

# CESIUM IMMOBILIZATION INTO POTASSIUM MAGNESIUM PHOSPHATE MATRIX

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The possibility of isomorphous substitution of potassium ions by cesium ions in the structure of potassium magnesium phosphate  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  (PMP) was shown. It was established, that the Cs included into the PMP matrix does not transfer to the environment during high temperatures heating process (1176 °C, 3 hours). Analysis of the IR absorption spectrum of the PMP sample has demonstrated that an increase in the amount of additive of the cesium chloride resulted in the shift of the main bands in the spectrum to the low-frequency region with average shift value  $10 \text{ cm}^{-1}$ , which indicates the strengthening of bonds in the crystal lattice of matter. The calculated degree of substitution of potassium by cesium during energy release process in the PMP matrix at the level of vitrified high level wastes is about 4%, i. e. the PMP matrix should correspond to the formula  $\text{K}_{0.96}\text{Cs}_{0.04}\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ .

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## INTRODUCTION

In the process of water cooled nuclear power reactors operations, a large number of liquid radioactive waste are formed, and their activity, despite of low concentration, is determined by  $^{134,137}\text{Cs}$  and  $^{60}\text{Co}$  radionuclides [1].

High-temperature methods of radioactive waste (RAW) treatment, including vitrification, can provide the formation of environmentally stable solid products. However, in the process of high-temperature manufacturing of such products, volatile cesium can partially transfer into the gas phase. It is known that such process has began from heating temperature about 575 °C and almost completely cesium passes into the gas phase at 900 °C [2].

Therefore, the search and development of solid materials formed at low temperatures and provided a high safety barrier for cesium fixing are environmentally justified.

Furthermore, it should be taken into account that the main parameter characterizing the quality of solidified wastes is thermal stability. According to the requirements of standard GOST, solidified wastes should possess specific properties provided no changes in structure and chemical composition at temperatures up to 550 °C [3].

In addition, there is a risk of a fire in the underground radioactive waste storage and the temperature can increase to higher values. For example, two fire incidents took place in 2014 at a pilot plant for the isolation of waste (USA), which resulted in contamination of an underground ventilation system by plutonium [4]. According to such risks, it is necessary to carry out research on the heat resistance of materials of RAW matrices over a wide range of temperatures.

The aim of this study was investigation of synthesis of cesium-containing potassium magnesium phosphates and their thermal stability under high temperatures heating conditions.

## MATERIAL AND METHODS

The heat treatment of samples of potassium magnesium phosphate (PMP) was carried out in a high temperature furnace Nabertherm P310 (Germany) in air.

The phase composition of the material before and after heat treatment was investigated by X-ray diffraction methods (DRON-1.5, Cu  $K_\alpha$  with nickel filter for reduction of  $K_\beta$  component of the characteristic radiation) and infrared (IR) spectroscopy (IR spectrophotometer IKS-29 (LOMO)). Samples for the IR spectra recording were prepared in the form of transparent compressed tablets of mixture of KBr as the matrix and the tested substance (in the amount of 1%, weighed 100 mg). Spectra were recorded in the spectral range  $4000 \dots 400 \text{ cm}^{-1}$  (middle infrared area).

To determine the processes that occur during heating of the powders, differential-thermal analysis (DTA) by means of thermal analyzer SDT Q600 V20.9 Build 20 in the temperature range  $20 \dots 1300 \text{ °C}$  at a heating rate of  $10 \text{ °C/min}$  was made.

Elemental analysis of the PMP samples with the addition of 10 wt.% CsCl was carried out on a laser mass-spectrometer EMAL-2 with a high-resolution and two-focus by Mattauch-Herzog. The random error of the analysis results is characterized by the value of the relative standard deviation of 0.1–0.3.

## RESULTS AND DISCUSSION

### SYNTHESIS OF POTASSIUM MAGNESIUM PHOSPHATE

For the synthesis of potassium magnesium phosphate  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ , the following reagents were used:

- magnesium oxide  $\text{MgO}$ ;
- potassium dihydrogen phosphate  $\text{KH}_2\text{PO}_4$ ;
- distilled water ( $\text{pH} = 5.5$ ).

