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Адсорбція Cs^+ , Sr^{2+} на поверхні алюмосилікатів

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Анотація. За допомогою квантово-хімічних розрахунків (метод ab-initio) досліджено процес адсорбції цезію та стронцію на поверхні алюмосилікатів. Показано, що ці поверхні адсорбують Cs^+ , Sr^{2+} , також отримано детальну інформацію про розподіл зарядів та відстаней між атомами адсорбату та сорбента, розраховано сили зв'язку.

Adsorption of Cs^+ , Sr^{2+} on aluminosilicate surface

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Abstract. Using quantum-chemical calculations (ab-initio method) process of adsorption of cesium, strontium on aluminosilicate surfaces was investigated. It was shown that these surfaces adsorb Cs^+ , Sr^{2+} and detail information about charge and distance distribution between atoms of adsorbate and sorbent was obtained, bond forces were calculated.

1. Introduction

One of the main ecological problems in 30-km exclusion zone of Chernobyl Nuclear Power Plant consist in transport (migration) of radionuclides with ground and subterranean water. Actual sources of radioactive elements entering into ground and subterranean water are: the object "Shelter" carrying ecological and nuclear hazard and industrial territory surrounding it, points for temporary location of active wastes (temporary burials) and points for burial of radioactive wastes (permanent burials).

It is known that natural aluminosilicates - clay minerals of bentonite class - may be used as general purpose effective sorbents, in particular, for radionuclide sorbtion. Taking into account wide reserves of the stuff it is promising to use them for building waterproof ground constructions, i.e. radioecological barriers that can stop contaminating water bearing layers, rivers, lakes, and ground in the radioactive contamination regions of Chernobyl zone.

The sorption of radionuclides by natural minerals can be essentially improved by chemical modifying their surface when a clay mineral serves as a matrix for coating synthetic sorbents of high efficiency. The most effective sorbents for the sorption of radionuclides cesium and strontium (they are basic source for contamination in Chernobyl zone) are synthetic materials based on ferrocyanides of ferric (III), nickel (II), cupric (II) or other metals or their mixtures.

For creation of highly effective ferrocyanide sorption-barrier materials on clay matrix and guaranteeing of their optimum storage important there are detailed researches of interaction between radioactive elements water solutions and aluminosilicate surface.

With the purpose of searching effective sorbents for radionuclides in the given work the study on microscopic a level of the nature of interaction of radionuclides with a surface of aluminosilicate are carried out. Such examinations became possible in connection with occurrence in last years of power modern computers and the relevant quantum-chemical programs. Using such quantum-chemical programs in the given work adsorption of strontium and cesium with the surface of aluminosilicate is explored. It is optimized a structure of a system an adsorbate - adsorbent, places of localization of radionuclides set, charges on them and also charges on natural atoms of a surface are calculated. Adsorption energy Cs^+ , Sr^{2+} are obtained, forces of covalent bindings in system radionuclide - sorbent are calculated. Systemic carrying out of such examinations on various structures and received results will enable to predict directions of

modification of natural sorbtion materials with the purpose of increasing of effectiveness of adsorption of radioactive ions by them.

2. The technical approach

Theoretical calculations were performed using version PC GAMESS [1] of quantum-chemical calculation packet GAMESS (US) [2] (General Atomic and Molecular Structure System) basing on ab-initio method. Effective core potential (ECP) was used, in this method electrons of inner shells are excluded from calculations and their influence on valency electrons is replaced by ECP, which is parametrized to obtain observed atomic properties. This give us a possibility to take into account the most important contributions of relativistic effects and reduces computer calculation time because basis functions describe valency orbitals only. RHF (restricted Hartree-Fock) was used.

3. Adsorption of Cs^+ , Sr^{2+} on aluminosilicate surfaces.

Occurrence in last years of power modern computer and the relevant quantum-chemical programs enable from " the first principles " to explore interaction of radionuclides with a surface of different sorbents. Carrying out of such examinations will enable justified selection of known sorbents and also an opportunity to predict a direction of their modification with the purpose of increasing of effectiveness of adsorption of radioactive ions by them. Using such quantum-chemical programs in the given work adsorption of strontium and cesium on a surface of aluminosilicate is explored.

