# SORPTION PROPERTIES OF MAGNESIUM-POTASSIUM PHOSPHATE MATRIX

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Sorption characteristics of fine-dispersed magnesium-potassium phosphate ceramics $KMgPO_4 \cdot 6H_2O$ for immobilization of $^{137}Cs$ was investigated. The Cs specific capacity 2.97 mg/g at pH=4 was detected. The high selectivity of the ion exchange of $KMgPO_4 \cdot 6H_2O$ out of dilute solutions was caused by various values of hydration radii of potassium and cesium. There is change in solution pH in dynamics studies toward higher values, apparently due to leaching of movable potassium out of ceramics. The high chemical and radiation resistance of ceramic are confirmed.

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## 1. INTRODUCTION

The significant amount of radioactive waste had accumulated in the world. Radioactive waste was formed as a result of the operation of nuclear power plants, reprocessing of spent nuclear fuel, using of radioactive sources in science, technology, medicine. Therefore there is necessity of radioactive waste disposal. The total release of radioisotopes into environment from nuclear fuel cycle are $\sim$350 thousand Ci for atmosphere and $\sim$10,000 Ci for hydrosphere on GW of electric power per year. Among the radioactive waste generated during reprocessing, the most widespread are liquid radioactive waste [1,2]. In Ukraine, on the territory of nuclear power plants (except of the Chernobyl NPP) remains about 31 thousand m$^3$ of low-level, 1,786 m$^3$ of intermediate-level and 166 m$^3$ high-level radioactive solid wastes, 12,280 m$^3$ of liquid radioactive wastes [3-5]. As a result of the operation of LWR-1000 1.8 t/year fission products are being produced. During operation LWR-1000 transuranium isotopes are being produced with rate 0.48 t/year. Half-lives of transuranium isotopes much more of half-lives of fission products of uranium. Therefore the activity of transuranium isotopes after 1000 years exceeds activity of fission products of uranium in 10$^5$ times.

The significant amount of highly concentrated salt melt with radioactive waste is kept on nuclear power plants. Salt melt contain considerable quantity isotopes of $^{132,137}Cs$ and $^{90}Sr$. Therefore, processing salt melt by means of sorbents can essentially decrease volumes of keeping of radioactive waste.

Long-term storage of HLW in liquid form is extremely risky, therefore IAEA regulations require to isolation of waste into special materials [6]. In this case, for disposal of spent nuclear fuel is used combined protection. Such protection allowing reliably isolate of waste. One of the components of this protection are materials on based of phosphate systems ($KMgPO_4 \cdot 6H_2O$) that will prevent release of radioactive isotopes into biosphere. The $KMgPO_4 \cdot 6H_2O$ (Ceramicrete) is formed through an acid-base reaction between calcined magnesium oxide (MgO) and potassium hydrogen phosphate ($KH_2PO_4$) in aqueous solution:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O.$$
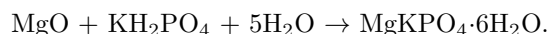
Matrix of magnesium-potassium phosphate is used to form composition of waste which similar concrete. This composition is very stable. $KMgPO_4 \cdot 6H_2O$ is a well-defined analogue of Struvite; where cation $K^+$ replaces the $NH_4^+$ ammonium cation. This ion replacement is possible, as ionic radii $K^+$ and $NH_4^+$ are almost identical.

Possibility of sorption of radioactive waste and, especially, $^{137}Cs$ and $^{90}Sr$, are being researched intensively. Use of Ceramicrete for the immobilization of $^{137}Cs$ and $^{90}Sr$ is economically advantageous as compared with other matrices for of radioactive wastes.

In the present study, we have analyzed an important data set of fine-dispersed magnesium-potassium phosphate ceramics ($KMgPO_4 \cdot 6H_2O$) during ion exchange by using $^{132}Cs$ isotope. We researched selectivity and ion exchange capacity of ceramics towards radiocesium and we established kinetic characteristics of ionite.

