Vitrification of Radioactive Hospital Waste
Incineration Ash - 9149

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ABSTRACT

Vitrification of a hospital Cs contaminated waste incineration ash, by comelting with Na borosilicate glass and encapsulation procedure ware studied. Mechanism of the sintering and melting of heat treated ash and glass mixtures, as well as accompanying recrystallization processes were studied. The influence of incorporation of Cs and CaO as characteristic components of ash on the change of structure of the glass and its properties were studied. CaO increases the tendency of glass for crystallization. Cs is incorporated into the newly forming crystal phases which are aluminosilicates (Na, Ca- plagioclase and nepheline), and Ca -borates. The influence of chemical and phase composition change on Cs leaching was investigated. Experimental results were compared with MD simulation of glass structure data.

INTRODUCTION

High level radioactive wastes [HLW] from both the nuclear power industry and military nuclear programmes are currently immobilised by vitrification. Borosilicate glass is providing the very suitable medium for the majority of the species present in these wastes [1,2]. It prevents leaching of radio nuclides by water- an immobilisation effect. Environment protection and increase of disposal cost makes that vitrification of the low level nuclear waste [LLW] lately is finding favour [3].

The LLW resulting from the use of radioactive isotopes in medicine, industry, laboratories and other purposes can be immobilized by vitrification. Management of such waste begins with combustion reducing their amount. According to [4] paper, PCV and cotton combustion ash containing radio isotopes, is suitable for vitrification and ceramization by incorporating it into the composition of boro-aluminosilicate glass, similar to those used in nuclear power industry. The ash is mixed with glass powder and sintered or remelted at $1100 - 1300^0C$ [4,5,6]. The paper presents the results of model studies of the hospital waste contaminated with radioactive ^{137}Cs.

As the object of the investigations there has been chosen the determination of the influence of Cs and CaO as a characteristic component of ash, after combustion of these waste on the structure and properties of borosilicate glass. The effect of introducing Cs_2O or Cs_2O and CaO on the properties of boro-aluminosilicate glasses is little known, as it is not used in traditional glass manufacturing.

These components have different crystallochemical parameters. Cesium is characterized by great ionic radius $r_{Cs} = 1.74$ Å, the coordination number in relation to oxygen CN = 8 and the iconicity of chemical bond with oxygen, according Görlich $i_G = 0.832$[7].

Thus it is considerably different form Na which shows $r_{Na} = 1.02$ Å, and CN = 6 in relation to oxygen and the iconicity of bond with oxygen Na-O, $i_G = 0.870$. Ionic radius of Ca^{2+} at CN 6 , $r_{Ca}= 1.00$ Å, and ionicity Ca – O bond $i_g = 0.707$ [7].

EXPERIMENTAL

The chemical composition of the reference borosilicate glass (glass 1) and its Cs containing modification (glass 2) applied in experiments are shown in Table I. CaO was added to the composition of the glasses at the expense of diminishing of SiO_2 and B_2O_3 content as it is characteristic component of ash. The other ash components: SiO_2, Al_2O_3 are already present in the reference glass composition (glass 3 and 4). In the glass 2 and glass 4, a part of Na_2O (5 mass %) was replaced by Cs_2O.

Table I The chemical composition of the investigated glasses in (mass %).

Sample	SiO_2	B_2O_3	Al_2O_3	CaO	Na_2O	Cs_2O
Glass 1	56.0	15.0	8.0	-	21.0	-
Glass 2	56	15.0	8.0	-	16.0	5.0
Glass 3	48.5	7.5	8.0	18.0	18.0	-
Glass 4	48.5	7.5	8.0	18.0	13.0	5.0

The glasses ware obtained by meting of batch composed of quartz sand, Na, Ca and Cs carbonates, boric acid and aluminum oxide of chemical grade purity. A batch was melted at 1200^0C for 2 hours in an alumina crucible, cooled and crushed in to 0.3 – 0.1 mm grain size.

