Vitrified waste combustion ash crystallization
Mössbauer spectroscopy study

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Mössbauer spectroscopy has been applied to determine the content and position of Fe2+ and Fe3+ in the structure of vitrified municipal waste incineration ashes as well as its change with temperature increase. The Fe clustering and incorporation into the structure of pyroxene which is crystallising in the glass were studied.

Introduction

Storage of the increasing amount of waste has become a serious problem of modern civilization. This refers in particular to municipal waste, the storage of which occupies on increasing number of areas and requires expensive protection measure to prevent the spreading of toxic substances. This makes the cost of their storage increase permanently. In this situation the combustion of municipal waste as well as of some industrial waste has become an increasingly common practice. However, in the combustion process the furnace ashes and fly ashes are produced being the solid combustion products. The combustion of waste is going at temperature usually not exceeding 1200^0 C and in the solid combustion waste there remain then the heavy metals and the cancirogenic dioxanes and furanes, in a form easily washed away by the ground waters.

The vitrification process has found wide application in the radioactive waste disposal. The waste from nuclear power plants are stored in a vitrified from as components of chemically resistant borosilicate glasses. Experience gained at vitrification of nuclear waste is applied in the neutralization of waste resulting from the combustion of substances containing toxic components.

In order to improve the economic effectiveness of the vitrification process the obtained glass should be processed and converted into valuable goods. It can be processed by way of controlled crystallization into glass – ceramic materials of high strength parameters, intended to be used in the building industry for the construction of roads, as well as for the production of wall and roof tiles[1].

It has been demonstrated that vitrified and powdered ashes, afterwards condensed by compression and heated at the temperature of about 900 – 1000^0C is foaming, producing a porous insulating material known as foamed glass[2]. The advantage of the vitrified ash is that it foams without an addition of special foaming agent, usually soot, and the obtained foamed glass has now become an insulating, valuable material on account of its fire resistance.

Scope of study

The main goal of the study was obtaining the foam glass strenghtenning, by controlled crystallization of vitrified municipal ash. This process is influenced strongly by changes of the iron aggregation process. Due to this Mössbauer spectroscopy has been applied to determine the position of iron Fe^{2+} and Fe^{3+} in the structure of glass and crystalline phase and its change with temperature increase. The results was supported by SEM – EDS and thermal analysis study.

Materials

Thermal reactions of vitrified ash obtained from the municipal combustion plant where investigated. The object of investigation were also furnace ashes from a waste combustion plant in Warsaw and from a combustion plant of hospitals waste in Łódz. The chemical composition of these ashes is similar it changes in the range SiO_2 46 – 49 %, CaO 13 – 20 %, MgO 1.5 – 3.0 %, Fe_2O_3 (total) 5 – 15 %, Al_2O_3 12 – 15 %, Na_2O 5 – 7 %, K_2O 1.1 – 1.2 (wt %). The ashes from Warsaw and Łódz plants were melted in a laboratory furnace at 1450^0C and the obtained melt was vitrified by pouring it onto a steel plate.

Foamed glass was obtained from vitrified and powdered ash by heating at 900^0 and 950^0C for 6 min. The material contains spherical pores of air stick in the matrix formed by partly recrystallized glass. The crystallizing phase is the monoclinic pyroxene diopside- hadenbergit type $(Ca,Mg,Fe^{2+},Fe^{3+},Al)_{1-x}[Si_2O_6]$. On the surface of pores the clacium olivine $CaFeSiO_4$ was also found.

Mössbauer study

The Mössbauer spectroscopy can be useful technique 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. That parameters are closely related to the hyperfine interaction parameters like: isomer shift (IS), quadrupole splitting (QS) and hyperfine magnetic field (H_{hf}).

The isomer shift is related to the valency and coordination number. In case of glassy samples for Fe^{3+} ions in tetrahedral symmetry IS is in the range of 0.2 – 0.4 mm/s and in octahedral symmetry in the range of 0.4 – 0.6 mm/s. For Fe^{2+} (T_d) the isomer shift is < 1.0 mm/s and for Fe^{2+} (O_h) > 1.0 mm/s.

The quadrupole splitting is useful for evaluating the coordination number, too. The QS of Fe^{3+} (T_d) is in the range of 0.7 – 1.0 mm/s wherease that of Fe^{3+} (O_h) is 0.3 – 0.9 mm/s.

To determine the hyperfine interaction parameters there were measured mössbauer spectra of vitrified municipal waste ash, foamed glass from vitrified ash at 900^0C and 950^0C, which are shown at Fig. 5, 6, 7 and hyperfine parameters are summarized in Table 2.

The Mössbauer effect was measured at the 14.4 keV emission of a ^{57}Co source in Rh. The spectrometer was calibrated using α - Fe foil at room temperature and IS values are quoted to this standard.

The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ration can be evaluated directly from the relative areas of the spectra components. This ratio values are about 94 %, 34 % and 53 % for municipal waste ash sample and foamed at 900^0 and 950^0C respectively. Spectrum of foam glass (foaming temperature 900^0C) except of two paramagnetic doublets consist of two more sextets (clustered iron) that can be only seen at low temperatures. Direct comparison of the area under Fe^{3+} doublets and area under the two fitted sextets gives a good estimate of the percentages of isolated and clustered Fe^{3+} ions. It means that this sample consists of about 34 % isolated Fe^{2+}, 43 % of isolated Fe^{3+} and 23 % of clustered Fe^{3+}.