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## 2. MATERIALS AND METHODS

The ceramics of $KMgPO_4 \cdot 6H_2O$ was milled in a planetary mill and was in the range about 1 micron. $CsNO_3$ sample (30 mg) was irradiated by bremsstrahlung with $E_{max}$=23 MeV, I=700 mA. The reaction of $^{133}Cs(\gamma,n)^{132}Cs$ was used to activating of cesium. The irradiated sample of $CsNO_3$ was dissolved in 250 ml of distilled water. The crushed samples of $KMgPO_4 \cdot 6H_2O$ (1 g) was placed in solution of $CsNO_3$ (50 ml). Solutions with various pH were researched. Dissolution of $CsNO_3$ and ion exchange were carried out at room temperature. After sorption of cesium by $KMgPO_4 \cdot 6H_2O$ during 29.5 hours the $^{132}Cs$ activity of ionite was measured. The sorption of $^{132}Cs$ was carried out during 315.5 hours. Activity of $^{132}Cs$ was measured by Ge(Li)-detector (volume 50 cm$^3$ and energy resolution of 3.2 keV at 1333 keV line).

## 3. RESULTS AND DISCUSSION

Caesium content in ceramics after sorption 29.5 and 315.5 hours relatively pH is shown on Fig.1.
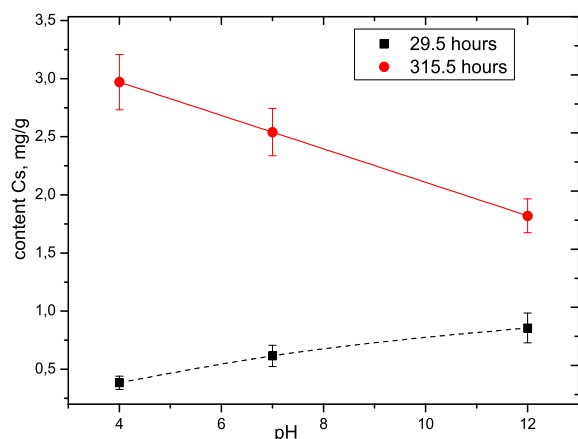


***Fig.1.*** *The concentration of cesium in samples of $KMgPO_4 \cdot 6H_2O$ after ion exchange for 29.5 and 315.5 hours*

Feature of ion exchange of cesium which replaces the potassium in $KMgPO_4 \cdot 6H_2O$ is small rate of exchange in the initial period (29.5 hours) for the high acidity of a solution. However, high ion exchange capacity of cesium in $KMgPO_4 \cdot 6H_2O$ was detected for high acidity of a solution after equilibrium establishment. After an ion exchange during 315.5 hours the acidity of initial solution with pH=4 were changed to pH=7 and with pH=12 to pH=11.

In order to establish of balance between $KMgPO_4 \cdot 6H_2O$ and $CsNO_3$ the ion exchange is being realised. In this case, part of the ions A(K) are being replaced by ions B(Cs) in ionite, and part of ions B(Cs) is being replaced by A(K) in solution:

$$\overline{A} + B \leftrightarrow \overline{B} + A. \qquad (1)$$
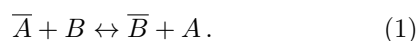
Efficiency of use of ion exchange is characterized by ability of counterions to the separation A and B, i.e. its selectivity. $T_B^A$ separation factor is being determined by the following equation:

$$T_B^A = (\overline{m}_A/\overline{m}_B)/(m_A/m_B) = (\overline{C}_A/\overline{C}_B)/(C_A/C_B), \qquad (2)$$

where $\overline{m}_A$, $\overline{m}_B$ – molal concentration of counterions before contact with the solution; $m_A$, $m_B$ – molal concentration of counterions after the establishment of equilibrium; $\overline{C}_A$, $\overline{C}_B$ – concentration of counterions before contact with the solution, $C_A$, $C_B$ – concentration of counterions A and B after the establishment of equilibrium. The value of selectivity for $KMgPO_4 \cdot 6H_2O$ at pH=4 was 174.6. For dilute solutions (in this case the cesium concentration was $6.1 \cdot 10^{-4}$ mol/l) at equilibrium the ionite preferably absorbs counterions [7].