Hospital waste incineration ash has the composition in mass %: CaO – 39.9, SiO_2 – 22.2, Al_2O_3 – 13.5, Fe_2O_3 – 7.72, SO_3 – 4.52, TiO_2 – 3.02, P_2O_5 – 2.56, Cr_2O_3 – 0.89, ZnO – 0.68, Na_2O – 0.61, BaO – 0.54, NiO – 0.36, Cl – 0.24, K_2O – 0.13, CuO – 0.13, MnO – 0.11.

Glass transformation and crystallization was measured by differential scanning calorimetry (DSC) method. Measurements were carried out using Perkin Elmer DTA/DSC – 7 heat flow differential scanning calorimeter. Pure Al and Au were used for temperature and heat calibration. The transformation temperature Tg, was measured at the half of the specific heat capacity change step, registered on DSC curve. Value of specific heat capacity change ΔC_p ($J \cdot g^{-1} K^{-1}$), accompanying glass transformation, was calculated using Perkin Elmer Pyris Thermal Analysis Software Library program.

Phase composition of samples were investigated by x-ray diffractometry (XRD) using DRON 1.5 apparatus and Cu K radiation. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were applied also in the study. Glass and glass-ash mixture samples heat treated at characteristic temperatures, indicated by DSC curves were subject of investigations.

RESULTS

Influence of Cs and CaO on borosilicate glass properties

The obtained investigation results have shown that the introduction of relatively small amount of Cs_2O (5 % mass) instead of Na_2O induces considerable changes in the structure and the thermochemical properties of boroaluminosilicate $Na_2O – B_2O_3 – Al_2O_3 – SiO_2$ glass.

FTIR spectrum of $Na_2O – B_2O_3 – Al_2O_3 – SiO_2$ glass is characterized by an intensive band of Si – O – Si bridges of silicate network at 1000 cm^{-1}, 729 cm^{-1}, and a band 1407 cm^{-1} of [BO_3] groups which occur in its structure. The band connected with the cation modifier Na^+ occurs at 458.8 cm^{-1}. Introduction of Cs_2O causes the shifting of the main band to 1017cm^{-1} and the glass modifiers band to 455.9 cm^{-1}. It means that the presence of Cs^+ influence on the degree of polymerization of the network.

Introduction of Ca into the glass causes the appearance besides the Si-O-Si band (1021 cm^{-1}) the band at 946 cm^{-1}, which is characteristic for silicate and aluminate glasses, containing calcium [8] and it indicates the formation in the network   domains containing this element; in the similar way there may be

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interpreted the shifting of the band [BO_3] to 1422 cm^{-1}. The band connected with the cation modifiers becomes also shifted to 471 cm^{-1}.

Hence the presence of Cs_2O, even in the amount of 5 mass % instead of Na_2O causes the modification of the glass structure. It is stronger when simultaneously Cs_2O and CaO are introduced; which is observed as the shifting of the band Si-O-Si toward higher values from 1000 cm^{-1} (glass 1) to 1021 cm^{-1} (glass 4).

