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Low-temperature immobilization of actinides and other components of high-level waste in magnesium potassium phosphate matrices

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A B S T R A C T

The magnesium potassium phosphate (MPP) matrices formed by the room-temperature reaction of MgO and KH_2PO_4 solution were used for immobilization of simulated liquid alkaline high-level waste (HLW) containing actinides, fission and corrosion products. Novel procedures of solidification of HLW simulants were developed to increase stability of the MPP matrices to leaching radionuclides (Pu, Np, Am, Cs, Sr, Tc, I and Se), matrix-forming (K, Mg and PO_4) and admixture components (NO_3, NO_2, Na and others) as well as hazardous elements (Pb, Cr, Zn and others) according to the ANS, PCT, TCLP standards. Density (~1.7 g/cm^3), compressive strength (>20 MPa), radiation resistance of the matrices and chemical yield of radiolytic hydrogen (0.004 molecule H_2/100 eV) were determined. The phase composition of the matrices and distribution of radionuclides were studied by XRD and autoradiography correspondingly.

1. Introduction

The use of nuclear energy resulted in accumulation of huge amounts of liquid HLW containing environmentally hazardous elements like plutonium and other actinides as well as fission and corrosion products. Therefore it is very important to choose optimum methods and matrices for immobilization of such waste. The present technology of solidification of HLW by vitrification does not ensure complete immobilization of radionuclides because of low hydrothermal stability of glass [1,2]. As an alternative the incorporation of radionuclides into crystalline phases that are analogs to natural minerals and having high radiation and chemical stability (e.g., pyrochlore, zircon, and zirconolite) is considered as an alternative way for vitrification [3–5]. Various methods were proposed for preparation of mineral-like matrices, e.g., cold pressing and sintering [6], hot pressing [7] or induction melting in cold crucible [8].

Crystalline magnesium potassium phosphates which are analogs to natural phosphate minerals (having great physicochemical stability in geological medium [9]) could be used as host matrices for HLW immobilization. Phosphates are extremely insoluble [10] in groundwater and this would ensure their good isolating properties. The compound is formed under ambient conditions (room temperature) as a result of exothermic acid–base reaction between MgO and KH_2PO_4 [11]. The reaction is governed by

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O.$$

Therefore aqueous HLW could be directly tempered by introduction of binding agents. The process is characterized by low-power inputs, simplicity of realization and mobility of the solidification process as well as minimization of secondary radioactive waste. Compared to cementation there are perceptible advantages: possibility of solidification of liquid wastes within the wide range of pH, high loading capacity towards HLW components [12]. During the last years interest in the use of binding phosphate materials has risen. The scientists of ANL (USA) offered the use the phosphate materials (Ceramicrete) for immobilization of low-level and technetium-containing simulant waste solutions [13,14] as well as for incorporation of Pu-containing ash [15], in Khlopin Radium Institute (Russia) and INEEL (USA) possibility of incorporating of simulant of low-level ash remainder of combustible radioactive waste into iron phosphate matrices was studied [16].

This paper presents the results obtained on immobilization of liquid HLW simulants into MPP matrices. Special attention was given to the study of chemical stability of the matrices under conditions of different temperatures and leachants as major criteria of applicability for environmentally safe HLW disposal.

2. Experimental procedure

The chemical and radionuclide compositions of liquid HLW simulants that were used for incorporation to MPP matrixes are presented in Table 1. The H-1 and M-1 solutions correspond to the

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Table 1
Chemical and radionuclide compositions of HLW simulants.