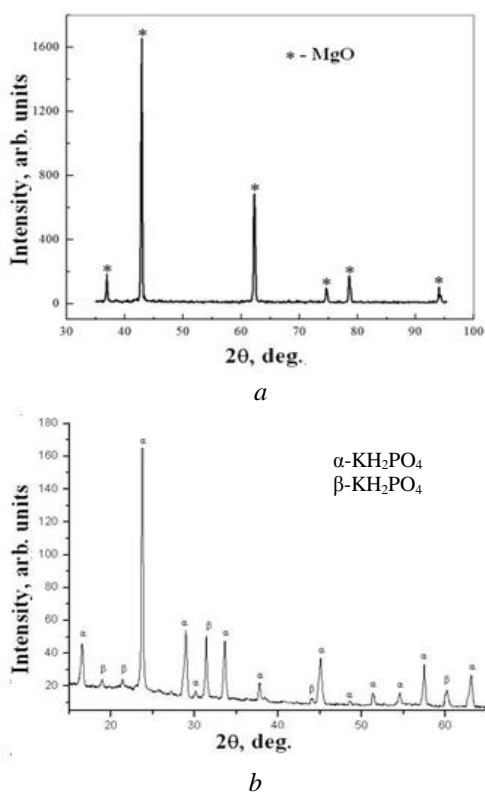
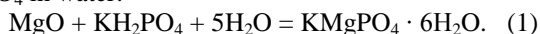


Fig. 1. X-ray diffraction patterns of initial components of PMP samples: a – MgO, heat treated at 1300 °C during 1 hour; b – KH<sub>2</sub>PO<sub>4</sub>

PMP samples were obtained under normal conditions (atmospheric pressure, room temperature) as a result of the acid-base reaction between MgO and KH<sub>2</sub>PO<sub>4</sub> in water:



To reduce the rate of reaction of magnesium oxide with potassium dihydrogen phosphate, the MgO powder was heat treated at 1300 °C for 1 hour in air. The magnesium oxide obtained after heat treatment is characterized by a strongly pronounced periclase structure (Fig. 1,a). The diffractogram of the second component, potassium dihydrogenphosphate, is shown in Fig. 1,b. It can be seen that along with the main phase of KH<sub>2</sub>PO<sub>4</sub> (pH = 4.46), a certain amount of the concomitant less reactive phase of K<sub>2</sub>HPO<sub>4</sub> is also presented and characterized by higher pH values

In the case of synthesis of cesium-containing PMP samples, cesium chloride CsCl was used as a starting reagent.

X-ray phase analysis (XRD) of the obtained PMP samples revealed that the x-ray lines are corresponded to the crystalline hexahydrate of potassium and magnesium double orthophosphate KMgPO<sub>4</sub> · 6H<sub>2</sub>O (ASTM 35-0812) (Fig. 2,a). The density of the obtained PMP samples is 1.7...1.8 g/cm<sup>3</sup>.

The behavior of the PMP samples under heating process was determined using DTA/TG analysis (Fig. 4,a). It was found that the endothermic peak at a temperature of 120 °C corresponds to the dehydration of potassium-magnesium phosphate according to the following reaction [5]:

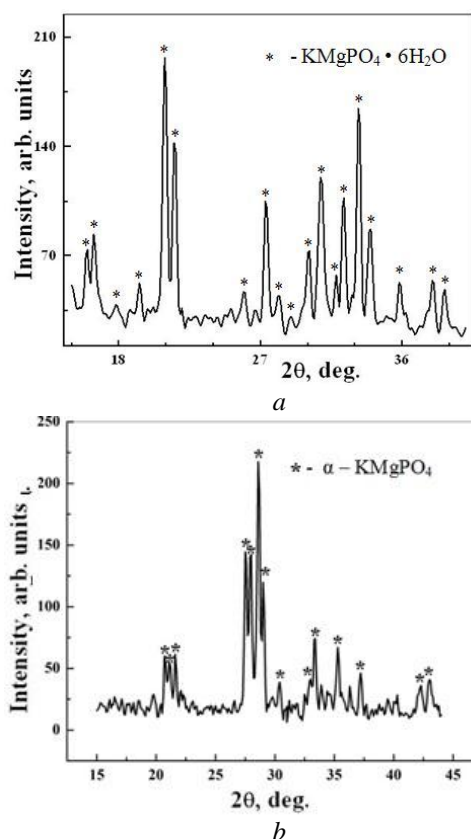


Fig. 2. X-ray diffraction patterns of PMP samples: a – without heat treatment; b – heat treated at  $T = 1300$  °C,  $\tau = 45$  min

This process is confirmed by a weight loss (~ 40%) on the TG curve, which corresponds to a decrease in the stoichiometric amount of bound water. A small exothermic peak near 400 °C seems to correspond to the reversible  $\alpha$ -KMgPO<sub>4</sub> →  $\beta$ -KMgPO<sub>4</sub> phase transition detected by the authors [6] during heat treatment of K-struvite single crystals of MgKPO<sub>4</sub> · 6H<sub>2</sub>O at a temperature of 362 °C.

After heat treatment of the PMP samples at a temperature of 1300 °C for 45 min, the lines of dehydrated potassium-magnesium phosphate phase  $\alpha$ -KMgPO<sub>4</sub> are observed (see Fig. 2,b). These data are in good agreement with the data of XRD analysis of synthesized anhydrous phosphate KMgPO<sub>4</sub> with the addition of Eu [7].