All glasses gives spectra consisting of paramagnetic doublets which are a superposition of lines from Fe^{2+} and Fe^{3+} of diffrent coordination number and position.

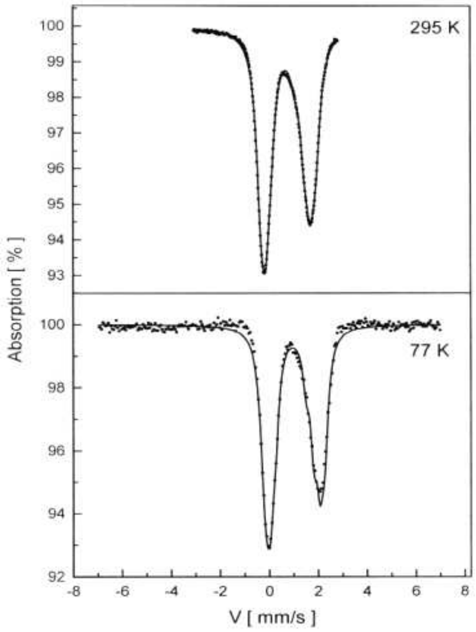

Fig. 1. ^{57}Fe Mössbauer spectrum of vitrified municpal waste ash.

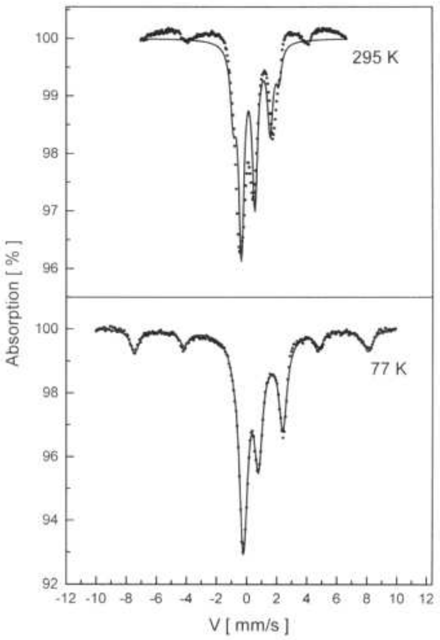

Fig. 2. ^{57}Fe Mössbauer spectrum of foam glass from municipal waste (900 C).

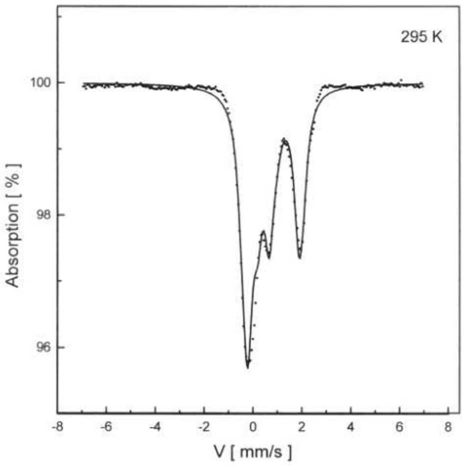

Fig. 3. ^{57}Fe Mössbauer spectrum of foam glass from municipal waste (950^0 C).

Table 1. Hyperfine interaction parameters

Vitirfied municipal waste ash at 77 K

Area [%]	QS [mm/s]	IS [mm/s]	Oxidation state and coordination
8.2	2.194	1.568	Fe^{2+} (O_h)
22.8	2.161	1.214	Fe^{2+} (O_h)
18.8	1.826	1.207	Fe^{2+} (O_h)
17.1	1.917	0.982	Fe^{2+} (O_h)
6.0	1.677	0.536	Fe^{3+} (T_d)
10.8	1.888	0.763	Fe^{2+} (O_h)
16.3	2.550	1.196	Fe^{2+} (O_h)

Foamed glass (foaming temperature 900^{0}C) at 77 K.

Area [%]	QS [mm/s]	IS [mm/s]	$\mu_0 H_{hf}$ [T]	Oxidation state and coordination
42.7	0.979	0.467	–	Fe^{2+} (T_d)
34.2	2.830	1.238	–	Fe^{2+} (O_h)
20.3	0.003	0.459	50.68	Fe^{3+} (O_h)
2.8	0.140	0.623	46.55	Fe^{3+} (O_h)

Foamed glass (foaming temperature 950^{0}C) at 295 K.

Area [%]	QS [mm/s]	IS [mm/s]	Oxidation state and coordination
25.6	0.833	0.472	Fe^{3+} (O_h)
21.8	0.954	0.122	Fe^{3+} (T_d)
16.2	1.735	0.994	Fe^{2+} (T_d)
36.4	2.354	0.989	Fe^{2+} (T_d)

Conclusions

Mössbauer spectroscopy is a helpful tool of phase transition in Fe – rich glass study. It makes possible to study the Fe aggregates formation and disappearing it with temperature as well as Fe valency change.

Fe aggregates in glass are nucleator for fine crystals of silicates formation. Thus the process of nanocrystallisation of glass is dependent of them.

The conducted investigations have shown that the thermal transitions in vitrified ashes begin with the formation of Fe clusters already at about 700^0C. Around these clusters there takes place the crystallization of fine pyroxene grains and at 800^0C the material is recrystallized to a great degree. At 750^0 - 850^0C there follows the crystallization of the fine grained pyroxenes of the first generation. At 850 - 950^0 formation the generation of pyroxenes with well shaped prismatic crystala. 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. The result is the excess of oxygen, which can be released and participates in the swelling of the glass powder at the temperature of its sintering. This makes it possible to obtain foamed glass from vitrified waste.

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