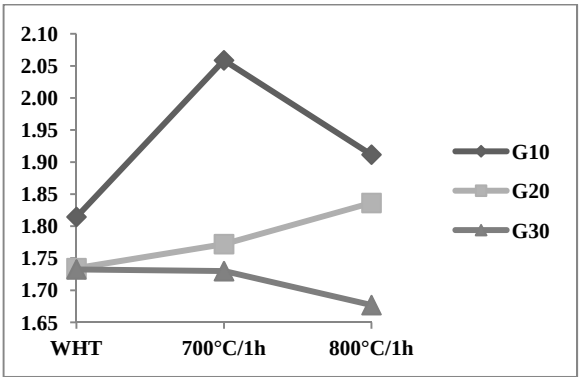

Fig. 1. Specific gravity (g/cm^3). WHT means without heat treatment

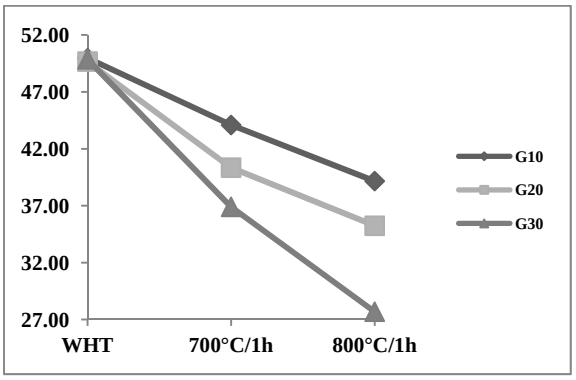

Fig. 2. Water absorption (%).WHT means without heat treatment

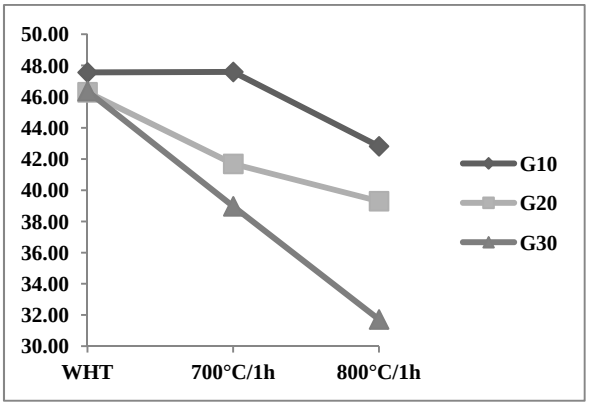

Fig. 3. Total Porosity (%).WHT means without heat treatment

B. *Microstructure*

The SEM images in Fig. 4 and 5 describe the characteristic morphology of geopolymer produced from municipal solid waste incineration ashes: geopolymers apperas as highly heterogeneous matrices (see Fig. 4). SEM Observations of the samples confirmed the relatively high porosity of the geopolymers caused by surface fracture and by boundaries between many different grains (Fig.4.).

Fig.5. shows the morphology changes as a consequence of heat treatment. Black parts correspond to holes and pores in the material which appears a bit more porous after heat treatment, but this needs to be confirmed by systematic SEM observations.

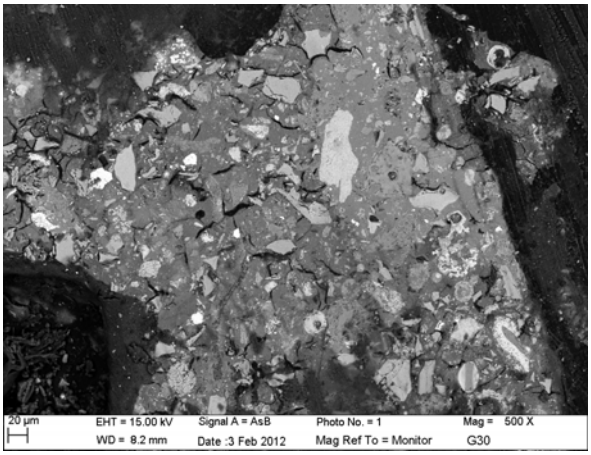

Fig. 4. Microstructure of sample G30 without heat treatment

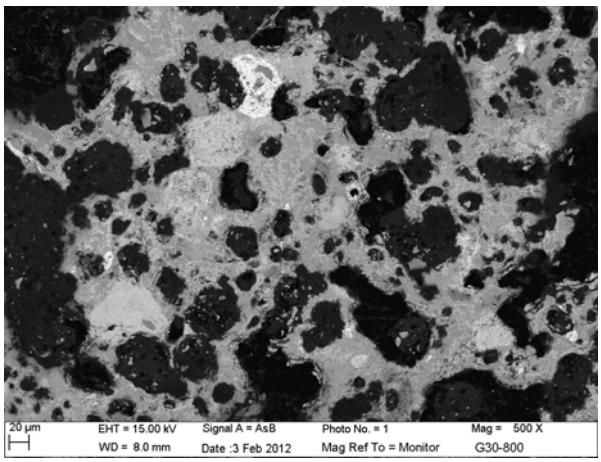

Fig. 5. Microstructure of sample G30 with heat treatment at 800°C

X-Ray Diffraction reveals the presence of a major amorphous part in all samples without heat treatment. As shown in Fig.6., the crystallization is higher when the amount of waste glass is lower. At room temperature, sample G10 presents 3 bragg peaks whereas sample G30 displays only 1 peak; after 800°C treatment, G10 presents more diffraction peaks than G30. With increasing temperature, the peak intensity increases, resulting in a higher crystallinity. Although it is difficult to assign a mineral phase for each peak, we could identify the main crystalline structure at 700°C and 800°C, which are lazurite ($(Na,Ca,K)_{7.8}[Si_6Al_6O_{24}][SO_4,S,Cl]_2 \cdot H_2O$) with cubic symmetry and wollastonite ($CaSiO_3$) with triclinic symmetry.