### CESIUM-CONTAINING POTASSIUM MAGNESIUM PHOSPHATE MATRIX

To carry out experiments on the incorporation of cesium into the PMP matrix, weighed samples of the initial reagents were used for the following reactions:

- 10 wt.% CsCl + 90 wt.% (MgO + KH<sub>2</sub>PO<sub>4</sub>);
- 15 wt.% CsCl + 85 wt.% (MgO + KH<sub>2</sub>PO<sub>4</sub>).

From the data of XRD analysis of PMP samples with cesium, it can be seen that the obtained material is identified as potassium-magnesium orthophosphate, which in general form can be represented as K<sub>1-x</sub>Cs<sub>x</sub>MgPO<sub>4</sub> · 6H<sub>2</sub>O (Fig. 3). In addition, lines of magnesium chloride phosphate Mg<sub>2</sub>PO<sub>4</sub>Cl were observed on the diffractograms. It can be seen that with an increase in cesium content (from 0 to 10% by weight

CsCl and up to 15% by weight CsCl), a small shift of the main X-ray lines  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  toward smaller angles occurs (see Figs. 2,a; 3,a,b). This is typical for the case of substitution of atoms of material by other atoms with large ionic radii. In our case, the potassium atoms are replaced by cesium atoms. As can be seen from Tabl. 1, the replacement of alkali ions is accompanied by insignificant changes in lattice parameters, while the crystal structure remains unchanged.

Table 1

Lattice parameters of PMP and PMP +10 wt.% CsCl samples

Composition	Lattice parameters		
	a	b	c
$\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ [8]	6.903	6.174	11.146
$\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$	7.6178	6.8512	12.2876
$\text{K}_{1-x}\text{Cs}_x\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$	7.646	6.8748	12.2575

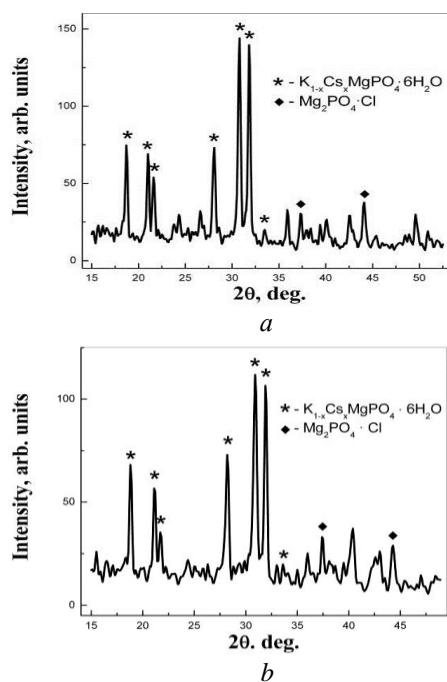


Fig. 3. X-ray diffraction patterns of samples: a – PMP+10 wt.% CsCl; b – PMP+15 wt.% CsCl