Waste simulator	H-1	H-2	M-1	M-2
Density, g/cm^3	1.43	1.31	1.28	1.17
Solids, g/L (wt%)	745 (52)	498 (38)	450 (35)	183 (16)
Content of main components in waste simulator, g/L				
NO_3^-	167.6	264.6	99	82.6
NO_2^-	113.1	0.3	38	
Na^+	256.0	85.1	295.5	24.0
OH^-	83.7	43.7	90.5	
CO_3^{2-}	12.5	19.3		
Fe^{3+}		33.4		10.3
Al^{3+}	39.7	16.3	8.0	
Cl^-	9.2	0.2	6.0	
Cs^+	0.02	0.06		
Sr^{2+}	0.3	16.1		15.7
SO_4^{2-}	0.3	1.9	13	24.2
Cr	CrO_4^{2-} – 2.9	Cr^{3+} – 0.24	CrO_4^{2-} – 7	Cr^{3+} – 0.25
Pb^{2+}	0.07	0.01		
Cd^{2+}	0.003	5.0		
K^+	7.4	0.2		13.6
Zn^{2+}	0.01	0.1		
Ni^{2+}		2.4		2.4
Zr^{4+}		5.0		
Ce^{3+}	0.9	8.2		
Specific activity of nuclides, Bq/L				
^{239}Pu	1.2×10^8	3.5×10^8		
^{237}Np	1.2×10^8	2.4×10^6		$\sum\alpha$ – 1.3×10^5
^{241}Am		8.0×10^8		
^{90}Sr	2.1×10^7	5.1×10^8	1.5×10^6	
^{137}Cs	2.4×10^7	1.2×10^7	5.8×10^{10}	
^{99}Tc	6.3×10^8	1.9×10^9		
I	^{131}I – 1.1×10^7		^{129}I – 2.3×10^6	
^{75}Se	2.7×10^6			

supernatants from HLW repositories of Hanford (USA) and PA 'Mayak' (Russia) and H-2 and M-2 solutions correspond to sludges from the same sites. Earlier [17] it was established that neutralization of simulated alkaline supernatants and introduction of chemicals converting Tc, I, Cs, Se into their poorly soluble forms into HLW are required for enhancement of efficiency of immobilization of wastes. Concise description of the technique of synthesis of MPP matrices are presented below.

The experiments were carried out in a glove box equipped with exhaust. To the desired pH 8–9 the H_3PO_4 solution upon stirring was gradually added to the initial simulated supernatants H-1 and M-1. For separation of I^- anions (and partly Tc) AV-17 resin in a Cl^- form (3.5 wt%) was introduced into the mixture, that was then stirred for 24 h. For precipitation of Cs (and as well as Sr) $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.5 wt%) and $NiSO_4 \cdot 7H_2O$ (0.35 wt%) were introduced, and the mixture was stirred for 15 min. After that $Na_2S \cdot 9H_2O$ (2.1 wt%) was added followed by stirring of the mixture to stabilize some elements in low-valence states (e.g., Tc(IV), Cr(III)). The mixture obtained was solidified by addition of KH_2PO_4 followed by MgO (components in stoichiometric ratio, e.g., H-1 (mL)/KH_2PO_4 (g)/MgO (g) = 2:3:1) upon continuous stirring. Analogous procedures except preliminary neutralization and AV-17 introduction were carried out for solidification of simulated sludges.

Chemical resistance of synthesized MPP matrices was determined according to the immersion test ANS 16.1 [18] on leaching with distilled water at 25 °C. Determination of radionuclides content in the leachates was performed by the methods of radiometry (α- and γ-spectrometers 'Canberra') and of liquid-scintillation spectrometry (GreenStar). The values obtained were used for calculation [19] of 'effective diffusivity', D (cm^2/s) (Eq. (1)) and leachability indexes, Li (Eq. (2))

$$D = \pi \left[\frac{a_n/A_0}{(\Delta t)_n}\right]^2 \left[\frac{V}{S}\right]^2 T, \tag{1}$$

$$\mathrm{Li} = \frac{1}{10}\sum_1^{10}\left[\log\left(\frac{1}{D}\right)\right]_n, \tag{2}$$

where V is the sample volume, cm^3; S is the geometric surface of the sample, cm^2; $T = [0.5(t_n^{1/2} + t_{n-1}^{1/2})]^2$ is the 'mean time' of the leaching, s; a_n is the activity of the nuclide passed into the solution during leaching time interval 'n' (corrected, taking into account radioactive decay); Σa_n is the cumulative activity of the radionuclide passed into the solutions as a result of leaching; A_0 is the total activity of given nuclide in washing water after 30 s washing before the beginning of the first leaching; $\Sigma(\Delta t)_n = t_n = t$ is the total leaching time, beginning from the first leaching, s; $(\Delta t)_n = t_n - t_{n-1}$ is the duration of leaching interval 'n', s.