Typically, the ion exchange is the result of stoichiometric process: for each equivalent of counterions of A which emerges from the ionite into ion exchanger enters of the equivalent of counterions. Because of condition of electrical neutrality the stoichiometric exchange means that opposite diffusion fluxes of counterions A and B are equal at any time and in any part of the ionite. If one of the two counterions is more mobile, its flow must first be large, which cause short-lived space charge and thereby create an electric field (diffusion potential). Therefore, the rapid ions were decelerated and slower ions were being accelerated by electric field. Thus, the flow is being equalized.

The diffusion flux of particles $\Phi_i$ of i-th class, according to Fick's first law is expressed as follows:

$$\Phi_i = -grad C_i. \qquad (3)$$

The variation in time of concentration of the i-element is associated with condition of continuity of a flux (second Fick's law):

$$\frac{\partial C_i}{\partial t} = -div\Phi_i. \qquad (4)$$

For a system with spherical symmetry and for the case of constant coefficients of diffusion from equations (3) and (4) we can derive the following equation:

$$\frac{\partial C_i}{\partial t} = -D_i \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} \right). \qquad (5)$$

For gel kinetics chosen solution does not contain elements of A, and the ion exchanger contain element of A with varying concentrations: $r>r_0$, t=0,

$C_A(r)$=0,

$r \leq r_0$, t=0, $\overline{C}_A(r) = \overline{C}_A{}^0(r)$=const.

Usually, the neglect of ion concentration in solution A is impossible for the solution with final volume. Running water is absent in this volume also. The condition $\overline{CV} \ll CV$ (C– total concentration of counterions A+B in the equivalent; $\overline{V}$ – the volume of ion exchanger; V – volume of solution) in this

case are not executed, so the boundary condition for the solution are:

r=r$_0$, t>0, $\overline{C}_A$(r)=$\overline{C}_A$(t),

$$\overline{C}_A(t) = \frac{3\overline{VC}}{r_0 VC} \int_0^t (\Phi_A(t)dt). \tag{6}$$

This condition follows from the material balance -d$\overline{Q}_A$=dQ$_A$ and equilibrium conditions at the phase boundary.

The solution of equation (5) has following analytical expression [7]:

$$U = \frac{\overline{Q}_A^0 - \overline{Q}_A(t)}{\overline{Q}_A^0 - \overline{Q}_A^\infty} = 1 - \frac{2}{3\omega} \sum_{n=1}^\infty \frac{exp(-S_n^2\tau)}{1 + S_n^2/9\omega(\omega + 1)}, \tag{7}$$

where $\omega=\overline{CV}/CV$; $\tau=\overline{D}t/r_0^2$; $S_n$ – the roots of the transcendental equation $S_n ctg S_n = 1 + S_n^2/3\omega$; $\overline{Q}_A^\infty = \overline{Q}_A^0 \omega/(\omega+1)$ – number of ions remaining in the ion exchanger after the establishment of equilibrium, U – value of transformations achieved at time t to the transformations that have been established at equilibrium (Fig.2).
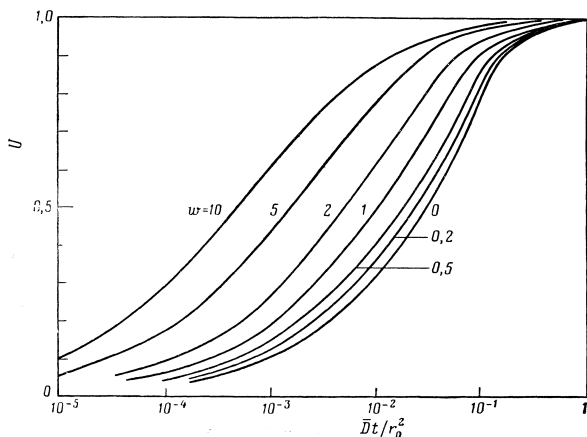


**Fig.2.** *Ion exchange in a solution of limited volume in a case of gel kinetics [7]*

For the above experimental conditions, the value of $\overline{CV}$/CV is equaled 0.76. In the case of ion exchange during 315.5 hours the value of $Dt/r_0^2 = 0.18$ is correspond to implementing of equilibrium on the level of 0.95 (see Fig.2). The evaluation of half-equilibrium time for conditions that were used in the experiment is 50 hours at room temperature and particle size of KMgPO$_4$·6H$_2$O 1 micron. The value of the diffusion coefficient D was used out of [8].