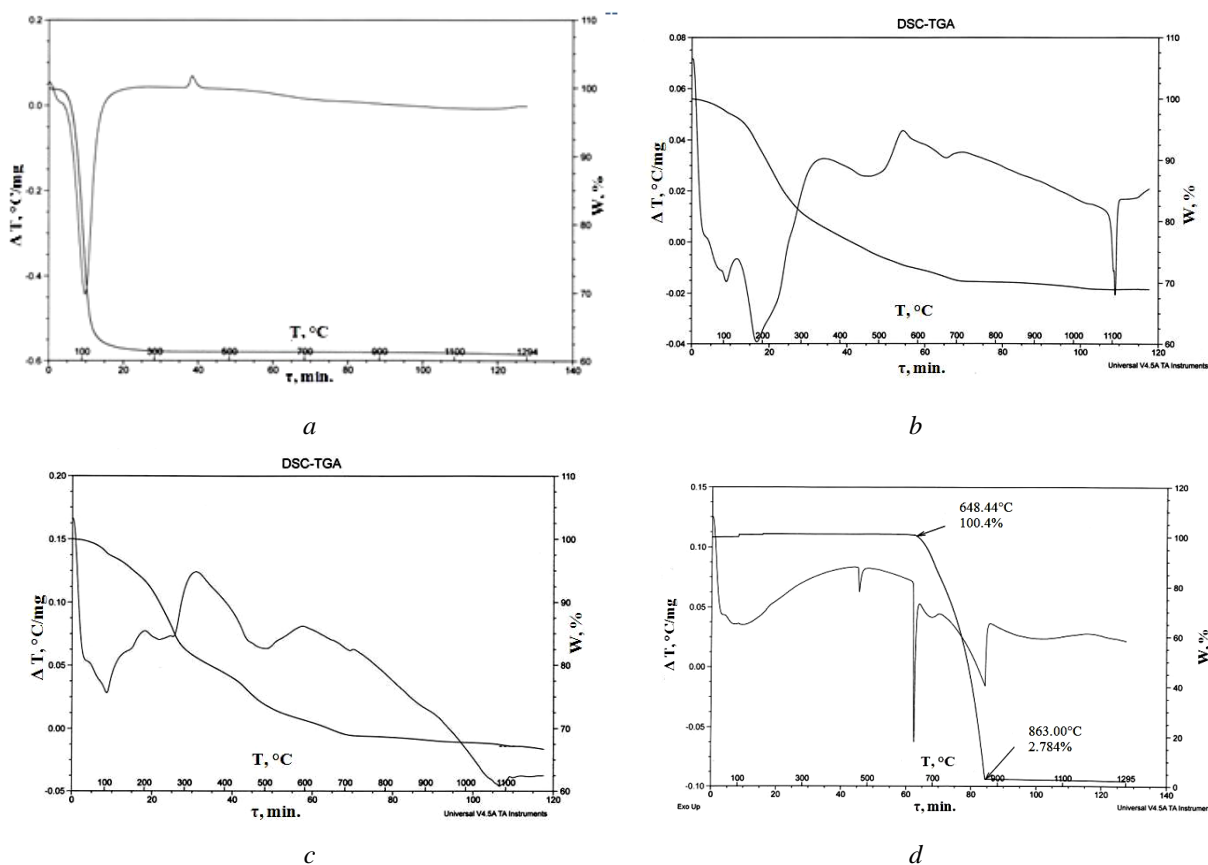


Fig. 4. DTA/TG analysis of samples: a – PMP; b – MP + 10 wt.% CsCl; c – PMP + 15 wt.% CsCl; d – CsCl

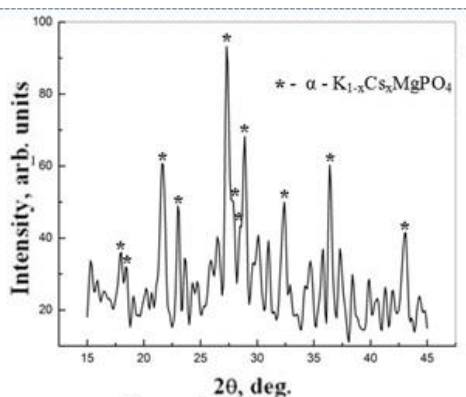


Fig. 5. X-ray diffraction patterns of PMP+10 wt.% CsCl sample after heat treatment at  $T = 1050\text{ }^{\circ}\text{C}$ ,  $\tau = 2.5\text{ hours}$

To determine the behavior of cesium-containing potassium-magnesium phosphates during heating process DTA/TG analysis of PMP + 10 wt.% CsCl and PMP + 15 wt.% CsCl was made. The DTA/TG analysis data (see Fig. 4,b,c) show no weight loss of PMP samples with cesium during heating process up to 1200 °C. The exception is the weight loss associated with the removal of water in the temperature range 0...700 °C. Above 700 °C the weight of the samples remains practically unchanged; while CsCl completely evaporates in the temperature range 648...863 °C (see Fig. 4,d). This process indicates that the potassium magnesium phosphate matrix can reliably retain cesium during the temperature increase up to 1200 °C. Endothermic peaks at temperatures of 1106 °C (see Fig. 4,b) and 1080 °C (see Fig. 4,c) are probably caused by the melting of the sample material without loss of their weight.

Analysis of the diffractogram of the PMP sample + 10 wt.% CsCl after treatment at a temperature of 1050 °C showed that the lines of anhydrous phosphate  $\text{K}_{1-x}\text{Cs}_x\text{MgPO}_4$  (Fig. 5) are expanded under the action of high temperature.

Heat treatment of PMP samples with cesium of 2...3 g weight were made in air at temperatures of 700, 1050, and 1176 °C with different holding times: 1, 2.5, and 3 hours, respectively. Samples were placed in boats

made from  $\text{Al}_2\text{O}_3$ . The carried out experiments have shown that weight loss was about 27...28% after heat treatment at 700 °C. The results are well corresponded to the removal of crystallization water. With a further increase in temperature up to 1150 °C, weight loss of the samples was about 1%. Near this temperature, the process of samples material melting took place. Appearance of the sample PMP + 10 wt.% CsCl in the boat after heat treatment at 1176 °C and holding time 3 hours is shown in Fig. 6.

Elemental analysis of PMP samples with the addition of 10 wt.% CsCl was performed using an EMAL-2 laser mass spectrometer. The results of elemental analysis of PMP + 10 wt.% CsCl are presented in Tabl. 2. From the table data, it can be concluded that with increasing of the processing temperature the amount of cesium in the PMP samples remains practically unchanged. It should be noted that the cesium content in the PMP sample also remains almost the same after heat treatment at 1176 °C and the holding time 3 hours. These conditions are corresponded to the sample melting process.