Leaching resistance of MPP matrices was determined in accordance with TCLP [20] requirements and analysis was performed by the ICP method (spectrometer 'Jarrel-Ash Division ICAP 9000'). Chemical durability of the matrix towards leaching of the main components (K^+, Mg^{2+} and PO_4^{3-}) was determined at 90 °C according to PCT [21], the results were used for a calculation of normalized leaching rate NR [g/(m^2 day)]

$$NR = \frac{i \cdot V}{S \cdot f \cdot d}, \tag{3}$$

where i is the concentration of the element or ion in the leachant, g/L; V is the volume of leaching water, L; S is the surface area of the crushed sample, m^2; f is the fraction of species in waste form; d is the leaching time, days. Specific surface area of the crushed MPP matrices (H-1 – 4.9; H-2 – 7.1; M-1 – 15.3; M-2 – 17.4 m^2/g) was determined by the BET method [22] (adsorbate – Ar).

X-ray diffraction of the matrices was done using diffractometer 'Dron-4-13' using Co Kα radiation. Mathematical treatment, pictorial representation of the results and substance identification were realized by using complex program TRFA containing card index JCPDS (PDF-2). Radiation resistance of MPP matrices was determined after irradiation on CPU-90 facility with ^{60}Co source (the dose rate 160 rad/s, total absorbed dose 2.8×10^8 rad). In order to determine distribution of radionuclides over the matrices volume the method of autoradiography was used. There were specially prepared MPP matrices with the individual nuclides (specific activity ~1000 Bq); the polished samples were placed on Retina XBM film and exposure during 4–11 days.

For the study of radiolytic hydrogen release, MPP matrix (24.7 g) containing 1.1 wt% of ^{239}Pu (^{241}Am admixture was 0.1 wt% of ^{239}Pu quantity) was prepared. Gases and volatile constituents released during solidification and curing of the matrix were analyzed on gas–liquid chromatograph (carrier gas – He) within 4 weeks. At that two types of chromatographic columns – with Porapac-Q and with molecular sieves having pore size of 5 Å – were used, and the analysis was performed at column temperatures 25 and 80 °C. The released gas phase was additionally analyzed by IR-spectrometry using Specord-M 80.

3. Results and discussion

As a result of the performed experiments, homogeneous MPP matrices with density of 1.6–1.8 g/cm^3 and with compressive strength about 30 MPa (standard cement compound strength ⩾5 MPa [23]) were prepared (Table 2). It was established that increase of the matrices volumes up to 200 L (Fig. 1) did not result in noticeable change of these physical parameters. It was shown that the matrices obtained were radiation-resistant as their mechanical strength and X-ray diffraction patterns did not change after irradiation. No considerable change in the parameters determined by

Table 2
Physical properties of MPP matrices produced by solidification of HLW simulants.

Properties	H-1	H-2	M-1	M-2
Volume, L	0.03–1	0.03–1	0.03–20	0.03–200
Density, g/cm^3	1.6–1.7	1.7–1.8	1.8	1.8
Waste loading, wt%	35	44	43	34
Compressive strength, MPa	25–55	40–55	>20	>20

Fig. 1. MPP matrix obtained by solidification of M-2 (PA Mayak, Russia).

standards leaching procedures (Table 3) for the matrices with different volumes was revealed.