As is known, silicates and aluminosilicate are good sorbents for radioactive waste products. Among them it is necessary to choose silicates with stratiform structure that is enlarged – montmorillonite and vermiculite which will consist of trilaminar packets in which one layer Al - Fe - Mg octahedrons is linked with two layers silicate tetrahedrons [3-5]. In interpacketes gaps of such sorbents several layers of molecules of water with radionuclides are adsorbed. Thus the structural cell is increased along an c axis (which perpendicular to layers) with on 0.3 - 1.4 nanometers. Therefore interpackets gaps of these minerals can be viewed as plate micropores which sizes vary during adsorption. Natural zeolites - clinoptilolit, mordenite, faujasite, chabazite, and other are used also for cleaning radioactive waters. In particular, in structure of chabazite there are major elliptic hollows with a cross-section $1.1 * 0.66$ nanometers. The

hollows are joined among themselves by windows with size $0.37 * 0.41$ nanometers, forming a three-dimensional grid of channels which allow to diffuse easily to ions and molecules with sizes in ~ 0.40 nanometers. In clinoptilolite structure there are four types of channels of elliptic section. In particular, channels along an c axis have the size $0.705 * 0.425$ and $0.46 * 0.395$ nanometers [3]. Clinoptilolite has high selectivity to cations of the large sizes. The recommendation on education long-lived isotope ^{137}Cs from sewage of nuclear energy stations are based on this property of clinoptilolite and other natural zeolites. At decontamination of 380 m^3 radioactive water is necessary 0.7 m^3 of clinoptilolite to reduce contents ^{137}Cs and ^{90}Sr in it to permissible norm.

Basis of structure of aluminosilicate is quartz SiO_2 . Aluminosilicate are crystals where in a matrix of silicate some atoms of silicon are substituted by aluminium Al^{3+} which similar to Si^{4+} is in a tetrahedral environment of oxygen ions. Thus we simulated a surface of aluminosilicate (or a surface of their hollows) for quantum-chemical calculations. The surface was simulated by clusters which size is determined by possibilities of the modern computers.

Using quantum-chemical programs in the given work adsorption of Cs^+ and Sr^{2+} ions on a surface of aluminosilicate is explored. Detail information about charge and distance distribution between atoms of adsorbate and sorbent was obtained, bond forces were calculated, adsorption energy are found. To model aluminosilicate surface we used cluster, with crystal alpha quartz as the basis.

The central silica atom in such initial cluster was replaced by aluminium [6]. To saturate the free oxygen bonds hydrogen atoms in optimal position were added. Two possible construction of cluster were taken into consideration – with one external OH group and three internal aluminium bonds, and case when there are two OH groups and two internal aluminium bonds. The chemical formulas of such clusters one can write down as : $\text{AlSi}_2\text{O}_2(\text{OH})_8$ in first case, and $\text{AlSi}_3\text{O}_3(\text{OH})_{10}$ in second. These clusters represented on pictures 1 and 2 accordingly.

In this work calculations were performed using version PC GAMESS of quantum-chemical calculation packet GAMESS (US) (General Atomic and Molecular Structure System) basing on ab-initio method. Quantum-chemical calculations in case of Sr and Cs elements are well simpler as for uranium, therefore basis functions MINI are reliable enough. RHF method was used, total spin of the system was taken as zero, total charge of the system in case interaction with strontium +1 (in comparison to module of electron charge), in case of caesium the system considered as electro-neutral.

