

ION EXCHANGE IN PHOTOACTIVATED INORGANIC MATTERS

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The effects of monovalent and bivalent impurities on the diffusive mobility sodium, caesium and strontium in magnesium potassium phosphate hexahydrate and clinoptilolite were analysed. It was determined that ratio of diffusion coefficients of sodium concerning caesium and strontium are in antagonistic dependence on the caesium and strontium content in a matrices on the basis of magnesium potassium phosphate hexahydrate. It is established that the diffusion process in the magnesium potassium phosphate hexahydrate is due to the Frenkel. The influence of the diffusion of impurity elements as a function of the ionic radius and the ion position in the crystal lattice of clinoptilolite has been studied.

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1. INTRODUCTION

The present article compares the more important natural zeolite and ceramic based material (MgKPO₄) for the immobilization of ion Cs⁺. There have been many articles published both on zeolite and magnesium potassium phosphate hydrate which devoted to this problem, however, the use of radiation to modify the properties of these materials is relatively unreported [1-3].

Zeolites are inorganic solids consisting of enclosed regular cavities or channels of well-defined size and shape that are widely used in industry in separation processes, such as catalysts and in nanoreactors [4]. A major diversity of properties of zeolites is caused by its structural singularities. The crystalline skeleton, for example, clinoptilolite, consists of tetrahedrons [(Si,Al)O₄] and has a substratified constitution and two-dimensional system of channels. In this skeleton which has the subzero charge, the part of ions Si⁴⁺ is substituted by ions Al³⁺, that is compensated by presence of such cations as Na⁺, K⁺, Ca²⁺, Mg²⁺, etc. These cations can easily be substituted by cations of other metals. Canals and vacuities of a crystalline skeleton clinoptilolite are filled «zeolite water». In case of a dehydration of «zeolite water», clinoptilolite is selective sorbent of Cs⁺ and Sr²⁺ ions at the expense of coincidence of the dimensions of hollows of a clinoptilolite skeleton and of ionic radii of Cs⁺ (0.181 nm) and Sr²⁺ (0.132 nm). The kinetic characteristic of a sorption consists of interior diffusion of ions with coefficient $\sim 10^{-11}$ cm²/s and of

exterior diffusion with coefficient $\sim 10^{-5}$ cm²/s. Taking into account it, nanosize of clinoptilolite particles leads to increase of a rate of an ion exchange and to rise of adsorption capacity.

Potassium magnesium phosphate hydrate are formed by reaction between magnesium oxide (MgO) and potassium dihydrogen phosphate (KH₂PO₄) in solution governed by reaction: MgO + KH₂PO₄ + 5H₂O → MgKPO₄·6H₂O Such potassium magnesium phosphate hydrate have good mechanical strengths, good chemical stability and can be used for immobilization of radioactive waste in other matrices.

The irradiating of magnesium potassium phosphate hexahydrate influences the ionic exchange which has some the singularities [5] (Table 1). With an increase of an exposure dose the process of a leaching of ions from magnesium potassium phosphate hexahydrate decreases owing to structural modifications.

Table 1. The loss weight of ceramic samples after leaching during 858 hours, %

Leaching samples	Loss weight	Irradiation
KE+10%CaSiO ₃ +0.3%H ₃ BO ₃	14.6%	e ⁻ 100 MGy
KW+10%CaSiO ₃ +0.3%H ₃ BO ₃	18.5%	e ⁻ 100 MGy
KW+10%CaSiO ₃	19.9%	γ 1 MGy
KE+10%CaSiO ₃ +0.3%H ₃ BO ₃	21.6%	γ 1 MGy

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The essential differences note in the diffusion of univalent and divalent ions. Obviously, this is connected with near of Cs^+ and K^+ radii (0.181 and 0.152 nm, accordingly). Radius Na^+ much less also is 0.116 nm. It is necessary to notice that irradiation of magnesium potassium phosphate hexahydrate as by electrons, and bremsstrahlung lead to decrease of Cs^+ diffusion coefficient at increasing of its content in a matrix. The similar mechanism of diffusion becomes perceptible and for Sr^{2+} ion. The value of diffusion coefficient Sr^{2+} depends on the quantity of its content in magnesium potassium phosphate. The most considerable modifications of Sr^{2+} diffusion coefficient, more than in 10 times, are observed at an irradiating of magnesium potassium phosphate hexahydrate by bremsstrahlung to doses 1 MGy.