The obtained results according to ANS, PCT and TCLP (Table 3) allowed drawing the conclusions:

- MPP matrices are able to strongly retain actinides Pu, Np, Am (ANS: Li 13–14) not only by solidification of LLW [11–13], but also liquid highly saline HLW;
- the matrices achieved high resistance towards Cs leaching (ANS: Li 11.4–13.0; for concrete Li ~9 in Ref. [24]), that indicated to potentialities of immobilization of Cs, Sr-fraction of HLW after spent nuclear fuel reprocessing;
- it was established the possibility of low-temperature immobilization of waste containing volatile radionuclides (Li 9–11 for Tc and I) and contaminants;
- the results obtained on hydrothermal resistance of MPP matrices according to PCT indicate low leaching rate for all components of the matrices (NR of sodium for borosilicate glass JHCM 2.7×10^{-2} g/(m^2 day) in Ref. [25]);
- comparison of the results obtained according to standard TCLP testing with UTS limits [26] indicated that the MPP matrices are capable to fix hazardous contaminants rather strongly.

It was shown that initial MPP matrix material was identified as hexahydrate of potassium magnesium phosphate [27] (Fig. 2). Increase of salt content in the waste effected the phase composition of the matrix material: new phases which probably are hydrated nitrates were formed. Analysis of the diffraction patterns revealed lattice distortion of the initial matrix material on solidification of the solution with high content of sodium. This phenomenon may due to the formation of crystal phase of $Na_xK_{1-x}MgPO_4 \cdot nH_2O$ (where $0 < x \leqslant 1$) having variable composition with isovalent potassium–sodium substitution.

Table 3
Chemical stability of MPP matrices found according to standard procedures.

Components	H-1	H-2	M-1	M-2
ANS 16.1 (90 days, distilled water, 25 °C, monolith sample)				
Leachability index				
^{237}Np	12.8	13.6		
^{239}Pu	13.5	14.4		$\sum\alpha$ – 12.9
^{241}Am		14.6		
^{90}Sr	10.9	13.2	11.1	
^{137}Cs	11.4	11.5	13.0	
^{99}Tc	9.9	10.0		
^{131}I	11.2		7.9	
^{75}Se	9.6			
PCT (7 days, distilled water, 90 °C, particles size 100–200 mesh)				
Normalized leaching rate, g/(m^2 day)				
Mg	4.1×10^{-6}	7.1×10^{-7}	6.6×10^{-5}	1.6×10^{-5}
K	1.9×10^{-2}	1.1×10^{-2}	2.4×10^{-2}	2.4×10^{-2}
PO_4	6.3×10^{-3}	1.8×10^{-3}	7.2×10^{-3}	9.5×10^{-3}
Na	1.7×10^{-2}	9.3×10^{-3}	2.4×10^{-2}	2.1×10^{-2}
NO_3	3.1×10^{-2}	1.9×10^{-2}	3.8×10^{-2}	2.6×10^{-2}
Ce	6.6×10^{-6}	1.2×10^{-6}		
Cs	7.3×10^{-4}	$<1.1 \times 10^{-4}$		
Sr	2.2×10^{-4}	$<2.0 \times 10^{-6}$		
Zn	$<1.2 \times 10^{-2}$	$<4.5 \times 10^{-4}$		
Cr	8.5×10^{-5}	4.2×10^{-5}		
Ni	7.0×10^{-5}	2.6×10^{-6}		
Cd	1.8×10^{-3}	2.5×10^{-7}		
Pb	7.3×10^{-4}	1.1×10^{-3}		
TCLP (24 h, agitation, extraction fluid no. 1, particles size <1 cm, in brackets – UTS limits)				
Content of hazardous contaminants in leachates, ppm				
Cs	<0.05	<0.05		
Sr		0.05	0.07	8.0
Ce		<0.06		
Pb (0.75)	0.005	0.004		
Cr (0.6)	0.04	0.006	0.2	0.08
Se (5.7)	0.01			
Cd (0.11)	0.001	0.008		
Zn (4.3)	0.05	0.1		
Cu	0.006	0.02		
Co	0.001	0.001		
Ni (11)		<0.1	0.5	0.7

