Vitrified waste incineration ashes
Thermal transformations and industrial utilization

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The crystallization processes occurring in vitrified municipal waste incineration ashes during heating, as a basis for fine crystalline glass- ceramics and fire resistant foam glass were studied. Pyroxene crystallization is accompanied by glass structure components redistribution. Due to Ca and Fe incorporation into pyroxene structure, surrounding glass is poorer in them and enriched with Si and Al. Heat treated ash properties are the cumulative effect of crystallized phase properties and properties of residual glassy matrix.

Vitrification as municipal waste neutralization method

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 combustian process, there remain heavy metals and the carcirogenic dioxanes and furanes in a form easily washed away by ground waters. Mixing of the ashes with cement and pelletization of the mixture to reduce the leaching of the toxic substances does not guarantee permanent protection against this hazard. Vitrification is one of the promising technology for inertisation of this residue.

The advantages of the method of waste neutralization by way of vitrification are as follows:

The chemical composition of the glasses may change in a wide range and due to this many waste combustion ashes can be vitrified in their original form or with appropriate additions, which may be the waste or other by-products. They modify the ash composition to make its vitrification easier or applicable for recycling..

Through appropriate selection of glassy ash composition it is possible to make it completely resistant to water, and the hazardous components present in the glass not washable into the environment.

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 temperature 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.

The plasma processing of industrial waste is used in the USA and France to neutralize asbestos waste products, in the USA and Australia - to neutralize hazardous toxic waste; in Japan 70 % of municipal waste are neutralized in combustion chambers and a considerable amount of the ashes is vitrified.

Thermal plasma reactor for combustion and vitrification of wastes from hospital and other hazardous wastes has been constructed[1].

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 municipal waste incineration utilization is mainly considered. These materials can be obtained by bulk crystallization of glassy ash[2], or by viscous flow sintering of glass powders and crystallization[3]. Microstructure of glass-ceramics obtained by a bulk as well as sintered powder crystallization has been the subject of detailed studies[4].

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.[5]

Glassy ash shows high crystallization ability. Investigations have been undertaken on the behavior of vitrified ashes during heating and the processes occurring in them, especially on the crystallization accompanying the formation of the foam glass. Crystal phase development with the temperature increase was the subject of a detailed study. The obtained results are the subject of this paper.

Investigated materials

Thermal reactions of vitreous ash from the municipal combustion plant Von Roll, Germany as well as furnace ashes from a waste combustion plant in Warsaw and from a combustion plant of hospitals waste in Lodz were examined. The ashes from both these plants were melted in a laboratory furnace at 1450°C and the obtained melt was vitrified by pouring it onto a steel plate. The chemical composition of these ashes is similar (Table 1). They are Ca and Fe rich aluminosilicate glasses.

Vitreous ash homogeneity has been studied by SEM and EDS methods. It has been revealed that the glassy ashes contain several inhomogenities. They are inclusions of elementary carbon of the dimension 20 – 50 um, 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 um size of Ca and Fe silicates, free CaO and chlorides (KC1 and $CaCl_2$) are locally visible. Places enriched with Cu hace been identified.

Table 1. Chemical composition of vitrified waste combustion ashes

Component	hospital waste Łódz	municipal waste Warszawa	municipal waste von Roll (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

Vitrified glass crystallization

DTA curves of glasses indicate that the glass transformation temperature (T_g) changes from 600 to 700°C, and the temperature of the exothermic crystallization peak (Tc) , changes from 860 to 969°C depending on the chemical composition of glass. Tc corresponds to the maximum rate of crystal phase volume increase. TG curve of the Von Roll glass, which is the reaches in FeO, indicates on an increase of the sample weight at 500 - 800°C due to iron oxidation

DTA curves shows that the reduction of iron content by removing pieces of metalic iron (deironed ash from Warszawa plant, Fe_2O_3 content 3.1 wt.%) causes the increase of the Tg temperature by 80°C, and the Tc temperature increases from 913 to 969°C. The reduced content of iron oxides, which are the modifiers, causes the increase of the viscosity of the glass, slowing down the crystallization process. Iron is also an essential component of the crystallizing pyroxenes.

Microscopic optical investigations of the progress of bulk crystallization in solid pieces of glass, carried out on samples heated for 2 hrs in a gradient temperature furnace, have shown that this process begins above the transformation temperature (650°C). Above 725°C the sample starts to crystallize, but the process is slow, at 750^0C , 24 hours heating is necessary to obtain 50% bulk crystallization of the sample. Above 850°C there takes place the growth of the well shaped pyroxene crystals, which take the form of prismatic, dark colored crystals of rhombohedral cross - section. They are surrounded by colorless glass.