Apparently, in the course of an irradiating of samples the part of magnesium oxide (MgO) is dissolving in phosphoric acid (Table 1) [6]. Hydration radius of Mg^{2+} (0.426 nm) is more than radius of Sr^{2+} (0.412 nm). Ions Mg^{2+} are in a structure of potassium magnesium phosphate hydrate in the form of an octahedron with 6 molecules of water (Fig.1).

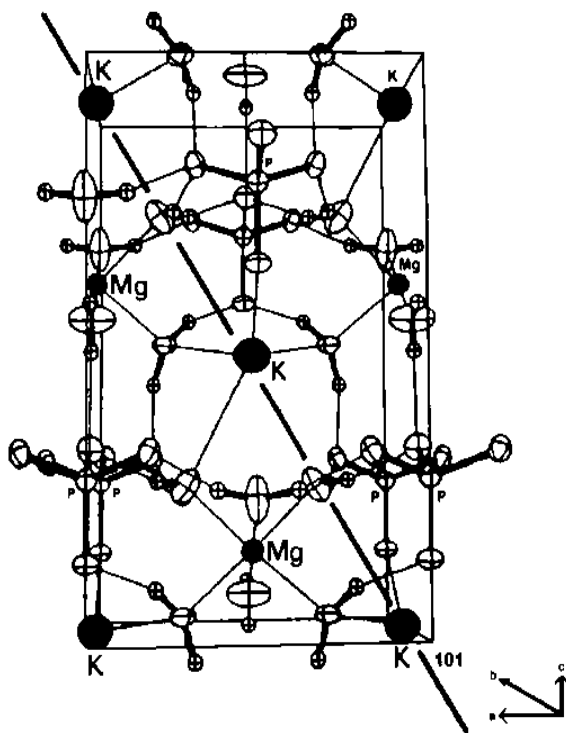


Fig.1. Projection of the crystal structure of the potassium analogue of struvite along the b -axis rotated 180° in the plane of the paper. It shows that the sites occupied by the K^+ ion which, like the NH_4^+ ion, lie on the (101), (103), (200), and (002) planes, and diffraction from these planes should be most affected by the replacement of NH_4^+ by K^+ . The trace of the 101 plane through the K^+ ions is marked [7]

It transpires that a well-defined potassium analogue $[\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}]$ of struvite exists, where K^+

replaces the NH_4^+ ammonium cations. These two compounds are isostructural with the existence of a complete isomorphous series from 100% K^+ to 100% NH_4^+ struvite. This ion replacement is possible, as the ionic radii of K^+ and NH_4^+ are almost identical (0.152 vs 0.151 nm).

The purpose of this article is establishment of the mechanism of diffusion of univalent ions in magnesium potassium phosphate hexahydrate depending on the content of divalent elements, and also investigation of changes of value of diffusion coefficients from an impurity content in samples. Also, the study of the influence of ion location in a crystal lattice of clinoptilolite on their diffusion was the purpose of this article.

2. MATERIALS AND METHODS

Samples on the basis of magnesium potassium phosphate hexahydrate with imitators "Hanford-1" KE basin sludge and 10% $\text{CaSiO}_3 + 0.3\%\text{H}_3\text{BO}_3$, "Hanford-1" KW basin sludge and 10% $\text{CaSiO}_3 + 0.3\%\text{H}_3\text{BO}_3$, "Hanford-1" KW basin sludge and 10% CaSiO_3 , "Hanford-1" KE basin sludge and 10% $\text{CaSiO}_3 + 0.3\%\text{H}_3\text{BO}_3$ and clinoptilolite were irradiated by electrons and bremsstrahlung to dose 100 MGy and 1 MGy, accordingly.

After an irradiation, the leaching of samples was realized in the distilled water at temperature 37°C . pH of the solution of leaching was 9.5. Ge(Li)-detector was used for comparison of the γ -spectra of these samples before and after irradiation (Fig.2).