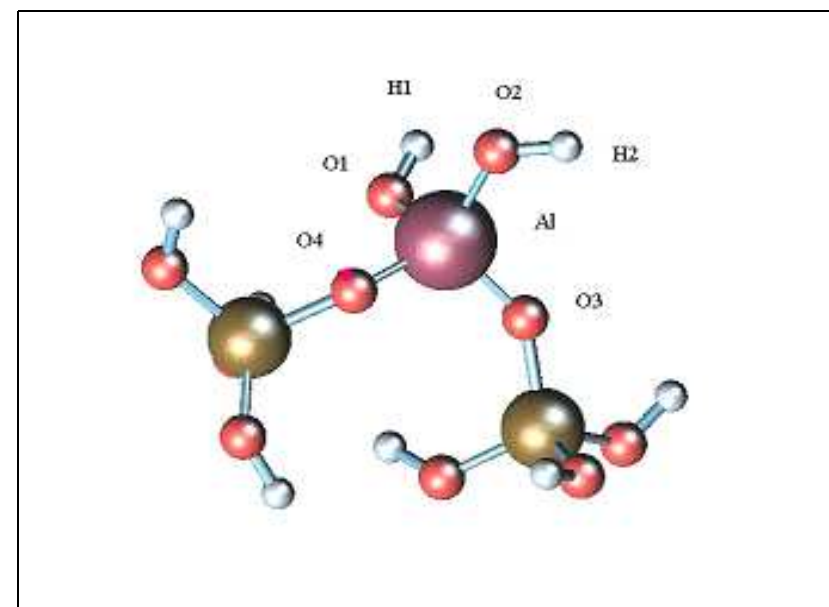


fig. 1 Model cluster $\text{AlSi}_2\text{O}_2(\text{OH})_8$.

Equilibrium geometry, charges of atoms and comparative value of bonds of model cluster $\text{AlSi}_2\text{O}_2(\text{OH})_8$.

$D(\text{Al}-\text{O}1)=1.772 \text{ \AA}$	$Q(\text{O}1)=-0.80 \text{ e}$
$D(\text{Al}-\text{O}2)=1.746 \text{ \AA}$	$Q(\text{O}2)=-0.78 \text{ e}$
$D(\text{Al}-\text{O}3)=1.611 \text{ \AA}$	$Q(\text{O}3,\text{O}4)=-0.94 \text{ e}$
$D(\text{Al}-\text{O}4)=1.607 \text{ \AA}$	$Q(\text{Al})=1.40 \text{ e}$
$\angle \text{O}2-\text{Al}-\text{O}1=112.09^\circ$	$Q(\text{H}1)=-0.19 \text{ e}$
$Q(\text{H}2)=-0.20 \text{ e}$	
bond order($\text{O}1-\text{H}1$)=0.95	bond order($\text{O}2-\text{H}2$)=0.94
bond order($\text{Al}-\text{O}2$)=0.65	bond order($\text{Al}-\text{O}1$)=0.61

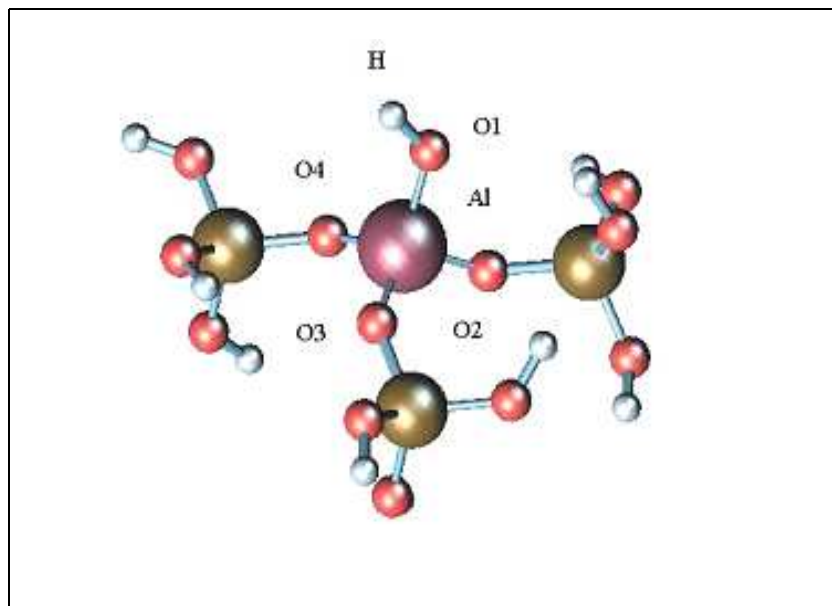


fig. 2 Model cluster $\text{AlSi}_3\text{O}_3(\text{OH})_{10}$

Equilibrium geometry, charges of atoms and comparative value of bonds of model cluster $\text{AlSi}_3\text{O}_3(\text{OH})_{10}$