The paper presents the results of research on cesium immobilization in a chemically stable matrix based on potassium-magnesium phosphate. In other words, Cs can be included in the crystal structure of struvite-K using acid-base reaction-synthesis of PMP at room temperature. The addition of cesium chloride during the reaction leads to changes in the unit cell size of the resulting phosphates, and confirms the partial replacement of potassium by cesium. The PMP samples have kept the rhombic crystalline structure during this process. The resulted PMP matrix is heat-resistant and Cs doesn't transfer to environment even after high temperatures heating.

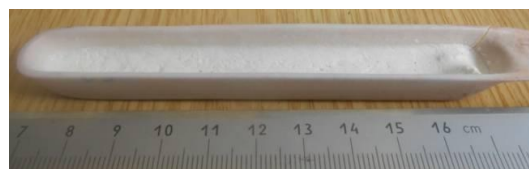


Fig. 6. Molten sample of PMP + 10 wt.% CsCl after heat treatment 1176 °C and holding time 3 hours

Table 2

Elemental analysis of PMP +10 wt.% CsCl samples after heat treatment process

Temperature and time of heat treatment process	Content of elements, wt. %										
	K	Mg	P	O	Cs	Cl	Na	Al	Si	Ca	S
700 °C, 1 hour	9.9	24.1	14.6	30.8	10.27	5.9	3.5	0.02	0.17	0.07	0.67
1050 °C, 2.5 hours	7.15	25.5	21.1	32.3	10.3	0.03	2.43	0.36	0.12	0.12	0.59
1176 °C, 3 hours	17.04	22.5	14.7	30.4	10.75	0.03	3.33	0.83	0.18	0.09	0.15