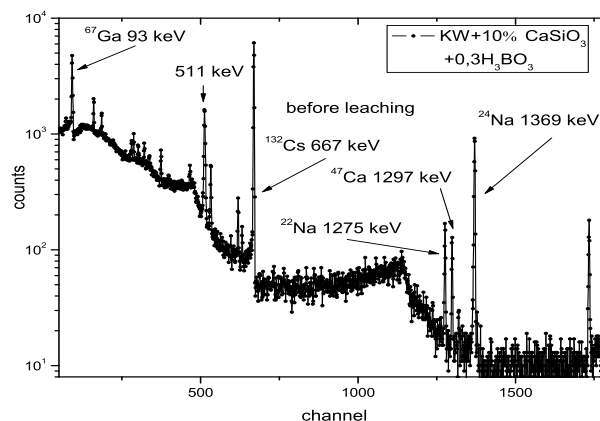


Fig.2. Energy spectrum of the sample of potassium magnesium phosphate hydrate after an irradiation on the electronic accelerator before leaching [5]

3. RESULTS AND DISCUSSION

The diffusion coefficients Na, Cs and Sr in samples of magnesium potassium phosphate hexahydrate were calculated from expression:

$$q = \frac{2}{\sqrt{\pi}} c_o \sqrt{Dt},$$

where D – diffusion coefficient, c_o – concentration of a studied element in substance.

The diffusion coefficients of sodium in magnesium potassium phosphate hexahydrate demonstrate high similarity. Perhaps this is connected with a much smaller sodium radius relative to potassium radius (0.116 vs 0.152 nm). The ratio of the values sum of sodium diffusion coefficient regarding values sum of caesium and strontium diffusion coefficients largely characterize the behavior of Cs^+ and Sr^{2+} ions. It can be seen, if the strontium content in matrix is large then the diffusion coefficient of caesium in matrix on

the basis of magnesium potassium phosphate hexahydrate (Tab. 2) is higher. On the other hand, the greater the amount of caesium, the greater diffusion coefficient of strontium in ceramics on the basis of magnesium potassium phosphate hexahydrate. The strontium has more strong opposite effect of diffusion regarding caesium and potassium since strontium is not isomorphic impurity in a matrix on the basis of magnesium potassium phosphate hexahydrate.

Table 2. The sum of ratios of the diffusion coefficients of sodium relative to caesium and strontium and content of caesium and strontium in the ceramic samples

	KE+10%CaSiO ₃ +0.3%H ₃ BO ₃ electrons, 100 MGy	KW+10%CaSiO ₃ +0.3%H ₃ BO ₃ electrons, 100 MGy	KW+10%CaSiO ₃ γ -radiation, 1 MGy	KE+10%CaSiO ₃ +0.3%H ₃ BO ₃ γ -radiation, 1 MGy
$\sum D_{Na}/D_{Cs}$	15.87	28.3	34.6	14.7
content Cs, g/g	$1.6 \cdot 10^{-4}$	$5.25 \cdot 10^{-4}$	$5.15 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
$\sum D_{Na}/D_{Sr}$	15.76	5.98	2.56	32.7
content Sr, g/g	$9.97 \cdot 10^{-3}$	$4.63 \cdot 10^{-3}$	$4.37 \cdot 10^{-3}$	$1.09 \cdot 10^{-2}$

The strength of the ion-dipole interaction of water molecules with cation decreases with increasing radius of the cation coordinated by the molecule. Therefore it can be expected that the low-temperature diffusion will be realised in hydrate of barium, and high-temperature – in hydrate of magnesium. But in real conditions, there is no complete confirmation of this dependence on the radius of the cations. It is necessary to notice that diffusion rate depends not only on the energy state and not only from the chemical nature of cations and anions which are the nearest neighbours of a molecule of water. There is another parameter, for example, physical, or entropic which is connected with разупорядоченностью in a locating of atoms. Character of atomic packaging of K, Mg and PO₄ in magnesium potassium phosphate hexahydrate possesses specificity which is bound to the extreme dimensions of these ions. From the laws of dense atomic packing, it is known that particles with high various sizes it is difficult to package in an unambiguous way. Ambiguity in the arrangement of atoms creates internodes that can participate in the formation of migration paths penetrating the whole crystal in a solid. In other words, we can say that enhanced diffusion in crystalline hydrates is in need of not only a suitable energy but also a suitable space. Such space is in MgKPO₄·6H₂O. Magnesium potassium phosphate hexahydrate has a low specific gravity of 1.7 g/cm³.

The content of impurities in the magnesium potassium phosphate hexahydrate also has a significant effect on diffusion processes, according to A Lydyard's theory [9]. The alloying of ionic NaCl crystals by Sr^{2+} ions leads to a decrease in the diffusion coefficients of anions, which is proof of the presence of Schottky defects [10]. In our case, cation diffusion

is suppressed, indicating a different diffusion mechanism in potassium magnesium phosphate hydrate, according to the Frenkel diffusion mechanism [11].