The effect of additions to the $Na_2O - B_2O_3 - Al_2O_3 - SiO_2$ glass on its thermochemical properties is demonstrated by the DSC measurements (Fig. 1). The glass shows a broad double effect on the plateau above the transformation step, which is indication of the low degree of chemical homogeneity of the glass structure. Just behind there appears a poor effect of crystallization. CaO does not change T_g, but it increases the change of the specific heat capacity ΔC_p accompanying the glass transformation, the value of which can be the index of the structural changes accompanying the transformation (number and force of the broken bonds, components rearrangement) [9] Cs_2O increases T_g of the glass and ΔC_p of transformation. ΔC_p of reference glass 1 increases from 0.718 J·g^{-1}K^{-1} to 0.875 J·g^{-1}K^{-1} for Cs_2O containing glass 2. The temperature of the DSC crystallization peak increases from 690^{0}C to 715^{0}C. The presence of Cs_2O in glass containing Ca increases T_g but diminishes ΔC_p of the transformation. ΔC_p of glass 3 and glass 4 containing CaO have properly values 0.718 J·g^{-1}K^{-1} and 0.875 J·g^{-1}K^{-1}. In general, replacement of a part of Na by Cs, especially together with introduction of Ca, increases the thermal stability of the primary glass structure, which is in agreement with its modification indicated by the changes in FTIR spectra.
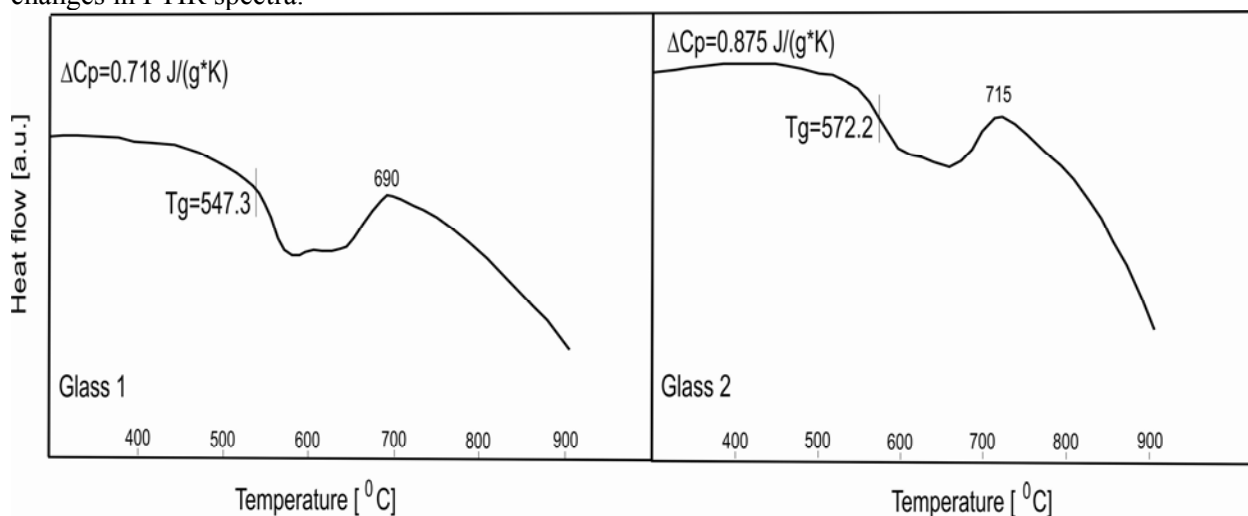

Fig. 1 DTA curves of glasses 1 and 2.

Moreover introduction of Ca^{2+} increases the glass tendency for crystallization above the temperature of transformation Tg. As the first, at 690^{0}C, i.e. at the stage of glass softening, the ring silicate $Na_4Ca_4[Si_6O_{18}]$ (columbeite) is formed and at 780^{0}C the wollastonite $CaSiO_3$ crystallizes. Introduction of Cs_2O changes the course of crystallization, which becomes a single stage crystallization; then pollucite $Cs[AlSi_2O_6]$ with wollastonite crystallize.

In calcium –free reference glass (Table I, glass 1) there crystallizes the high temperature variety of quartz stabilized by Al and Na admixtures and nepheline $Na[AlSiO_4]$. The presence of Cs_2O increases the temperature of crystallization and increases its intensity.

SEM investigations and EDS spectra have confirmed the results of XRD studies. According to EDS in the reference calcium – free glass (glass 1), Cs is incorporated as an admixture into the structure of the

newly formed crystal phases (high quartz, and nepheline). In CaO containing glass Cs is localized in wollastonite and pollucite structure.

Observations of the behavior of glass samples in a heating microscope show that the introduction of Cs_2O into the glass, instead of the part of Na_2O, increases a little its softening as well as the melting temperature, whereas it reduces the flow temperature, which means faster depolimerization of the network resulting in the drop of the molten glass viscosity at high temperatures. The presence of CaO makes flowing interval longer. It is the effect of the stiffening of the primary structure of the glass at the low. Crystallochemical parameters of Ca^{2+} (r_{Ca} = 1.00 Å, CN=6, i_g=0.707) causes that it forms more covalent less flexible bonds with Si^{4+} through the oxygen bridge than Na^+ and Cs^+. It means that oxide bridges in the glass structure becomes more rigid but at the same time more susceptible to break what gives network de-polymerization effect at high temperatures. Diminishing of viscosity visible as flowing of sample, is the result of this.