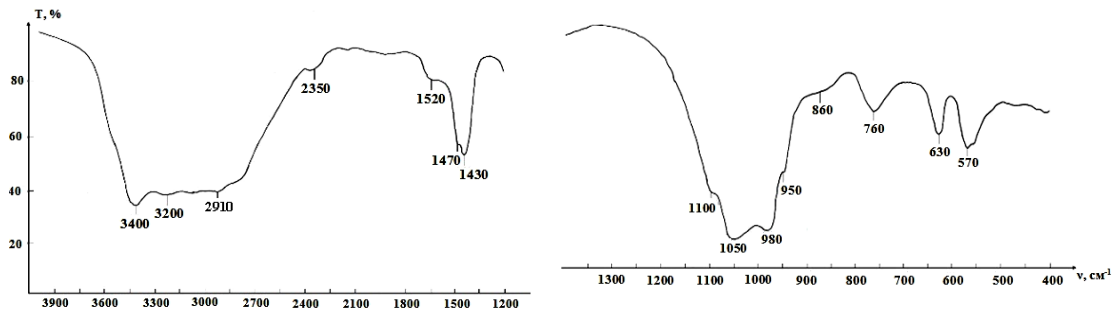


Fig. 7. IR absorption spectrum of PMP sample

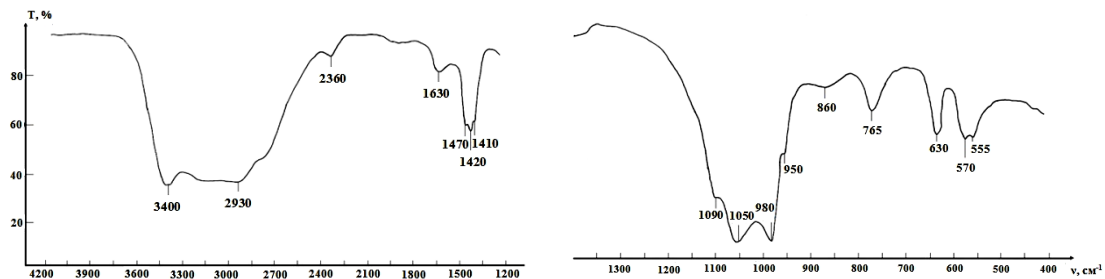


Fig. 8. IR absorption spectrum of sample with PMP + 10 wt.% CsCl composition

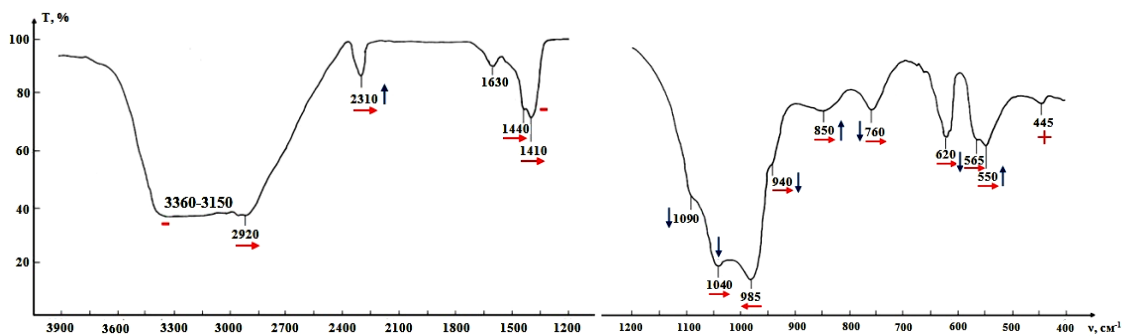


Fig. 9. IR absorption spectrum of sample with PMP + 15 wt.% CsCl composition

### IR SPECTROSCOPY OF THE POTASSIUM MAGNESIUM PHOSPHATE MATRIX

Analysis of the IR absorption spectrum of the PMP sample showed that the main bands of the IR spectrum correspond to potassium magnesium phosphate  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ : 570, 630, 760, and 1050  $\text{cm}^{-1}$  [9] (Fig. 7) in a good agreement with XRD data (see Fig. 2,a). However, bands of other compounds are also present in the spectrum:

1. The doublet of 1430 and 1470 and the strong band of 3400  $\text{cm}^{-1}$  are probably caused by the formation of magnesite ( $\text{MgCO}_3$ ), since this frequency range is characteristic for vibrations of the complex anion of  $\text{CO}_3$  and OH groups in the structure of this mineral [10]. The formation of carbonate phases containing  $\text{CO}_3^{2-}$  ions can be caused by the absorption of atmospheric carbon dioxide during the synthesis and storage of PMP samples.

2. The band 860 and the band 950, 980, 1100  $\text{cm}^{-1}$  are caused by the vibrations of  $\text{P}(\text{OH})_2$  and the complex  $\text{PO}_2$  ion in the phosphate structure, which may be products of incomplete synthesis.

According to the IR spectrum the phase composition of the PMP sample + 10 wt.% CsCl, is the same as for the PMP sample without the addition of CsCl, since all the bands in the spectrum are coincided (Fig. 8). The difference lies in the fact that the intensity of all the bands corresponding to phosphate phases has increased substantially, and the maxima have become narrower and more precise. Such changes in the spectrum are associated with a higher degree of crystallinity of this sample. The data on XRD analysis of PMP samples without additives and with the addition of CsCl also demonstrate the increase in crystallinity (see Figs. 2,a; 3). The bands corresponding to the carbonate phase (magnesite) retained the same shape and intensity.

The overall view of the IR spectrum of the PMP + 15 wt.% CsCl sample (Fig. 9) is, in general, similar to the spectrum of the sample with the addition of 10 wt.% CsCl (see Fig. 8). However, it is necessary to note the following differences:

1. The main bands corresponding to the  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  phase (565, 620, 760, and  $1040\text{ cm}^{-1}$ ) are shifted to the low-frequency region of the spectrum by  $5\text{--}10\text{ cm}^{-1}$ , and the intensity is slightly reduced. Such a shift of the absorption bands to the low-frequency region can be caused by an increase in the mass of atoms in the process of the isomorphous substitution of a part of the K atoms by the Cs atoms [12].

2. There are significant changes in bands associated with the carbonate phase (magnesite), in the region of  $1400\text{--}1500\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  (see Figs. 8, 9). Instead of a band with a triple maximum ( $1410$ ,  $1430$ , and  $1470\text{ cm}^{-1}$ ), a doublet of bands of the same intensity,  $1440$  and  $1410\text{ cm}^{-1}$ , is formed, which is shifted to the low-frequency region by  $10\text{--}30\text{ cm}^{-1}$ . In addition, the  $3400\text{ cm}^{-1}$  band corresponding to the stretching vibrations of H-O-H in the magnesite structure of  $\text{MgCO}_3$  disappears. These changes may be associated with an increase in the symmetry of the crystal lattice of the carbonate phase, which is caused by a decrease in the water content. In general, it can be noted that with an increase in the amount of the addition of cesium chloride, all the main bands in the spectrum undergo a shift to the low-frequency region by average value about  $10\text{ cm}^{-1}$  (Tabl. 3). This fact indicates the strengthening of bonds in the crystal lattice of material. An exception is the  $1630\text{ cm}^{-1}$  band corresponding to the deformation vibrations of H-O-H, which remains unchanged. The intensity of the band  $1090\text{ cm}^{-1}$  associated with the products of incomplete synthesis is apparently reduced due to a decrease of the products amount. This process is confirmed by the shift of the band  $985\text{ cm}^{-1}$  associated with this phase to the high-frequency region.