The ionic radius of gallium is 0.076 nm, which is less than the ionic radii of sodium and potassium (0.116 and 0.152 nm, respectively). Therefore, interstitial gallium diffusion must be significant. However, gallium is not an isomorphic impurity in magnesium potassium phosphate hexahydrate. Therefore, the diffusion coefficient of gallium in magnesium potassium phosphate hexahydrate should differ from the diffusion coefficients of magnesium and potassium. The sum of the ratio $\sum D_{Na}/D_{Ga}$ is less than 5%, therefore can suggest that the diffusion of gallium in magnesium potassium phosphate hexahydrate is realized by another mechanism than for impurities of sodium and caesium. Apparently, the diffusion of sodium, caesium, potassium in magnesium potassium phosphate hexahydrate realize by the Frenkel mechanism.

The diffusion coefficients Na, Ca, K, Mn and Rn in clinoptilolite were calculated in the same way like for magnesium potassium phosphate hexahydrate with use of leachate of samples (Fig 3).

On Fig.4 the diffusion coefficients of ions in clinoptilolite are presented. Clinoptilolite belongs to microporous materials and its properties are in many respects similar magnesium potassium phosphate hexahydrate. Diffusion mobility in clinoptilolite is in many respects determined by steric factors. Also, it is supposed that diffusion of cations in clinoptilolite is realized by the interstitial mechanism despite a high vacancy concentration in it [12]. The ionic radii of sodium and potassium are equal 0.116 and 0.152 nm that determines their site and bond with a lattice of clinoptilolite (Fig.5) [13].

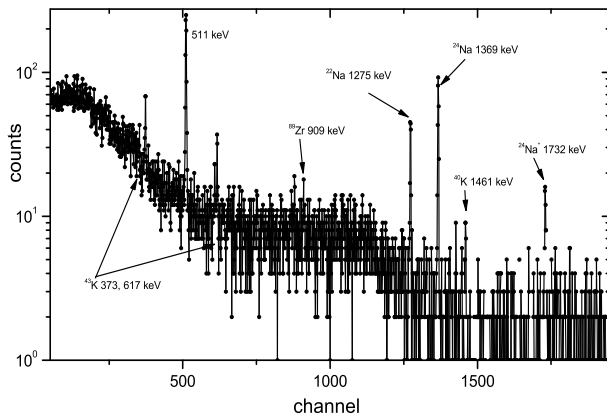


Fig.3. The energy spectrum of clinoptilolite leachate

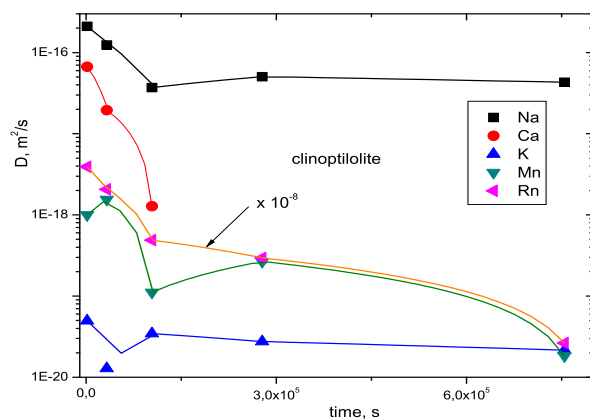


Fig.4. Diffusion coefficients of Na, Ca, K, Mn and Rn in clinoptilolite

The potassium ion is in position A1 in coordination with 6 atoms of oxygen and 3 molecules of water, and the sodium ion is in positions A1 and B in coordination with 2 atoms of oxygen and 5 molecules of water. We will notice that cation bonding distances for sodium are 0.258 nm for site A1 and 0.267 nm for site B. The cation bonding distances for potassium is 0.31 (2 bonds), 0.297 (2 bonds), 0.316 (2 bonds) for site A1. The stronger connection of potassium ions with atoms of a skeleton clinoptilolite also causes lower diffusion mobility of potassium (see Fig.4).

Diffusion mobility of manganese (the ionic radius of 0.0395 nm) a little more than for potassium. The manganese is bound with only 2 atoms of oxygen (A3-site) in a skeleton clinoptilolite. However, as a result of small ionic radius manganese is bound to 6 molecules of water and with strong enough bonds [13]. The cation-water distance for Mn^{6+} is only 0.22 nm. One can propose what the hydration complex $[Mn(H_2O)_6]^{2+}$ diffuses as the whole.

