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THERMOCHEMISTRY OF VITRIFIED WASTE INCINERATION ASHES CRYSTALLIZATION

L. Stoch[*], *B. Procyk and P.Stoch*

AGH, University of Science and Technology, Faculty of Material Science and Ceramics, Cracow, Poland

Thermochemistry of crystal phase formation in vitrified municipal and hospital waste combustion ash and Ca, Fe pyroxene crystallization mechanism are presented. Pyroxene structure is capable of accumulate heavy metals and toxicants contained in ash. Due to this vitrification and crystallization is one of most effective method of immobilization dangerous contaminant of waste.

Keywords: *crystallization, glass, thermochemistry, vitrification, waste incineration ash*

Introduction

Increasing amount of municipal waste has become one of the serious problems of human civilization. Accordingly the significance of municipal solid waste incineration is continuously increasing. Incineration reduces the volume of wastes by 90%, but it leaves a considerable amount of ash as solid residue. In the solid products of the low temperature fluidal combustion process, there remain heavy metals and the carcirogenic dioxanes and furanes in a form easily washed away by ground waters. Storing of the ashes in landfill sites not guarantee permanent protection against this hazard. Vitrification is one of the promising procedure for inertisation of this residue [1].

For this reason, in the developed countries, vitrification of the solid remainders of waste combustion is increasingly used as the most effective method to neutralize their toxic properties. This refers in particular to the remainders of the combustion of wastes from hospitals considered to be particularly dangerous.

Vitrification of wastes may be carried out in a standard tank furnace or in specially adopted furnaces, heated with electricity, utilizing the Joule effect, in the induction furnaces or arc furnaces. Recently, the plasma waste vitrification process in which thermal plasma is utilized, has become more and more popular. The plasma process which enables vitrification at the temperature up to 2000°C is especially advantageous for waste combustion ashes processing. At this temperaturę there takes place the decomposition of dioxanes and furanes and removing of many toxic elements (Pb, Cd, Hg and others) which escape from the melt and are trapped by special filters, while others remain in the melt and become incorporated into glass structure for good.

Vitrification is an energy consuming process and its use can be justified if high quality products are made of glassy ash. Up to now obtaining glass-ceramic materials as a method of vitrified waste utilization is considered [2–4]. Microstructure of glass-ceramics obtained by a bulk as well as sintered powder crystallization has been the subject of detailed studies [5, 6].

Lately it has been demonstrated that vitrified and powdered ash, afterwards densified by compression at the temperature of about 900–1000°C is foaming, producing a porous insulating material similar to a foam glass. The advantageous property of the vitrified ash is that it can foam, even without any addition of a special foaming agent, usually soot, and the obtained foamed glass has now become an insulating, valuable material on account of its fire resistance [7].

Glassy ash shows high crystallization ability. Investigations have been undertaken on the behavior of vitrified ashes during heating and the processes occurring in them. Crystal phase development with the temperature increase was the subject of a detailed study. A special attention was paid to function of iron as a characteristic component of vitreous ash in crystallization process The obtained results are the subject of this paper.

Experimental

Materials and methods

Thermal reactions of vitrified ash from the municipal combustion plant Von Roll, Germany (A) as

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[*] Author for correspondence: stoch_l@poczta.onet.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

well as furnace ashes from a waste combustion plant in Warsaw (B) and from a combustion plant of hospitals waste in Lodz (C) were examined. The furnace ashes were melted in a laboratory furnace at 1450°C and the obtained melt was vitrified by pouring it onto a steel plate.

Crystallization of vitrified ash was investigated on samples grained to 0.1–0.3 mm by DSC.The crystal phase formation was studied using X-ray diffraction (XRD), scanning electron microscope (SEM) energy dispersive spectroscopy (EDS) system as well as transmission electron microscopy (TEM). Mössbauer spectroscopy has been applied to determine the content and position of iron in the structure of vitrified ash as well as their change with temperature increase.

Results and discussion

The chemical composition of the ashes is similar (Table 1). XRD and EDS analysis have proved that calcium silicates Ca_2SiO_4 and wollastonite $CaSiO_3$ are the main components of the ash. They are accompanied by calcium aluminate $Ca_3Al_2O_6$. Presence of the Al_2FeSi_2 and pieces of metallic iron are also observed. Dissipated particles of carbon occur too, what indicates for reductive condition in the burning chamber. Vitrified ashes are Ca and Fe rich aluminosilicate glasses. Their homogeneity has been studied by SEM and EDS methods. It has been revealed that the glassy ashes contain several inhomogeneities. They are inclusions of elementary carbon of the dimension 20–50 μm, and small quantities of very fine C particles are dispersed in the bulk of glass. Droplets of glass of the high SiO_2 or SiO_2 and Al_2O_3 content are common. Grains of a few μm size of Ca and Fe silicates, free CaO and chlorides (KCl and $CaCl_2$) and iron sulfide are locally visible. Small quantities of C are also dispersed in the bulk of glass. Places enriched with metallic Cu, Fe and Al have been identified [8].