#### ENERGY RELEASE OF THE POTASSIUM MAGNESIUM PHOSPHATE MATRIX CONTAINED $^{137}\text{Cs}$

To determine the degree of substitution of K for Cs from the point of view of the permissible heating limit of the PMP matrix for the immobilization of cesium, the following calculations were made. During the process of the radioactive cesium inclusion into the potassium magnesium phosphate matrix, problems will be arisen due to the heating of the obtained material and associated with the radioactive decay of cesium. There will be necessary to organize the heat removal from canisters with HLW during their storage. To estimate the degree of heating of the PMP matrix during the immobilization of cesium, calculations were made of the specific energy release at the maximum degree of substitution of potassium with cesium. For such

calculations, material of composition corresponded to the formula  $\text{CsMgPO}_4 \cdot 6\text{H}_2\text{O}$  was used.

For this purpose, the specific energy release in the PMP matrix was calculated on the basis of the data [13] of the energy parameters of the decay of  $^{137}\text{Cs}$  (half-life 30.17 years) and its  $^{137\text{m}}\text{Ba}$  daughter product (2.55 min), which are given in Tabl. 4. Based on the conception that all potassium is replaced by cesium, and all cesium is represented by the  $^{137}\text{Cs}$  isotope, this value was  $150\text{ W/kg}$ . In the calculations it was assumed that the total energy released by  $\beta$ - and  $\gamma$ -radiation during the decay of one  $^{137}\text{Cs}$  nucleus is about  $0.75\text{ MeV}$  [13], and all this energy is absorbed by the PMP matrix.

However, since the chemical properties of all the isotopes of the same chemical element are the same, during the process of cesium separation from the stillage bottoms by chemical methods, cesium will be obtained as a mixture of isotopes. To estimate the isotope composition of cesium in the stillage bottoms of nuclear power plants, it was assumed that the accumulation of long-lived cesium isotopes during fission of uranium by thermal neutrons is from 6.23 to 6.7% [14]. According to some assumption that the release of cesium from bottoms will be carried out, for example, after 30 years of soaking (during this time, exactly half of the  $^{137}\text{Cs}$  decays and the shorter-lived isotopes decay almost completely), this mixture will have an isotopic composition close to that given in Tabl. 5.

The energy release of  $^{135}\text{Cs}$  was not taken into account for the further calculations, since it is four orders of magnitude lower than  $^{137}\text{Cs}$  energy release. After 30 years removal from the reactor the  $^{137}\text{Cs}$  isotope (see Tabl. 4) will represent only 19% of the total cesium. Based on this fact, the energy release in the PMP matrix with such an isotopic composition will be approximately five times less than in the matrix, in which all the cesium is represented by the radioisotope  $^{137}\text{Cs}$ , and will be  $\sim 28\text{ W/kg}$ . This energy release is several times higher than the energy release in glass containing radioactive waste obtained after chemical processing of spent nuclear fuel (SNF) of power reactors. According to our estimates, which are based on the initial data [15, 16], 30 years after fuel unloading from the reactor, the energy release of vitrified HLW obtained after SNF processing is about  $1.5\text{ W/kg}$ . To reduce the energy release in the PMP matrix to the level of vitrified HLW, according to our calculations, it is necessary to reduce the degree of substitution of potassium by cesium to  $\sim 4\%$ , i. e. the PMP matrix should correspond to the formula  $\text{K}_{0.96}\text{Cs}_{0.04}\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ .

In the case of 10 wt.% substitution of potassium by cesium, the energy release of the PMP matrix is  $\sim 3.6\text{ W/kg}$ , which is almost 2.5 times higher than in vitrified HLW. This fact should be taken into account in the process of the storage organizing and final disposal of PMP matrix with cesium.

Table 3

Bands description in the IR spectra of potassium-magnesium phosphates

IR spectra, cm <sup>-1</sup>			Description of the bands [9–11]
KMgPO <sub>4</sub> ·6H <sub>2</sub> O	KMgPO <sub>4</sub> ·6H <sub>2</sub> O + 10 wt.% CsCl	KMgPO <sub>4</sub> ·6H <sub>2</sub> O + 15 wt.% CsCl	
570	555 570	445, 550 565	deformation vibrations in the phosphate structure M-O (M-metal)
630	630	620	
760	765	760	
860	860	850	stretching vibrations of P(OH) <sub>2</sub>
950 980 1050 1100	950 980 1050 1090	940 985 1040 1090	deformation vibrations of P(OH) <sub>2</sub> , stretching asymmetric vibrations of PO <sub>4</sub>
1430 1470	1410 1430 1470	1410 1440	vibrations of C-O in the magnesite structure MgCO <sub>3</sub>
1620	1630	1630	deformation modes of H-O-H
2360	2360	2310	stretching vibrations of H-O-H in KMgPO <sub>4</sub> ·6H <sub>2</sub> O structure
2910, 3210	2930	2920	
3400	3400	3360...3150	stretching vibrations of H-O-H in the magnesite structure MgCO <sub>3</sub>

Table 4

The main energy parameters of radionuclide <sup>137</sup>Cs decay and its daughter product <sup>137m</sup>Ba [13]

