Increase of the radiation-chemical resistance of glasses for radioactive waste immobilization

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Increase of the radiation-chemical resistance of glasses for radioactive waste immobilization: Matrix glass composition for a possible immobilization of radioactive waste is selected. Borosilicate glass is low-alkali and relatively low-melting. It has a sufficiently high initial chemical resistance. To improve radiation chemical resistance was used such additives: oxides of cerium, iron, and manganese. After irradiation by γ-quantum's (Co^{60}) with high-dose exposure, samples were tested for chemical resistance against water action. Experiments demonstrated the effectiveness of such additives.

Keywords: radionuclides, γ-rays, immobilization, glass matrix, radiation chemical resistance

INTRODUCTION

Nowadays it is quite common to bury radioactive wastes all over the world. The most ideal variant of matter for this purpose are glass and glass-ceramic, because they are practically pore-free and have relatively high radiation and chemical resistance. Priority takes borosilicate glass. It is an excellent waste solvent, easily produced and acceptable thermal, mechanical, physical characteristics are present. Primarily, one of the most important criterion in the development of composition for radioactive waste immobilization is chemical durability during groundwater action, which leads to glass surface leaching.

The interaction of high energy radiation results in breaking bonds within the glass material, leading to the formation of free electrons and holes [1,2]. Electrons and holes are trapped by existing defect in the glass structure [3]. This new formation “defect-electron (hole)” is characterized by low energy. Thus, they are able to re-absorb radiation. As a consequence, electron becomes excited and moves into a higher energy state [4]. Similar effect of the radiation is observed in the case of ion which valences are variable, for example Ce^{+3}, Fe^{+2}, Mn^{+2} and etc. In low oxidation state they are capable to capture holes and in high oxidation state – to capture energy electrons.

EXPEREMENTAL PART

Chemically pure reagents used for the batch preparation for the synthesis of assigned glass composition. Batch consisted of the following components: amorphous silica – SiO_2; boric acid – H_3BO_3; soda – Na_2CO_3; potash – K_2CO_3; chalk – $CaCO_3$. And pure oxides: barium – BaO; magnesium – MgO; zinc – ZnO. The components are weighted accurate within 0,1 gram, then chopped in a porcelain mortar and sifted through a sieve with mesh size of 0,5 mm. The matrix glass composition shown in Table 1.

Table 1 – The matrix glass composition

Component	Na_2O	K_2O	MgO	CaO	BaO	ZnO	B_2O_3	SiO_2
Contents, mass %	6	6	2	2	2	30	15	37

Additives were input in the amount of 2 % (in excess of 100 % for matrix glass). Such additives were: Ce_2O_3, FeO, MnO, Ce_2O_3+FeO.

Fireclay sagger used for glass melting. Samples were boiled at a temperature 1200°C during 2 hours inside the silit-furnace.

The obtained samples were irradiated on the Cobalt unit with absorbed doses D_1 = 5,3 MRad and D_2 = 11,8 MRad (isotope - Co^{60}, energy of one gamma-quantum E = 1,25 MeV). For all glasses, after the action of radiation appears centers of color, which visually can be detect. The samples were tested for chemical resistance, and its change under irradiation.

RESULTS AND DISCUSSION

The obtained solutions after glass leaching were tested by two different quantitative method of analysis:

1) Atomic-absorption analysis
2) Standard testing method for chemical resistance (titration by 0,01N HCl)

In the case of the first method, investigated concentration of ions Na^+, passed into solution during leaching, for non-irradiated samples and samples with absorbed dose 5,3 MRad. The analysis was carried out by the atomic-absorption spectrometer Perkin Elmer AAnalyst 300 with graphite furnace TGA-800. The results of the analysis are illustrated in the histogram in fig. 1.