It is known that the hydration radius of cesium (226 pm) is less than the radius of hydration of potassium (232 pm). Therefore, ionite preferably absorbs counterions with smaller equivalent volume [9,10]. Elastic grid of a matrix absorbing ions with smaller hydration radius will occupy a smaller volume. Owing to it the selectivity is increased with augmentation of a difference of the equivalent volumes.

Dependence of ion exchange capacitance of Cs in KMgPO$_4$·6H$_2$O versus values of pH of solution at equilibrium, apparently, due to additional release of potassium into solution that allows greater quantity of cesium to penetrate into ionite. The additional release of K cause neutralization of CsNO$_3$ solution with high acidity. In the initial period of contact of the solution with an ion exchanger the significant concentration of H$^+$ ions inhibits the transition of cesium ions into ionite.

## 4. CONCLUSIONS

1. The possibilities of fine-dispersed matrix of KMgPO$_4$·6H$_2$O for sorption of cesium were studied. The possibility of its use for the removal of cesium-137 out of solutions determined.

2. Large ion exchange selectivity towards cesium out of dilute solutions was detected.

3. Acceptable sorption properties of KMgPO$_4$·6H$_2$O matrix for cesium were being caused by difference of hydration radii of potassium and cesium.

4. Sufficiently good ion exchange capacity towards cesium of KMgPO$_4$·6H$_2$O was achieved. The ion exchange capacity towards cesium in the ionite was 2.97 mg/g at pH=4.

5. Dependence of ion exchange capacity of Cs in ionite of KMgPO$_4$·6H$_2$O versus pH of solution of CsNO$_3$ was determined.

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## СОРБЦИОННЫЕ СВОЙСТВА МАГНИЙ-КАЛИЙ-ФОСФАТНЫХ МАТРИЦ

*Н. П. Дикий, А. Н. Довбня, Ю. В. Ляшко, Д. В. Медведев, Е. П. Медведева, С. Ю. Саенко, В. А. Шкуропатенко, Р. В. Тарасов, И. Д. Федорец*

Исследованы сорбционные характеристики мелкодисперсной магний-калий-фосфатной керамики $KMgPO_4 \cdot 6H_2O$ для иммобилизации $^{137}Cs$. Обнаружена высокая емкость по цезию, которая составляет 2.97 мг/г при pH=4. Высокая избирательность ионного обмена из разбавленных растворов обусловлена различной величиной гидратационных радиусов калия и цезия в матрице $KMgPO_4 \cdot 6H_2O$. Зарегистрировано изменение pH растворов в динамике исследований в сторону более высоких значений, по-видимому, за счет выщелачивания подвижного калия из керамики. Подтверждены высокие химическая и радиационная устойчивости данной керамики.

## СОРБЦІЙНІ ВЛАСТИВОСТІ МАГНІЙ-КАЛІЙ-ФОСФАТНИХ МАТРИЦЬ

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Досліджені сорбційні характеристики дрібнодисперсної магній-калій-фосфатної кераміки $KMgPO_4 \cdot 6H_2O$ для іммобілізації $^{137}Cs$. Виявлено високу ємність по цезію, яка складає 2.97 мг/г при pH=4. Висока вибірковість іонного обміну з розведених розчинів обумовлена різною величиною гідратаційних радіусів калію і цезію в матриці $KMgPO_4 \cdot 6H_2O$. Спостерігається зміна pH розчинів у динаміці досліджень у бік більш високих значень, очевидно, за рахунок вилугування рухливого калію з кераміки. Підтверджено високу хімічну і радіаційну стійкість даної кераміки.