Diffusion mobility of calcium (the ionic radius of 0.114 nm) a little smaller than for sodium. Calcium bonds to three framework oxygen atoms and five water molecules in the B-channel realize in clinoptilolite. It is known that in a structure mutual substitution between Ca and Na takes place, the Na polyhedra tend to be larger than Ca polyhedra. With prolonged

leaching, the diffusion coefficient of calcium decreases substantially, which is possibly due to competition with sodium ions for locations in the crystal lattice of clinoptilolite.

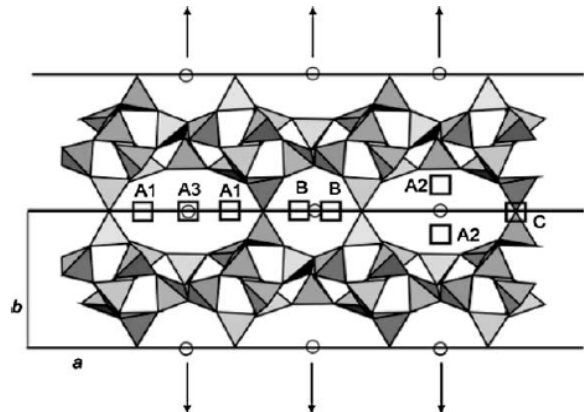


Fig.5. Polyhedral model of a portion of the heulandite structure projected parallel to the c-axis with squares representing the most important extra-framework sites. In addition, the prominent symmetry elements for space group $C2/m$ are shown: small circles=centre of inversion, heavy horizontal lines=traces of mirror planes, double-barbed arrows=twofold axes [13]

The diffusion of neutral radon in clinoptilolite is carried out by the Knudsen mechanism. Therefore, the diffusion coefficient of radon in clinoptilolite is more by 8-9 orders of magnitude with respect to other ions.

4. CONCLUSIONS

1. The sums of the ratio of diffusion coefficients of sodium concerning caesium and strontium are in antagonistic dependence on the caesium and strontium content in a matrix on the basis of magnesium potassium phosphate hexahydrate. The more of the strontium content correspond to the more of the diffusion coefficient of caesium in a matrix on the basis of magnesium potassium phosphate hexahydrate. The more of the caesium content correspond to the more diffusion coefficient of strontium in ceramics.

2. It is established that the diffusion process in the magnesium potassium phosphate hexahydrate is caused by the transition of ions from the site positions of the regular lattice to the interstices, that is, by the Frenkel mechanism.

3. The diffusion of gallium in magnesium potassium phosphate hexahydrate is realized by the Shottky mechanism.

4. The diffusion of cations in clinoptilolite is realized by the interstitial mechanism and is depended from ion positions in a crystal lattice of clinoptilolite.

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ИОННЫЙ ОБМЕН В ФОТОАКТИВИРОВАННЫХ НЕОРГАНИЧЕСКИХ ВЕЩЕСТВАХ

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Проанализировано влияние моновалентных и двухвалентных примесей на диффузионную подвижность натрия, цезия и стронция в гексагидрате фосфата калия магния. Определено, что отношения коэффициентов диффузии натрия относительно цезия и стронция находятся в антагонистической зависимости от содержания цезия и стронция в матрицах на основе гексагидрата фосфата калия магния. Установлено, что диффузионный процесс в гексагидрате фосфата магния обусловлен механизмом Френкеля. Изучено влияние диффузии примесных элементов в зависимости от ионного радиуса и занимаемой позиции в кристаллической решетке клиноптилолита.

ІОННИЙ ОБМІН У ФОТОАКТИВОВАНИХ НЕОРГАНІЧНИХ РЕЧОВИНАХ

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Проаналізовано вплив моновалентних і двовалентних домішок на дифузійну рухливість натрію, цезію і стронцію в гексагідраті фосфату калію магнію. Визначено, що відношення коефіцієнтів дифузії натрію щодо цезію і стронцію знаходяться в антагоністичній залежності від вмісту цезію і стронцію в матрицях на основі гексагідраті фосфату калію магнію. Встановлено, що дифузійний процес у гексагідраті фосфату калію магнію обумовлений механізмом Френкеля. Вивчено вплив дифузії домішкових елементів в залежності від іонного радіуса і займаної позиції в кристалічній решітці кліноптілоліта.