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ADSORPTION OF URANYL, CESIUM, STRONTIUM ON SiO_2 SURFACE

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ЛЬВІВ

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Адсорбція уранілу, цезію, стронцію на поверхні SiO_2

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Анотація. За допомогою квантово-хімічних розрахунків (метод ab-initio) досліджено процес адсорбції уранілу, цезію, стронцію на поверхні силікатів. Показано, що поверхня адсорбує UO_2^{2+}, Cs^+, Sr^{2+} та отримано детальну інформацію про розподіл зарядів та відстаней між атомами адсорбату та сорбента, розраховано сили зв'язків. Показано, що присутність гідратної оболонки уранілу суттєво понижує величину енергії реакції.

Adsorption of uranyl, cesium, strontium on SiO_2 surface

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Abstract. Using quantum-chemical calculations (ab-initio method) processes of adsorption of uranyl, cesium, strontium on silicate surface are investigated. It is shown that the surface adsorbs UO_2^{2+}, Cs^+, Sr^{2+} and detail information about charge and distance distribution between atoms of adsorbate and sorbent are obtained, bond forces are calculated. It is shown, that presence of a hydrated shell of uranyl essentially diminishs quantity of energy of reaction.

1. Introduction

In all complex of problems of a zone of alienation one of basic there is a utilization problem for waste which are formed after Chornobyl accident and localized in such following places as object "Shelter", points of a burial of radioactive waste, temporary storages or remained immediately in an environment. In a 30-kilometer zone of alienation there is presence of the permanent source of the radioactive contamination causes a permanent ecological problem connected with transport processes (migration) of radionuclides by ground and underground water of system "the water inlet of a short-range zone of the Chornobyl Nuclear Power Plant - the river Prypyat - a cascade of Dnipro reservoirs". In this connection actual there are investigations of ground sorption properties in a zone of alienation, and development of sorption materials on the basis of clay raw materials which could be applied in a zone as sorption-barrier systems on a trajectory of radionuclides migration.

These investigations are important for the elaboration of physico-mathematical model of radionuclide migration in ground water, which can be applied for the creation of radioecological barriers-trappers in the system "the water inlet of a short-range zone of the Chornobyl Nuclear Power Plant - the river Prypyat - a cascade of Dnipro reservoirs". It is known that natural clay minerals of bentonite class may be used as general purpose effective sorbents, in particular, for radionuclide sorption. 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 Chornobyl zone.

Problems of using natural minerals of bentonite class to deactivate radioactive fluids, are considered in a number of monographes [1-4]. It is also known that their technological and sorption properties might be much improved by thermal and chemical modifying [5-7]. Klinoptylolite, vermiculite, montmorillonite are those natural minerals which are most often used for radionuclide sorption. Their main drawbacks are relatively low sorption capacity (montmoryllonite), abrupt drop of selectivity as to radionuclide sorption in high-concentration salt solutions and the lack of filtrationproof and waterproof properties (klinoptylolite, vermiculite). Hence, even though Ukraine possesses large reserve of the raw material, its application to removing radioactive contamination by Chornobyl disaster is limited and that to the creation of effective radioecological barriers is impossible.

It is known, that sorption properties of clay raw material can be essentially improved by modifying of mineral surface by salts of metals Fe3+, Cu2+, Al3+, Cr3+, etc. when the clay mineral is used as a matrix for mapping of high-performance synthetic sorbents. Radioisotopes 137Cs and 90Sr are the basic sources of contamination in Chornobyl zone. The most efficient sorbents for sorption of cesium and strontium radioisotopes are synthetics on the basis of ferrocyanides of ferric (III), nickel (II), cupric (II) and other metals or their mixtures. Synthesis and preparation of such materials is described in [8-11].

For creation of sorption-barrier materials on clay matrix and guaranteeing of their optimum storage important there are also detailed researches of water solutions of radio-active elements. Problem complex formation and hydrolysis in water solutions for radionuclide ions participation is by article of researches on row extent of years. In greater measure such processes learned by chemical methods. For some time past there began also study of different physics aspects of these phenomena.

New computer programs use for quantum-chemical calculations allows to explore an adsorption of ions of strontium, cesium, uranyl with a hydrated shell on a surface of silicates which are the structure elements of clayey matrix and to optimize structure of system "an adsorbate-adsorbent". The purpose of such investigations is the comparative analysis of the adsorption performances of various explored materials taking into account the local effects caused by a microscopic structure of the ionic clusters and centres on a surface and a porosity of the material. Systematic carrying out of such investigations on various structures and the results obtained will enable to forecaste directions for natural sorption materials modifying with the purpose of their efficiency improvement for radioactive ions absorption.