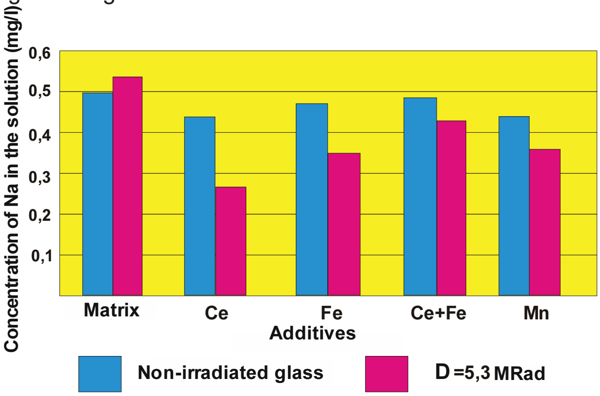

Fig. 1. The results of atomic-absorption analysis on ions Na^+, passed into solution during leaching, for non-irradiated samples and samples with absorbed dose 5,3 MRad

From the fig. 1, it follows that the amount of sodium, passed into solution, for all glasses, except the matrix, decreases after irradiation. Especially, such effect is significant for glass contained cerium oxide. Only for the matrix glass the amount of Na^+, passed into solution, increases under the action of radiation.

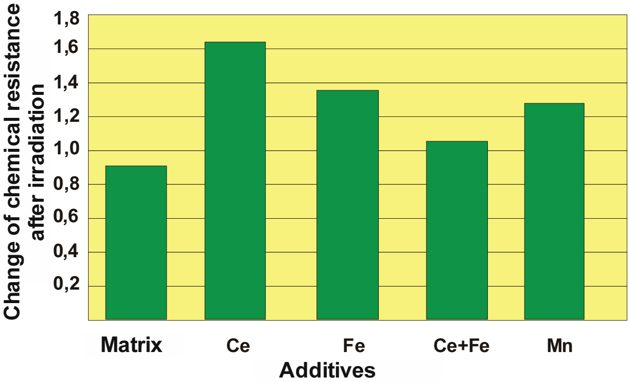

Fig. 2. Change of chemical resistance under irradiation relative to non-irradiated samples

Above-mentioned data's clearly illustrated in fig. 2. It presents the relative change in the chemical resistance of the samples after irradiation.

From the obtained data's, it can be logically assumed, that chemical resistance for all samples, except matrix glass, increasing after irradiation. However, the results by titration method of analysis, illustrated in fig. 3, indicates - it's not.

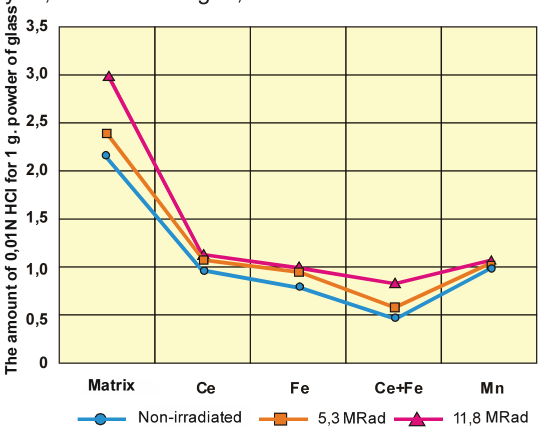

Fig. 3. Results by titration method 0,01N HCl

The chemical resistance of all samples decreases after irradiation. It's known, that in the case of titration by hydrochloric acid, determines all alkali and alkaline earth elements presents into solution, while atomic-absorption analysis, in our case, capture only one element – sodium. So, although atomic-absorption method indicates the amount of sodium, passed into solution during leaching, decreases, but the amount of other alkali and alkaline earth elements increases. In fact, it can be potassium, barium, calcium, magnesium (and maybe even zinc).

From the fig. 3, it follows that additives really increase chemical resistance of the matrix composition and reduces loss of chemical resistance under irradiation. Thus, we have improved not just chemical resistance, but radiation-chemical resistance of matrix glass composition.

CONCLUSIONS

We can conclude, the radiation-chemical resistance for glasses with the presence of different ions which valances are variable, more than without its presence, average in 3 times and even 6 times for glass contained combination of cerium and iron oxides. Such glass better for radioactive waste immobilization, than matrix glass, which selected as ready composition for burying radioactive waste. The best sample can be considered glass with presence combination of cerium and iron oxides. But, due to that it quickly lose its chemical resistance under irradiation, the best sample can be considered glass contained manganese oxide. It is cheap component and lose its chemical resistance under the action of radiation not significant at all.

It is worth noting, within this paper we have not extensively investigated the aspects of reducing the amount of sodium, passed into solution during leaching, under irradiation and mechanism of above-mentioned process. Also, there was not fully studying the composition of the liquid on the quantitative evaluation of other elements, for example: potassium, barium, calcium, magnesium and zinc.

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This paper has been reviewed