 Cesium leachability was determined by dissolving the glass samples of grain size 0.315 – 0.500 mm in deionized water at 98^0C per 60 min. The leachate was analyzed by ASA method. The results (Table II) indicate that Ca in the composition of Na borosilicate glass increases significantly leaching of Cs. It corresponds to an increase of diffusion coefficient of Cs from $2.55 \cdot 10^{-10}$ to $1.34 \cdot 10^{-9}$ cm^2/s in the presence of Ca (glass 4). Na diffusion coefficient is a little higher than Cs ($6.99 \cdot 10^{-11}$ and $7.19 \cdot 10^{-9}$ cm^2/s) and its leachability is higher as well. Diffusion coefficients were obtained using MD simulation with parameters described in [10,11].

Table II The leachability of selected components [$mg/1000cm^3$]

Sample	Na	Ca	Cs
Glass 1	75.8	-	-
Glass 2	5.35	-	13.1
Glass 3	80.9	38.2	-
Glass 4	59.3	33.0	78.2

Encapsulation of ash in borosilicate glass

Phase transitions and ash-glass component exchange during ash encapsulation have been studied. The studies were aimed at fixing of the minimal encapsulation temperature needed to initiate immobilization of Cs, which is present in the ash and become wash out-resistant.

The ash used in the tests was a product of burning of hospital wastes in a fluidal oven. Cs_2O (5% by weight) was added to the ash what stimulated the presence of the radioactive [137]Cs.

EDS analysis has proved that calcium silicates Ca_2SiO_4 and wollastonite are the main components of the ash. They are accompanied by calcium aluminate $Ca_3Al_2O_6$. Presence of the Al_2FeSi_2 was also observed. Dissipated graphite particles occur too, what indicates for reductive condition in the burning chamber.

Ash and glass were powdered down to the grain size of 0.063 mm. Then a mixture comprising 30% by weight of ash and 70% by weight of glass were prepared. Then the mixture was homogenized and activated for 2 hours being milled in attritor ball mill. Then the mixture was pelletized and heated at various temperatures per 3 hours in order to achieve sintering effect.

DTA curve (Fig. 2) of the prepared mixture indicate for exothermic reaction at about 470^0C caused by coal combustion and oxidation of reduced Fe and Si components. Broad endothermic effect caused by the glass melting is observed over Tg of the glass accounting for about 600^0. In temperature of about 750^0C it transits into exothermic effect of the reaction between glass and ash components causing formation of new compounds. Further temperature increase results in softening of the mixture, which is transformed gradually into partially re-crystallized melt.
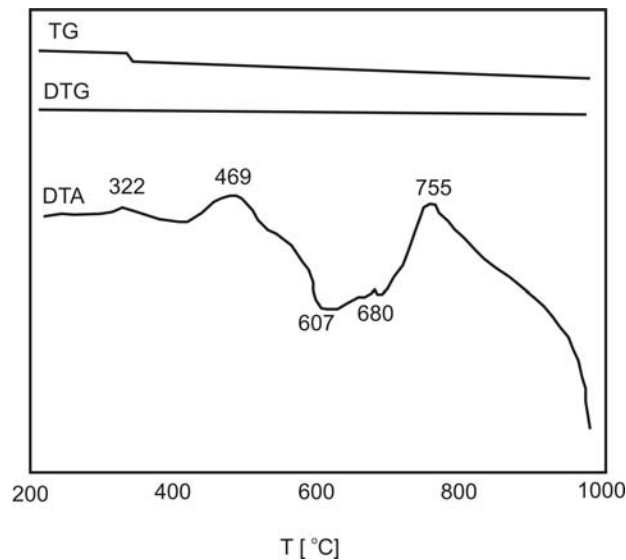
Fig. 2 DTA curve of the glass-ash mixture

Changes observed in the glass-ash mixture were monitored with use of SEM and EDS (Fig. 3, 4) method. Sinter composed of aggregates having diameter of several micrometers surrounded with the glass is formed at the temperature of 750^0. At higher temperature they are transformed into the glass with dispersed aggregates of the diameter lower than 1 m, which are relicts of sintered ash aggregates. Well-developed crystalline forms formed during the melt crystallization are also observed.