Type of radiation	Decay scheme	Frequency, %	Average energy release, MeV	Integral of energy release, MeV
β-particles	<sup>137</sup> Cs → <sup>137</sup> Ba	5.64	0.41626	0.023477
	<sup>137</sup> Cs → <sup>137m</sup> Ba	94.36	0.17432	0.164488
γ-quantums	<sup>137m</sup> Ba → <sup>137</sup> Ba	84.99	0.661659	0.562344
Sum of 1 decay:				0.750309

Table 5

The parameters of the cesium isotopes mixture with atomic masses 133, 135, and 137, generated by thermal fission of <sup>235</sup>U, at various time intervals after unloading from the reactor

Isotopes	T <sub>1/2</sub>	Fission yield <sup>235</sup> U, % [14]	Mixture content, %	
			one month after	30 years after
<sup>133</sup> Cs	Stable	6.70	34.4	~ 41
<sup>135</sup> Cs	2.3 · 10 <sup>6</sup> years	6.55	33.6	~ 40
<sup>137</sup> Cs	30.05 years	6.23	32.0	~ 19

## CONCLUSIONS

1. Potassium magnesium phosphate KMgPO<sub>4</sub>·6H<sub>2</sub>O was synthesized as a result of acid-base reaction between MgO and KH<sub>2</sub>PO<sub>4</sub> in water under normal conditions (atmospheric pressure, room temperature).

The evolution of the phase composition of potassium magnesium phosphate under heating to a temperature of 1300 °C has been studied.

2. The results of research on cesium immobilization in a chemically stable matrix based on potassium

magnesium phosphate are presented. The addition of cesium chloride during the reaction leads to changes in the size of the unit cell of the resulting phosphates, and confirms the partial replacement of potassium by cesium. The included into the PMP matrix Cs does not transfer to the environment during high temperature heating process.

3. Analysis of the IR absorption spectrum of the PMP sample showed that the main bands in the IR spectrum are corresponded to potassium magnesium phosphate  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ . With an increase in the amount of the cesium chloride addition, the main bands in the spectrum demonstrate a shift to the low-frequency region with average value about  $10 \text{ cm}^{-1}$ . This fact indicates the strengthening of bonds in the crystal lattice of obtained material and the isomorphous substitution of a part of the K atoms by the Cs atoms.

4. The calculations of the energy release of  $^{137}\text{Cs}$  in the PMP matrix have shown that to reduce the energy release in the PMP matrix to the level of vitrified HLW, the degree of potassium replacement for cesium should be about 4%, i. e. the PMP matrix should correspond to the formula  $\text{K}_{0.96}\text{Cs}_{0.04}\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$

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## ИММОБИЛИЗАЦИЯ ЦЕЗИЯ В КАЛИЙ-МАГНИЙ-ФОСФАТНУЮ МАТРИЦУ

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Показана возможность изоморфного замещения ионов калия в структуре калий-магниевого фосфата  $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$  (КМФ) на ионы цезия. Установлено, что включенный в КМФ-матрицу Cs не выходит в окружающую среду при нагревании до высоких температур ( $1176 \text{ }^\circ\text{C}$ , 3 ч). Анализ ИК-спектра поглощения КМФ-образца показал, что с увеличением количества добавки хлорида цезия основные полосы в спектре испытывают сдвиг в низкочастотную область, величина которого в среднем составляет  $\sim 10 \text{ cm}^{-1}$ , что свидетельствует об усилении связей в кристаллической решетке вещества. Рассчитанная степень замещения



калія на цезій при енерговиділенні в КМФ-матриці на рівні остеклованих високоактивних відходів становить ~4%, т. е. КМФ-матриця повинна відповідати формулі  $K_{0,96}Cs_{0,04}MgPO_4 \cdot 6H_2O$ .

## ІММОБІЛІЗАЦІЯ ЦЕЗІЮ У КАЛІЙ-МАГНІЙ-ФОСФАТНУ МАТРИЦЮ

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Показана можливість ізоморфного заміщення іонів калію в структурі калій-магнієвого фосфату  $KMgPO_4 \cdot 6H_2O$  (КМФ) на іони цезію. Встановлено, що включений в КМФ-матрицю Cs не виходить у навколишнє середовище при нагріванні до високих температур (1176 °С, 3 год). Аналіз ІЧ-спектра поглинання КМФ-зразка показав, що зі збільшенням кількості добавки хлориду цезію основні смуги в спектрі відчувають зрушення в низькочастотну область, величина якої в середньому становить ~ 10  $cm^{-1}$ , що свідчить про посилення зв'язків у кристалічній решітці речовини. Розрахована ступінь заміщення калію на цезій при енерговиділенні в КМФ-матриці на рівні остеклованих високоактивних відходів складає ~ 4%, тобто КМФ-матриця повинна відповідати формулі  $K_{0,96}Cs_{0,04}MgPO_4 \cdot 6H_2O$ .