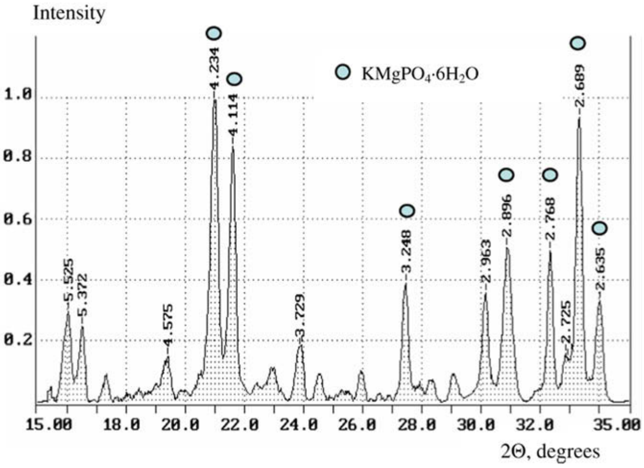

Fig. 2. X-ray diffraction pattern of MPP matrix.

Radionuclide distribution over the volume of the MPP matrices was different, and it depended not only on the radionuclide but also on a type of solidificated waste. After solidification of H-1 plutonium was concentrated in separate randomly distributed inclusions; in the matrices containing H-2 plutonium was uniformly distributed over the matrix volume, what is explained by co-precipitation of iron and plutonium hydroxides. It was established that distribution of technetium and iodine in the samples unambiguously corresponds with distribution of anionite granules (Fig. 3). Only small part of selenium was distributed over the volume, its basic quantity was mainly in the form of inclusions.

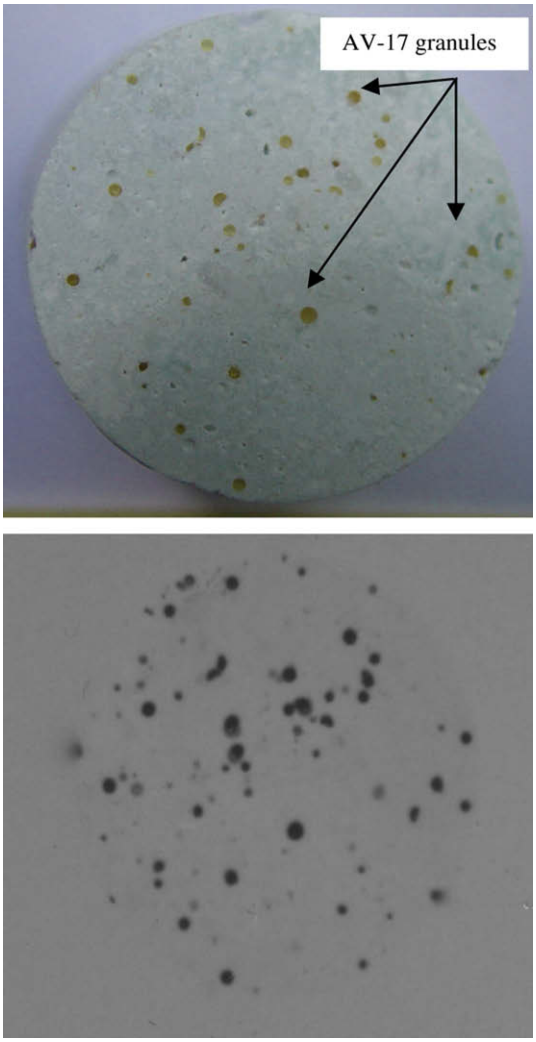

Fig. 3. Photograph (left) and autoradiograph (right) of MPP matrix prepared as a result of solidification of HLW simulant H-1 containing technetium and iodine.

Distribution of cesium and strontium in the MPP matrices obtained was uniform.

It was established that upon solidifying of HLW simulants composition of gas phase (O_2 – 21, N_2 – 78, CO_2 – 0.2, H_2O – 0.8 vol.%) corresponded to ambient air. After storing of MPP matrix containing 1.1 wt% of ^{239}Pu during 4 weeks (radiation absorbed dose 5.0×10^8 rad) release of radiolytic hydrogen was revealed: chemical yield 4.2×10^{-3} H_2 molecule/100 eV.

Thus the results of this investigation along with advantages of low-thermal method of preparation of MPP matrices gave demonstration of availability of the use of such materials for immobilization of constituents of actual liquid saline radioactive waste including HLW of radiochemical plants.

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