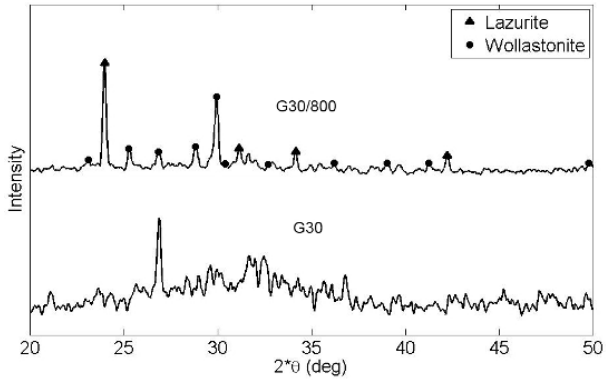

Fig. 6. X-ray diffraction of geopolymer samples G30 without heat treatment and at 800°C

TABLE II: BRAGG PEAKS OF THE MAIN CRYSTAL PHASES OBSERVED IN THE GEOPOLYMERS,

LAZURITE

hkl	d_{hkl} obs	d_{hkl} theo	I/I0 obs	I/I0 theo
4 -2 2	1,60	1,61	23,27	10,1
-1 4 0	1,83	1,83	20,30	42
3 -2 1	2,19	2,19	19,89	19
-1 0 3	2,31	2,31	20,01	27,3
2 0 2	2,48	2,48	20,53	14
-2 0 2	2,74	2,73	18,80	10,9
-1 -1 2	2,94	2,93	19,10	11,6
-2 2 0	2,98	2,98	100	100
1 0 2	3,10	3,09	39,72	47,6
-1 0 2	3,32	3,32	33,72	63,8
0 0 2	3,52	3,52	37,65	44,2
2 0 0	3,84	3,84	24,02	30,4

WOLLASTONITE

hkl	d_{hkl} obs	d_{hkl} theo	I/I_0 obs	I/I_0 theo
4 4 0	1,60	1,60	16,50	8,8
3 3 0	2,14	2,14	20,75	14,8
2 2 2	2,62	2,62	23,92	43,7
3 1 0	2,87	2,87	26,7	11
1 1 2	3,71	3,71	100	100

obs-Observed, theo-Theoretical

C. TCLP

The TCLP measurements were focused on two heavy metals, cadmium and lead. These two metals were present in FA in relatively high concentrations compared to others heavy metals.

A sample was shaken in a leaching liquor (diluted glacial acetic acid with pH=2.88±0.05) with the ratio L/S=20/l (kg) (Liquid/Solid) during 20 hours and then the leached solid sample was separated from the liquid part, which was analyzed.

Firstly we note that lead and cadmium behaved differently in terms of immobilization. The leaching rate of heavy metals appears to decrease when the initial amount of waste glass increases (Tab.2.). The first reason is that waste glass powder does not contain heavy metals in contrast to FA. Secondly, the former liquid transformed into glass after quenching is expected to strengthen the geopolymer then enhance the resistance to the leaching of heavy metals. It is observed that cadmium leaching is influenced by heat treatment: indeed increasing temperature induces higher amounts of Cd release. Samples without heat treatment met the restricted Cd leaching standards unlike samples synthesized at 800°C. On the other hand, it seems that heat treatment could lower the leaching rate of lead from these geopolymers.

TABLE III: LEACHED CHEMICAL ELEMENTS IN COMPARISON WITH LIMITS (PPM)

	Limits [9]	FA	BA	G10	G10/800	G20	G20/800	G30	G30/800
Cd	1	24	N.D	0,04	11,68	0,04	9,9	0,07	1,98
Pb	5	19,6	N.D	0,39	0,23	0,1	N.D	N.D	0,05

ND - Non Detected.

IV. CONCLUSION

Results showed that heat treatment in general improves different physical properties of geopolymers based on MSWI ashes and waste glass powder. The hypothesis of partial melting of waste glass powder is highly plausible as suggested by decreasing water absorption and porosity with increasing temperature. The higher the content of waste glass, the more water absorption and porosity decrease to 800°C.

The specific gravity rapidly increases in sample G10 at 700 °C, whereas it decreases in samples synthesized at 800 °C. For samples made of 20 wt% and 30 wt% waste glass, the change in specific gravity is less distinct.

With heat treatment, crystalline structures appear which make the geopolymer matrix double phased, keeping the amorphous part predominant. With these two components (glass and crystals) the material is expected to display better mechanical properties like tenacity, then inducing a higher immobilization efficiency.

The leaching results for lead clearly remain within the limits, and this indicates a possible industrial application [10]. Cadmium is released above the limits, possibly due to oxidation during heat treatment followed by a chemical reaction during the leaching test. Although heat treatment on geopolymers in order to recycle MSWI FA is at the first stage of investigation and development, the first experiments reveal that they are a promising economically solution due to possible applications such as construction materials which could be added to concrete as aggregates.

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