The XRD indicates that sintered glass-ash aggregates formed at the temperature of 750^0C are built of network silicates: albite - $Na[AlSi_3O_8]$, labradorite - $(Ca_{0.6}Na_{0.4})[Al_{1.6}Si_{2.4}O_8$] and anorthite - $Ca[Al_2Si_2O_8]$. Boron occur in form of sodium borosilicate – reedmergerite $NaBSi_3O_8$. Chemical composition and structure of theses phases indicate that they were formed in result of the exchange of the components between ash and glass grains via their diffusion. Network structure of plagioclases, which are the first crystallization products correspond in a considerable degree to the aluminosilicxate glass structure. From ash components only wollastonite was preserved. With the temperature increase, amount of Ca reach plagioclases is reduced in the aggregates, and amount of the wollastonite is reduced. Albite is the most resistant. Cs is kept in aggregates of the aluminosilicates. In surrounding glass matrix it appears when the aggregate is melted. Almost total reduction of the aggregates containing Ca is observed over the temperature of 800^0C and sodium aluminosilicates crystallize from the melt (nepheline $Na[AlSiO_4]$, melilities $CaNa)_2Al[(Al,Si)_2O_7]$). Remainders of albite and wollastinite are preserved. Boron crystallizes as reedmergerite.

Phase composition have influence onto Cs washout by water. Content of Cs dissolved in water in the room temperature is considerable as long as the ash aggregates are preserved. It drops to zero with their decay. However, total remelting of the sample is not necessary for Cs immobilization. Sintering of the pellets in temperature of $950\text{-}1000^0$ is sufficient. Temperature and sintering time depend on amount of Ca in the sinter.

Fe present in the ash expresses different behavior. Together with calcium it forms borates, which crystallize in form of prismatic crystals, which are hardly dissolved in the glass. However, presence of Cs in them has not been proved.
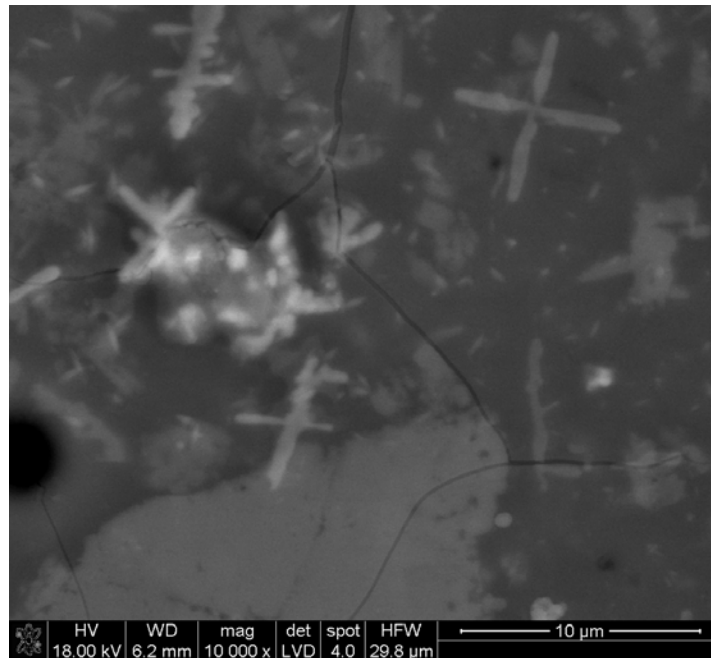
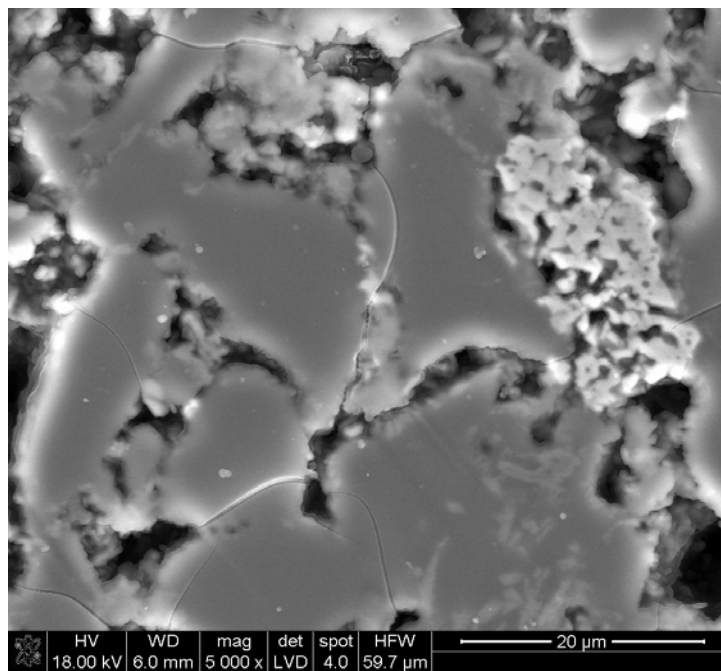**Fig. 3 SEM Ca borosilicates crystallization in glass- ash mixture, heat treated at 790^0C**