$D(\text{O1-H})=0.972 \text{ \AA}$	$D(\text{Al-O1})=1.759 \text{ \AA}$
$D(\text{Al-O2})=1.611 \text{ \AA}$	$D(\text{Al-O3})=1.607 \text{ \AA}$
$D(\text{Al-O4})=1.607 \text{ \AA}$	$\angle \text{O2-Al-O1}=109.42^\circ$
$\angle \text{O3-Al-O1}=116.32^\circ$	$\angle \text{O4-Al-O1}=102.78^\circ$
$Q(\text{H})=0.20 e$	$Q(\text{O1})=-0.79 e$
bond order(O1-H)=0.95	bond order(Al-O1)=0.63
bond order(Al-O2)=0.61	bond order(Al-O3)=0.61
bond order(Al-O4)=0.59	

After calculating the optimal position for strontium atom we discovered that its most advantageous for strontium to be near aluminosilica surface then far from it, comparison of complex energies in these two cases give us possibility to make such conclusion.

In case of Sr^{2+} interaction with $\text{AlSi}_2\text{O}_2(\text{OH})_8$ this energy profit is $dE=0.2987 \text{ hartree} \approx 8.1246 \text{ eV}$.

With all this going on such changes of geometry and charge takes place (see fig. 3)

- minor elongating external bonds $\text{Al-O}(\text{Al-O1}, \text{Al-O2})$
- major narrowing of angle $\angle \text{O1-Al-O2}$.
- repartition of charge in O-H bonds interacting with strontium (charge decreasing on oxygen and increasing on hydrogen).
- decreasing bonds values between aluminium atom and oxygen atoms which connected to strontium.

Energy profit in Sr^{2+} interaction to cluster $\text{AlSi}_3\text{O}_3(\text{OH})_{12}$ is $dE=0.22392 \text{ hartree} \approx 6.0906 \text{ eV}$. In this case, as one can see at figure 4, strontium in optimal position bonded to three oxygen atoms, one of these atoms belongs to aluminium and other two – to silica atom (at the same time bond that belong to aluminium is three times as much).

Also one can see elongating near-surface bonds Al-O and repartition of charge along O-H bond strontium (decreasing on oxygen and increasing on hydrogen).

Calculated energy profit in Cs^+ adsorption on $\text{AlSi}_2\text{O}_2(\text{OH})_8$ cluster is

$dE=0.11871 \text{ hartree} \approx 3.2289 \text{ eV}$. Configuration modification (distances and angles between interacting atoms) in case of caesium is not such big as it was for strontium (fig. 5). Equivalently one can say about charge modification in system.

In case of Cs^+ interaction with model cluster $\text{AlSi}_3\text{O}_3(\text{OH})_{12}$ calculated energy profit is $dE=0.1338 \text{ hartree} \approx 3.6394 \text{ eV}$

Optimal position of adsorbed atom, as well as it was for strontium, situated between three oxygen atoms, two of them connected to silica atom and one-to aluminium (see fig. 6). At the same time, in case of caesium, bond order is very small. Geometry and charge overpatching in cluster are next:

- repartition of charge in external O-H bonds (from oxygen to hydrogen) and its elongating.
- decreasing bonds values between aluminium atom and oxygen atoms ($\text{Al-O1}, \text{Al-O4}$).

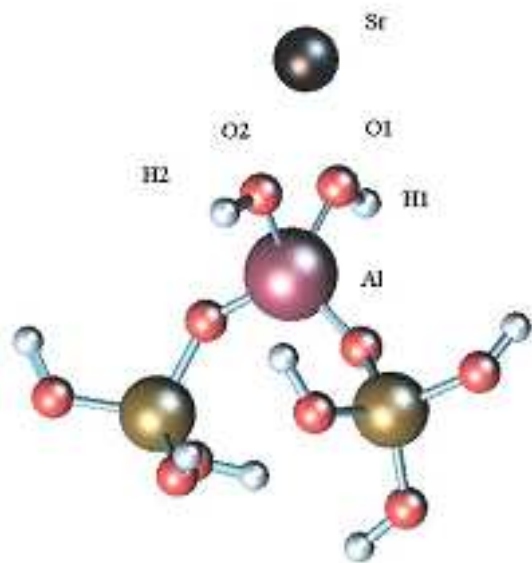


fig. 3 Sr^{2+} adsorbed on $\text{AlSi}_2\text{O}_2(\text{OH})_8$ complex.