DSC curves of vitrified ashes (Fig. 1) show the characteristic glass transformation deflection (T_g) and crystallization peak (T_c). Its temperature varies in a wide range depending on the chemical composition of the ash. Generally SiO_2 content increases but CaO and Fe_2O_3 decrease T_c temperature. Diminishing of Fe_2O_3 content by magnetic separation of metallic iron ash contaminations increases significantly T_c temperature the ash glass (Fig. 1 curves C and D).

Crystallization is also affected by the method of melting the ash. It is observed when comparing the crystallization curves of ash from combustion of hospital wastes in Lodz, melted traditionally in an

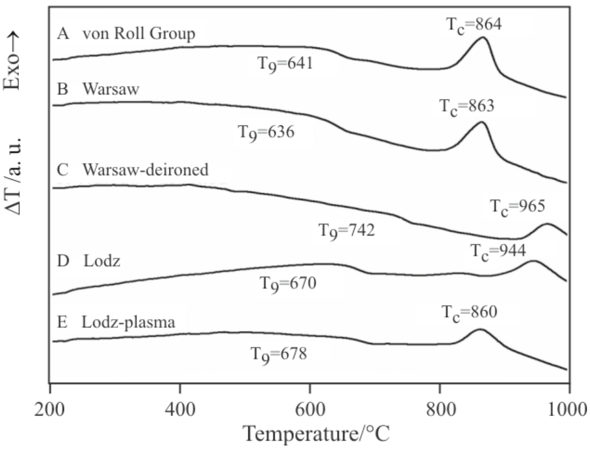

Fig. 1 DSC curves of the vitreous ashes

Table 1 Chemical composition of municipal waste combustion ashes/%

Component	Hospital waste ash Lodz	Municipal waste ash Warsaw	Vitreous municipal waste von Roll plant (Germany)
SiO_2	49.04	52.24	46.12
CaO	20.31	13.00	17.59
MgO	1.46	1.92	3.01
Al_2O_3	13.29	11.85	15.30
TiO_2	0.336	0.172	1.16
Na_2O	7.00	4.12	5.60
K_2O	1.11	1.22	1.22
ZnO	0.486	0.104	0.03
CuO	0.10	0.15	0.15
P_2O_5	1.43	0.83	0.11
Fe_2O_3 (total)	5.51	14.65	–
Fe(II) as FeO	0.136	1.408	6.93
Fe(III) as Fe_2O_3	5.36	13.09	1.15

electric furnace at 1450°C, with those of ash melted in a plasma furnace. Plasma melting reduces the crystallization temperature, which makes the vitrificate more susceptible to crystallization (Fig. 1, curves D and E).

Considering that during measurement the temperature increase was rapid (10 K min^{-1}), the appearance of crystallization peaks and their considerable intensity indicate that the vitrified ashes have a great tendency to crystallize when heated.

Bulk crystallization of vitreous ash is possible just above T_g temperature, but it needs a prolonged heating (6–12 h). A net of fine, crystals of micrometric size is formed then. At T_c temperature crystallization is rapid and big crystals of a rombohedric shape are formed.

Crystallization of vitrificate consists in the formation of crystals visible in electron scanning microscope (Fig. 2). According to XRD data they belong to pyroxens, group diopside ($CaMgSi_2O_6$) – hedenbergite ($CaFeSi_2O_6$) solid solutions series. From their composition determined by EDS method (Table 2) it follows that it is closer to another silicate of this group, the augite of the general formula (Ca, Mg, Fe^{2+}, Fe^{3+}, Al)($Si_{2-x}Al_x$)O_6]. Crystallization of glass at the temperature close to T_g transformation causes that crystals composition can differ from theoretical formula and be closer to that of glass what takes place in this case. The crystals contain a greater amount of iron (Fe_2O_3) and CaO, when compared with surrounding glass but contain less SiO_2 and Al_2O_3. EDS concentration profile demonstrating chemical elements distribution in crystal and surrounding glass (Fig. 3), suggests that at the temperature not far from T_g, when glass possess still high viscosity and its silicate network is preserved in a considerable degree, pyroxene structure formation consists in components glass structure modifiers – Ca, Fe, Mn, Cr and grouping them inside the network. Si concentration only slightly changes, and Al as silicate glass network component is partly expelled by coming in components to the crystal structure formation area, joining with the SiO_2 forming structural network of glass.

