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Influence of Na-Al-Fe-P glass alteration in hot non-saturated vapor on leaching of vitrified radioactive wastes in water

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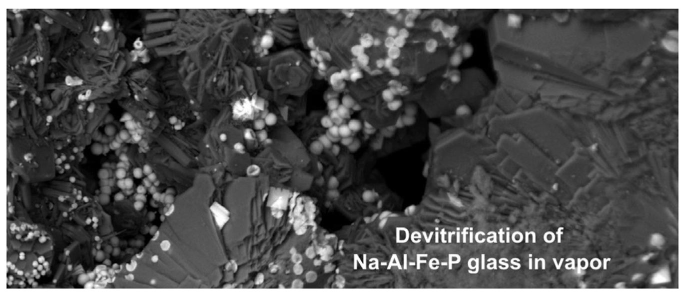
HIGHLIGHTS

- Heating in vapor leads to fast devitrification of Na-Al-Fe glass.
- Devitrification of the glass increases rate of its corrosion in water by two orders.
- Actinide simulators in water after interaction with devitrified glass are in colloidal form.

GRAPHICAL ABSTRACT



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ABSTRACT

Influence of preliminary heating in vapor on leaching of Na-Al-P-glass in water is investigated. The glass simulates industrial waste forms for solidification of high level liquid radioactive wastes used in Russia. Heating up to 300 °C in unsaturated vapor leads to transformation (devitrification) of pristine glass into four separate crystalline phases. The alteration takes place in whole volume of the monolithic glass sample. Experiments on leaching of altered and pristine glass in water are carried out. A ratio of estimated leaching rates of the altered and pristine glass can exceed two orders of magnitude. Fractions of radionuclide simulators in colloid of different size in leaching products are determined.

1. Introduction

Depletion of carbohydrates resources and restriction on greenhouse gases production place a limitation on development of power generation on the basis of fossil fuel firing. Renewable energy sources are not able to cover growing demand for electric power for the time being. Therefore, nuclear power plants as a source of electricity will remain necessary for relatively long time [1]. This is inevitably associated with solution of a problem of radioactive waste management. The most important part of the problem is caused by liquid high-level radioactive waste (HLW) derived at spent nuclear fuel processing. The liquid HLW are represented by highly radioactive strong acid or alkaline aqueous solution. Comprehensive analysis of the problem showed that the most

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effective solution at state-of-the-art capability is disposal of solidified HLW in underground repositories [2]. Solidification is carried out through incorporation of liquid HLW (sometimes after calcination) into a vitreous waste form such as B-Si-glass (France, U.K, U.S.) or Na-Al-P-glass in Russia [3–6].

Amount of vitrified HLW in Russia increased significantly with time (Fig. 1). In 2008, a preliminary decision was made to develop an underground repository in the Krasnoyarsk region (Siberia) for final disposal of radioactive waste including vitrified HLW [6,7]. It is expected that underground galleries of the repository with the disposed waste will be filled by groundwater through hundreds years after they will be loaded with solidified HLW and ultimately closed. Therefore chemical stability of the waste form at interaction with the groundwater is of great importance for prevention of radionuclides leaching and release into environment.

Experimental studies of Na-Al-P-glass leaching in aqueous solutions at different temperatures have demonstrated acceptable chemical stability of the waste form at thermal and geochemical conditions of underground disposal [8–12]. Samples of Na-Al-P-glass in these experiments were amorphous, however heating of the vitrified waste can lead to a partial crystallization of the glass [9,11,12]. A substantial heating of vitrified waste can take place during their storage in a temporary repository for 50 years until their heat generation rate decreases to an appropriate level [5,10]. Crystallization of the vitrified HLW can significantly accelerate its leaching by water.

Heating of Na-Al-P-glass in dry air up to 400 °C did not lead to any crystallization [9]. However experiments on borosilicate glasses of different composition showed that heating even up to 200 °C in saturated and sub-saturated water vapor ("vapor hydration test") led to a noticeable alteration of glass surface [13–18]. Consequent experimental studies of glass leaching in water showed that previous vapor hydration can exert a substantial influence on leaching rate. This was a reason to assume that heating of Na-Al-P-glass in a humid air below 400 °C can also lead to some alteration of the glass in contrast to its heating in dry air what can cause substantial changes in glass dissolution rate at its consequent leaching in water. An experimental examination of this assumption is the first objective of this study.