SEM of a sample crystallized for 4 hours at 950°C confirms the crystalline structure of the material. The main crystal phases are Ca, Fe pyroxenes with Al and Mn admixtures.

The analysis of changes in the concentration of the main components of a sample crystallized at 950°C shows that at places where pyroxene crystals occur, an increase in the concentration of Ca, Mg, Fe, Cr in them is observed. The surrounding glass becomes poorer in these components; this refers in particular, to Fe.This glass, on the other hand, is enriched with Si, alkalies and Al. Glass of such like composition has low crystallization ability and its viscosity should increse. Sufficiently high viscosity is necessary to make the glass foaming.

The conclusion of the investigations is that the crystallization mechanism of pyroxenes in the vitreous ash consists in the displacement of the cation modifiers in the glass structure within the silicate framework which itself undergoes only a rather small reorientation.

A specific feature of the vitrified ash bulk crystallization process is the formation long veins, formed by fine grains of CaO rich silicates (Ca, Fe, Mn $)_2[SiO_4]$ (monticellite) containing Al admixture. It differs from the pyroxene and glassy matrix in the lower content of Fe and Mn . Recent investigations indicate that the veins are formed at places of Cu colloidal grains precipitation. Cooper grains are the selectively acting nucleators for Ca ortosilicates formation.

The occurrence of veins formed of composite CaO, MnO, ZnO and Fe oxides was also observed in the crystallized ash. They are the effect of vitreous ash inhomogeneity.

Foam glass crystallization

The structure of foam glass obtained from vitrified ash by heating at 950°C for 6 min. consists of the spherical pores (about 90 vol.%) in the matrix formed by partly crystallized glass. EDS spectra show, that the crystallized phase is the Ca, Fe, silicate. As shown by XRD, it is monoclinic pyroxene of diopside structure type. On the surface of pores the calcium ortosilicate CaFeSiO4 (mellilite) has been also found. During crystallization a considerable portion of Fe is incorporated into the silicates structure and the glass becomes impoverished of this component. TEM and EDS studies indicate that pyroxene crystals contain approximately : 4 Na, 0.6 K, 0.6 Mg, 23 Ca, 30 Fe, 4 Mn, 7 Al, 1 Ti, 21 Si (atomic percent). Glass surrounding the crystals contains : 3Na, 1.3K 2 Mg, 24 Ca, 14Fe, 1.4 Mn, 10 Al, 1.5 Ti 34Si (atomic percent). This indicates that crystallization considerably changes the chemical composition of the glassy skeleton of the foam glass, making it more chemically durable and increasing its softening temperature. Mechanical strength is improved as well.

Foaming temperature of the studied vitrified ashes corresponds to the temperature of high crystallization rate and both processes can run parallelly.

Conclusions

Vitrified waste combustion ashes are Ca and Fe reach aluminosilcate glasses of high crystallization ability. Crystallization process starts at above 7500C and fine crystals (about 1 um long at 8000 C) of Ca,Fe- pyroxene of diopside structure are formed. Above 9000C coarse (about 10 um in size), prismatic crystals of rhombic cross-section, of the pyroxenes of second generation crystallize. The content and the size of crystals increases up to 9500 C, at higher temperature they are remelted.

A compact , fine crystalline structure of glass-ceramic materials of high mechanical strength can be formed when vitrified ash is heated at 8000 C. Through appropriate thermal treatment in the range 750 – 8000 C it is possible to obtain material of nanocrystalline structure.

Vitreous ash, powdered and mechanically densified, is able to foam at the temperature range 900 – 10000C. This property offer the possible to use it for the production of porous , insulating materials similar to foam glass. Foaming temperature of vitreous ash corresponds to the temperature of its highest crystallzation rate . Due to this , the obtained foamed glass-ceramic material posseses a higher chemical durability and temperature of softening as well as better mechanical properties, as compared with traditional foam glass.

Acknowledgments

The investigations were carried out with a financial support of the National Committee for Scientific Research of Poland, grant PBZ/KBN/13/TO8/99/34. SEM / EDS investigations were conducted at the Institute of Metallurgy and Material Science of Polish Academy of Science in Krakow under the supervision of prof. J. Dutkiewicz. Sample of Von Roll glass was sent kindly by prof. H. Hessenkemper, TU Bergakademie Freiberg.

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