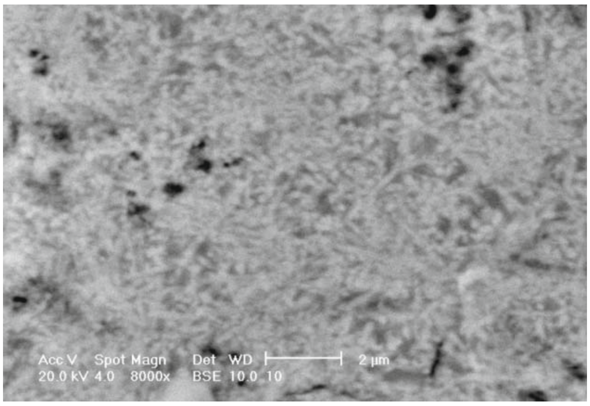

Fig. 2 Crystallization of vitreous ash C, after heating at 750°C (SEM image)

Table 2 EDS measured chemical composition (mass%) of pyroxene (augite) and surrounding glassy matrix (Fig. 4, point 3); vitreous ash A, crystallized at 950°C

Compound	Pyroxene	Glassy matrix
SiO_2	40.56	47.56
Al_2O_3	9.47	13.47
CaO	26.12	22.52
MgO	1.74	1.24
Fe_2O_3	16.28	9.36
MnO	1.62	1.10
Cr_2O_3	0.58	0.32
TiO_2	2.51	1.40
Na_2O	0.56	1.56
K_2O	0.75	2.12
SO_3	0.40	0.43

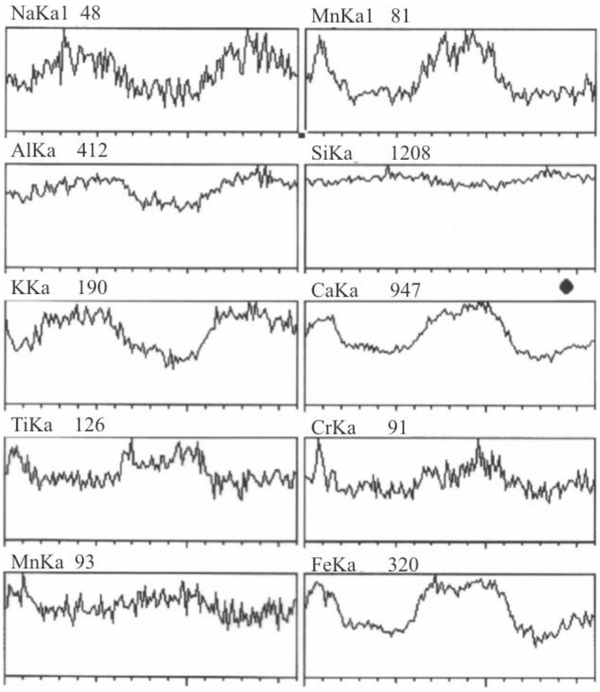

Fig. 3 EDS concentration profiles demonstrating chemical elements distribution in crystal and surrounding glass

It is visualized by EDS components concentration profiles. presenting chemical elements distribution in crystal and surrounding glass (Fig. 3).

The results indicate that crystal phase formation in ash vitrificates proceeds according to mechanism of amorphous structure ordering by diffusional rearrangement of components [9]. Acid-base strength of interactions (affinity) between acidic SiO_2 and basic oxides, increasing with the basicity degree of an oxide, as measured by ionicity of cation-oxygen decides about preferences of oxide incorporation into silicate network and the crystal structure formation.

The oxide basicity increase in the direction; Al_2O_3<FeO<MgO<CaO. This explains the diminishing content of Al, and increasing content of Ca and Fe in forming silicates structure as compared with their content in the parent glass structure.

Iron is the component easy changing its valency and position in the crystallizing compounds. Crystallization of glass in vicinity of metallic copper wire traces in vitrified ash (Fig. 3). Presence of metallic copper changes radically the chemical composition and type of phases crystallizing in its surrounding. Figure 4 shows the vein shaped crystallization around the remains of a copper wire. In its center, at places of the occurrence of metallic Cu, Ca reach silicates, from monticellite group, containing an admixture of Al are crystallizing and free CaO, also with an admixture Fe and Mn (Ca ferrites) are formed. The zone of the occurrence of Cu is distinguished by a reduced content of SiO_2 and iron when compared with their content in the surrounding core crystalline pyroxenes glass. On the boundaries of this zone the pyroxenes also poor in iron are crystallized. Further, iron containing pyroxenes and iron oxides precipitate. This iron to the outside migration can be explained as copper–iron electrochemical interaction and exchange of iron valency (oxidation–reduction process).