The main way of radionuclides migration in underground medium is their transport by groundwater. Radionuclides can be carried by the groundwater in dissolved form, as ions, or with colloidal particles (suspended particle of a size of 1–1000 nm). System of colloidal particles with substantial content of radionuclides is called radiocolloid. It can be referred to one of three groups according to its origin: intrinsic colloid, primary colloid and pseudocolloid [19,20]. The intrinsic colloids consist of particles composed to a significant extent of oxyhydroxides of radionuclides. The primary colloid represents colloid particles composed of leaching products of solid HLW. Pseudocolloid consists of colloid particles that existed in the groundwater before the contact with radioactive substances, and as a result of such interaction sorbs radionuclides.

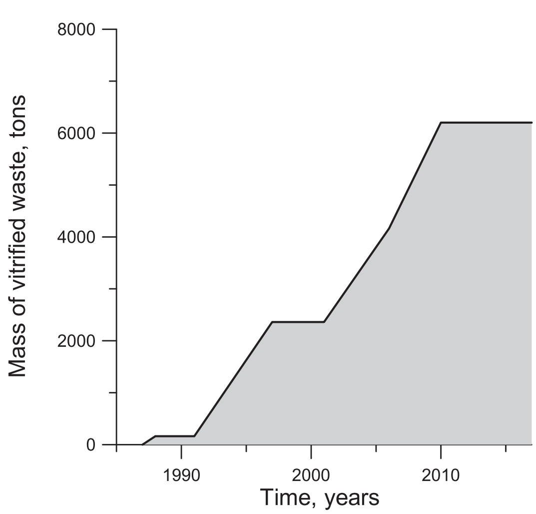

Fig. 1. Accumulation of quantity of vitrified HLW in Russia [6].

Velocity of spread of radioactive pollution depends on mobility of radionuclides in the groundwater. Field observations at sites of severe radioactive pollution evidence that mobility of radionuclides in groundwater in colloidal form can be much higher than in the form of ions [21–23]. As it follows from theoretical analysis, this can be caused by low sorption properties of rocks to radiocolloid particles [24,25]. As it follows from the existing classification, leaching of vitrified HLW can produce primary colloid. Since the colloidal form of radionuclides transport is the most mobile and, therefore, the most hazardous from ecological point of view, it is worthwhile to estimate ingress of radionuclides in the form of primary colloid into groundwater at leaching of Na-Al-P-glass taking into account the possibility of its alteration due to vapor hydration. This is the second objective of the study.

2. Experimental. Materials and procedure

Samples of Na-Al-Fe-P-glass for studies of vapor hydration were manufactured in an electric furnace at 1200 °C. Their composition (wt%): Na_2O (17.3), Al_2O_3 (14.0), P_2O_5 (51.1), Fe_2O_3 (5.5), NiO (1.1), SrO (2.1), Cs_2O (2.5), Ce_2O_3 (2.1), Nd_2O_3 (2.0), UO_3 (2.3) was close to vitreous waste form produced at Industrial Complex "Mayak" (Russia, South Urals) at solidification of liquid HLW. Experiments on vapor hydration of the Na-Al-P-glass were carried out in a titanium autoclave for 24 h. It was put in a thermostatically controlled chamber at a specified temperature. With this experiment completed, the autoclave was quenched. Specified vapor pressure was provided for through addition of calculated volume of deionized water into the autoclave before its closure. Samples in a form of monoliths were hanged by a titanium wire in the autoclave to avoid a contact with water at initial stage of heating and with hot condensate at quenching. A blank test was carried out with a glass sample in dry air at same temperature (300 °C).

Consequent experiments on leaching of Na-Al-Fe-P-glass were carried out in deionized water in the titanium autoclave with a teflon insert at a temperature of 90 °C. Such value was selected for following reasons. At first, it is assumed that temperatures in the underground repository for vitrified HLW in Krasnoyarsk region will not exceed this value. At second, leaching rate increases with temperature [8,9,11,12]. Therefore, data of such leaching experiment correspond to the worst case and can be used in conservative safety assessments of the mined underground repository of vitrified HLW.

Experiments on the simulated waste form were carried out with renewal of water in 1, 3, 10, and 30 days to reveal how leaching rate depends on time. Autoclave after each stage was cooled in flowing water opened. Solution from the autoclave was poured into germetic vessels and kept at 4 °C till ultrafiltration. Concentrations of elements in water after its interaction with the waste form during each of these time intervals was measured by inductively coupled plasma mass spectrometry (ICP MS). Experiments were carried out on samples of the altered glass after previous vapor hydration and pristine glass. Since concentration of comprising elements in the waste form are known their concentration in the water can characterize mass of the waste form which is leached from its unit surface per unit time. It can be estimated by formula