$D(\text{Al}-\text{O1})=1.817 \text{ \AA}$	$D(\text{Al}-\text{O2})=1.811 \text{ \AA}$
$D(\text{O1}-\text{Sr})=2.377 \text{ \AA}$	$D(\text{O2}-\text{Sr})=2.354 \text{ \AA}$
$\angle \text{O1}-\text{Al}-\text{O2}=89.73^\circ$	$Q(\text{H1})=0.25 \text{ e}$
$Q(\text{O1})=-0.85 \text{ e}$	$Q(\text{H2})=0.26 \text{ e}$
$Q(\text{O2})=-0.85 \text{ e}$	$Q(\text{Al})=1.36 \text{ e}$
$Q(\text{Sr})=1.88 \text{ e}$	
$\text{bond order}(\text{O1}-\text{H1})=0.93$	$\text{bond order}(\text{O2}-\text{H2})=0.93$
$\text{bond order}(\text{O1}-\text{Sr})=0.11$	$\text{bond order}(\text{O2}-\text{Sr})=0.11$
$\text{bond order}(\text{Al}-\text{O1})=0.53$	$\text{bond order}(\text{Al}-\text{O2})=0.55$

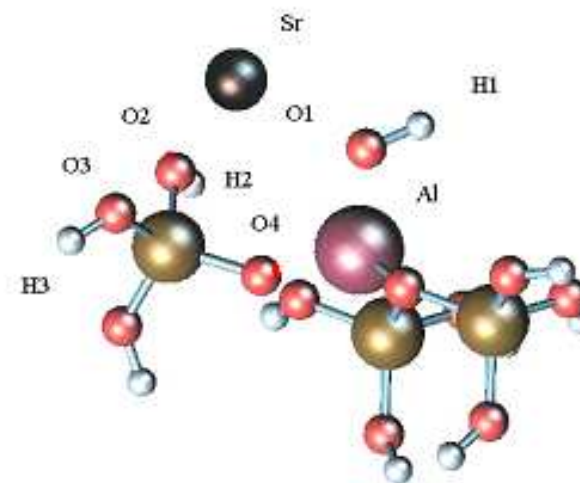
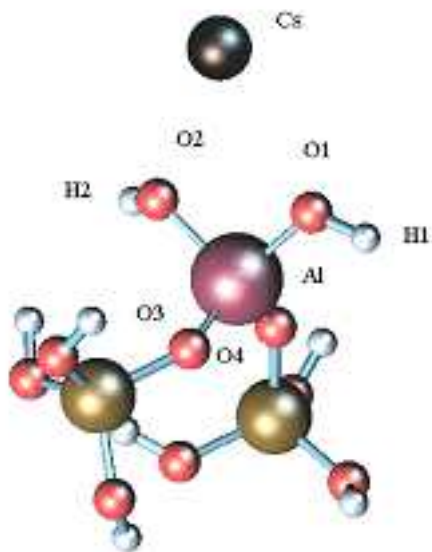
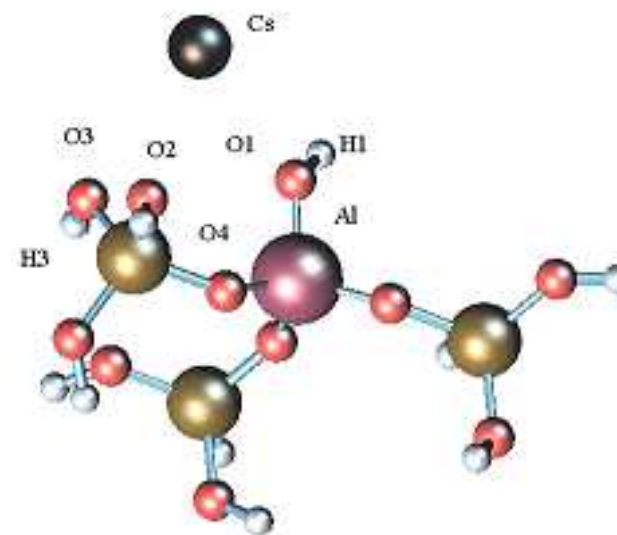


fig. 4 Sr^{2+} adsorbed on $\text{AlSi}_3\text{O}_3(\text{OH})_{12}$ complex.