Fig. 4 SEM of glass-ash mixture heat treated at 750^0C.

CONCLUSIONS

Encapsulataion of the hospital incineration ash with 5 wt.% Cs_2O admixture was studied. Heat treated glass and 30 wt.% of ash mixtures revealed that the process starts about 600^0C as sintering of glass and ash particles. Exchange of their components by diffusion takes place. Ca is incorporated into the glass, Na and B are diffusing from glass into ash.

About 750^0C chemically homogeneous sinter is formed. It is recrystallizing and material composed of microcrystalline aggregates surrounded by glassy matrix appears. The aggregates contain plagioclase feldspars (albite, bytownite and adesine) wollastonite and Na borosilicate reedmergerite. Cesium persists in the aggregates as component of aluminosilicates.

Aggregates are dissolving successively in molten glass. At the same time new generation of Ca borates and silicates crystallizes locally from Ca saturated melt. Chlorine from ash is preserved in as NaCl crystals, visible even in the samples heat treated at 1050^0C

Introduction of Cs into the basic glass $Na_2O – B_2O_3 – Al_2O_3 – SiO_2$ (waste glass) in order to immobilize its radioactive isotope, induces changes in the structure and in the properties of the glass. This results from considerable crystallochemical differences between Cs^+ and Na^+ as the glass structure modifiers. In the presence of even a relatively small amount of Cs_2O (5 mass %) substituting 5% Na_2O the stability of glass structure increases, which means, simultaneously the increase of the chemical durability of the glass. On the other hand above glass transformation temperature (Tg), cesium acts as the strong depolymeriser of network, increasing the tendency for crystallization of the glass. It becomes incorporated into the structure of the newly formed crystal phases such as the chemically resistant aluminosilicates (plagioclase feldspars, nepheline). A significant changes are induced by the introduction of CaO into the glass. It is diminishing chemical durability of borosilicate glass limiting the suitability of the borosilicate glass to inactivate the contamination. Crystallization of the glass, transforming it into glass-ceramic increases the chemical durability and reduces leaching of contaminants.

According to results presented above two procedures of combustion ash encapsulation in sodium borosilicate glass (waste glass) are possible: a. sintering of glass and ash mixture at temperature of softening of glass and formation of sinters composed of microcrystalline chemical resistant aluminosilicates and brosilicates and b. traditional remelting of glass and ash mixture. Due to inconvenient diminishing of chemical durability of glass by Ca, the content of ash in encapsulated mixture must be exactly adjusted to the chemical composition of ash.

ACKNOWLEDGMENTS

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