The Mössbauer spectroscopy is used for a long time as effective method of materials study [10, 11]. It has been used to determine the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio, coordination number, local symmetry of Fe nuclei and in same cases can give a good estimate of the percentages of isolated and clustered Fe^{3+} ions. The Mössbauer spectra of the vitrified ash samples revealed the changes of structural position of iron with temperature. Von Roll glassy ash contains Fe^{3+} (11% of total Fe atoms content) occupying octahedral (7%) and tetrahedral (4%) positions. Fe^{2+} (8 % of Fe atoms) has octahedral (48%) and tetrahedral (41%) position. Above T_g temperature, ordering of the Fe atoms distribution is observed. All tetrahedral Fe^{3+} and 1/4 of tetrahedral Fe^{2+} transforms into octahedral. In the structure of glass CN 6 is typical for components-modifiers and CN 4 for network-formers. Crystallization of glass changes the Fe distribution and all Fe^{2+} (83% of Fe atoms) becomes octahedral and all Fe^{3+} (17% of Fe atoms) has CN 4. This corresponds well to the possible positions of Fe in pyroxenes structure. The Fe^{2+} and Fe^{3+} clusters formation in glass, identified by the Mössbauer spectra, are not detectable by traditional phase analysis methods, probably due to small size and very low degree of crystallinity.

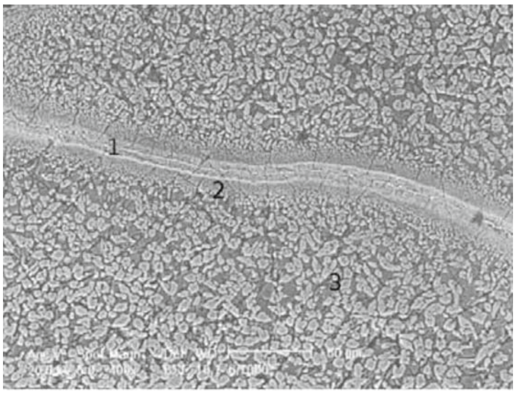

Fig. 4 Metalic Cu induced crystallization in vitrified ash at 950°C (SEM image). 1 – CaO and Ca silicate, metallic Cu containing vain, 2 – zone of fine crystalline Ca, Fe-pyroxenes surrounding the vein, 3 – coarse crystalline pyroxene (augite), and glassy matrix

The Mössbauer investigations have shown that the thermal transitions in vitrified ashes begin with the formation of Fe clusters already at about 700°C. Formation of magnetite, common in iron reach glass-ceramics from wastes is not observed here. Around these clusters there takes place the crystallization of fine pyroxene grains and at 800°C the material is recrystallized to a great degree. At 750–850°C there follows the crystallization of the fine grained pyroxenes of the first generation. At 850–950°C formation the generation of pyroxenes with well shaped prismatic crystal. The structure of pyroxenes prefers Fe^{2+}; the incorporation of iron into this structure causes the reduction of Fe^{3+} content, the amount of which decreases while the amount of Fe^{2+} is increasing.

Conclusions

Crystallization of the vitrified municipal and hospital waste combustion ash consists in the formation of Ca, Fe pyroxene close to augite (Ca, Mg, Fe^{2+}, Fe^{3+}, Al) $(Si_{2-x}Al_x)O_6]$ as the main crystal phase. Crystal phase formation in vitrificates proceeds according to mechanism of amorphous structure ordering by diffusional rearrangement of components. Interactions of acid-base character, between glass network forming SiO_2 and rest of components and Fe oxidation reduction processes are factors governing the glassy ash crystallization Augite structure is capable of accumulate heavy metals and many toxicants contained in ash. Due to this vitrification and crystallization is one of most effective method of immobilization dangerous contaminant of waste.

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References

1 O. Hjelmat, J. Hazard. Mater., 47 (1996) 345.
2 M. Romero, R. D. Rawlings and J. Ma. Rincon, J. Eur. Ceram. Soc., 19 (1999) 2049.
3 A. R. Boccaccini, J. Schawohl, H. Kern, B. Schunck, J. M. Rincon and M. Romero, Glass Technol., 41 (2000) 99.
4 A. A. S. T. Delben, F. L. Menezes, J. R. Delben, M. B. Coelho and R. F. Ribeiro, J. Therm. Anal. Cal., 87 (2007) 879.
5 W. Lynsawage, Ceram. Bull., 30 (1951) 21.
6 M. Pelino, C. Cantalini and J. Ma. Rincon, J. Mater. Sci., 32 (1997) 4655.
7 B. Procyk, J. Kucharski and L. Stoch, Pol. Ceram. Bull., 66 (2001) 124.
8 L. Stoch, Glass Technol., 45 (2004) 71.
9 L. Stoch and P. Stoch, J. Therm. Anal. Cal., 88 (2007) 577.
10 N. N. Greenwood and T. C. Gibb, Mössbauer spectroscopy, Chapman and Hall Ltd., London, 1971.
11 P. Stoch, J. Non-Cryst. Solids, 345 , 346 (2004) 153.

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