$D(\text{Sr}-\text{O1})=2.373 \text{ \AA}$	$D(\text{Sr}-\text{O2})=2.590 \text{ \AA}$
$D(\text{Sr}-\text{O3})=2.913 \text{ \AA}$	$D(\text{Al}-\text{O1})=1.831 \text{ \AA}$
$Q(\text{O1})=-0.85 \text{ e}$	$Q(\text{H1})=0.25 \text{ e}$
$Q(\text{O2})=-0.84 \text{ e}$	$Q(\text{H2})=0.35 \text{ e}$
$Q(\text{O3})=-0.82 \text{ e}$	$Q(\text{H3})=0.34 \text{ e}$
$Q(\text{Sr})=1.87 \text{ e}$	$Q(\text{Al})=1.44 \text{ e}$
$\text{bond order}(\text{O1}-\text{H1})=0.93$	$\text{bond order}(\text{Al}-\text{O1})=0.5$
$\text{bond order}(\text{Al}-\text{O4})=0.58$	$\text{bond order}(\text{Sr}-\text{O1})=0.13$
$\text{bond order}(\text{Sr}-\text{O2})=0.05$	$\text{bond order}(\text{Sr}-\text{O3})<0.05$

fig. 5 Cs⁺ adsorbed on AlSi₂O₂(OH)₈complex.

$D(\text{Al-O1})=1.769 \text{ \AA}$ $D(\text{Al-O2})=1.786 \text{ \AA}$
 $D(\text{O1-Cs})=2.889 \text{ \AA}$ $D(\text{O2-Cs})=2.919 \text{ \AA}$
 $\angle \text{O1-Al-O2}=100.43^\circ$ $Q(\text{H1})=0.22 \text{ e}$
 $Q(\text{O1})=-0.80 \text{ e}$ $Q(\text{H2})=0.20 \text{ e}$
 $Q(\text{O2})=-0.81 \text{ e}$ $Q(\text{Al})=1.38 \text{ e}$
 $Q(\text{Cs})=0.96 \text{ e}$
 $\text{bond order}(\text{O1-Cs}) < 0.05$ $\text{bond order}(\text{O2-Cs}) < 0.05$
 $\text{bond order}(\text{Al-O1})=0.62$ $\text{bond order}(\text{Al-O2})=0.58$

fig.6 Cs⁺ adsorbed on AlSi₃O₃(OH)₁₂complex.

$D(\text{Cs-O1})=3.204 \text{ \AA}$ $D(\text{Cs-O2})=3.062 \text{ \AA}$
 $D(\text{Cs-O3})=2.930 \text{ \AA}$ $Q(\text{O1})=-0.84 \text{ e}$
 $Q(\text{H1})=0.23 \text{ e}$ $Q(\text{O2})=-0.80 \text{ e}$
 $Q(\text{H2})=0.31 \text{ e}$ $Q(\text{O3})=-0.80 \text{ e}$
 $Q(\text{H3})=0.30 \text{ e}$ $Q(\text{Cs})=0.97 \text{ e}$
 $Q(\text{Al})=1.48 \text{ e}$
 $\text{bond order}(\text{O1-H1})=0.94$ $\text{bond order}(\text{Al-O1})=0.60$
 $\text{bond order}(\text{Al-O4})=0.59$

4. Conclusions

In this work using quantum-chemical calculations (ab-initio method) adsorption of cesium, strontium on aluminosilicate surfaces was investigated. Thus, using quantum-chemical calculations we showed that aluminosilicate surface adsorbs Cs^+ , Sr^{2+} and obtained a detail information about charge and distance distribution at adsorption, and bond forces between atoms. Calculated an adsorption energy of Cs^+ and Sr^{2+} ions in a following investigations will be utilised for model operation of a sorption part of the surface potential $U^a(z)$ at calculation of the nonuniform diffusion constant of ions in directions from a solution to a surface of sorbent. Also features of change of a charge on ions in an electrostatic part of the surface potential $U^a(z)$ will be taken into account. Calculated an adsorption energy and diffusion constants $D^a(z)$ for Cs^+ and Sr^{2+} ions will be important also at prediction of adsorption properties of the modified bentonitic clays by copper- and ferro-cyanide.

5. Acknowledgments

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АДСОРБЦІЯ Cs^+ , Sr^{2+} НА ПОВЕРХНІ АЛЮМОСИЛКАТІВ

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