2. Adsorption of uranyl with hydration shell on SiO_2 surface.

It is known that when hydrolysis is absent actinoide ions in water solutions are present as complexes $(M(H_2O)_n)^{z+}$ where z is a cation charge; n is a coordination (or hydration) number of central atom, M denotes actinoide ([12]). Uranium can be present in solutions as ions with four oxidization degrees: $+3, +4, +5, +6$. Stability of valency states of uranium in solution is as follows: $U(6)>U(4)>U(3)>U(5)$([13]), six valency uranium is the most stable, which is present in solution as uranyl ion $(UO_2)^{2+}$, hydrolysis of this ion takes place at $pH>3$ ([14]). Inclination of uranium to hydrolysis can be presented as $U(4)>U(6)>U(3)>U(5)$ ([13,15]). It is known that at presence of atmosphere air uranium of low valency in compounds slowly oxygenates to $((UO_2)^{2+})$. Compounds of six valence uranium transform in uranyl compounds at the presence of water, thus uranyl group is one of the most stable form in solutions [16]. In water solutions water molecules are situated in the equatorial plane of uranyl, perpendicular to the axial direction O-U-O. Such a bond is not strong but 5 or 6 such weak bonds are equivalent to one strong bond and their influence should be taken into account ([17]).

Theoretical investigations of different complexes with uranium are intensively carried out in last time, although direct comparison of calculated and experimental results is difficult for solutions. Computer calculations give us a possibility to take into account at least the influence of the nearest environment on investigated object. As example, in [17,18,19] processes of hydration and hydrolysis of uranyl were investigated using the quantum-chemical calculations. Also attempts of theoretical description of uranium behavior in water are carried out basing on the configuration model ([20]) and using molecular dynamics ([21]).

Quantitative calculations of adsorption of actinoides on surfaces are difficult, only in last years some progress was achieved. In [22] using the quantum-chemical calculations adsorption of uranyl on silver surface was investigated, there was revealed that some part of surface should be taken into account (adsorption did not take place when one atom was taken as a surface). We can assume that for other surfaces (SiO_2 for example) similar situation takes place. Influence of the presence of hydration shell of uranyl was also investigated, qualitatively adsorption picture did not change, only local minimum of the energy was more broad for the case of adsorption of hydrated uranyl and charge distribution changed. Together with quantum-chemical calculations adsorption of uranyl on silver and gold surface was experimentally confirmed [23], thus in this case quantum-chemical calculations agree with experiment.

Different complexes with ionic groups SiO_2 participation can be taken as a surface SiO_2. In many polimorphs of SiO_2 Si atoms are surrounded by tetrahedron of oxygen atoms. O-Si-O angle is close to an ideal bond angle in tetrahedron 109.28° [24,25]. Each oxygen atom is bonded with two silicon atoms and connects tetrahedrons between themselves. Alpha and beta quartz can be an example of such polimorphs.

It should be noted that in last time calculations of SiO_2 complexes are intensively carried out using quantum-chemical calculations as well as molecular dynamics method. The processes on the surface and inside different forms of SiO_2 are investigated [26-30], modeling of nanoparticle creation is carried out also [31], the processes in SiO_2 pores are modeled [31,32].

In this work calculations were performed using version PC GAMESS [33] of quantum-chemical calculation packet CAMESS (US) [34] (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. Basis 6-31G for atoms O, H, Si and basis LANL2DZ ECP for uranium atom were used. RHF (restricted Hartree-Fock) was used, this method gives good results for closed shells, total spin of the system was taken to be zero.

SiO_2 adsorbs hydrogen, thus we take a complex $Si_3O_4H_8$ as a surface SiO_2 (we take into account that surface is saturated by hydrogen bonds) [35], fig.1. In table 1 charge and distances in complex $Si_3\ O_4\ H_8$, obtained after geometry optimization by ab-initio method are showed, three H atoms were added to each of two extreme Si atoms to imitate surface; at calculations of adsorption these hydrogen atoms were fixed. All distances are in angstrom Å, angles are in degrees $^\circ$, charges are in comparison to module of electron charge |e|, bond order is in relative units (can be compared with bond order O-H ∼ 0.79 in water molecule H_2O).

In table 2 the charges and geometry of free uranyl are given. At adsorption on $Si_3O_4H_8$ (here we do not take into account the presence of hydration shell) hydroxyl groups are situated in equatorial plane of uranyl, then coordination of uranyl is equal 2 [35], fig. 2, tab. 3. It was revealed that addition of water molecule to uranyl is advantageous (the complex $Si_3O_4H_8UO_2H_2O$), energy gain is $dE = E(Si_3O_4H_8UO_2H_2O) - E(Si_3O_4H_8UO_2) - E(H_2O) = -0.094$ hartree

1hartree = 27.2 eV = 627.5095 kcal/mol

The complexes $Si_3O_4H_8UO_22H_2O$, $Si_3O_4H_8UO_23H_2O$, $Si_3O_4H_8UO_24H_2O$ were calculated also (fig. 4-7). Calculating in a similar way energy difference dE, it was revealed that complexes with five-coordinated uranyl (fig.6,7) are the most energy stable [36], equilibrium geometry and charges are given in tab. 4,5. Complex showed in fig. 7 has slightly lower energy than complex showed in fig. 6:
$dE= E(Si_3O_4H_8UO_24H_2O) - E(Si_3O_4H_83UO_2) - E(H_2O) = -0.038$ hartree

In the complex $Si_3O_4H_8UO_23H_2O$ uranyl is bonded with two hydroxyls and in the complex $Si_3O_4H_8UO_24H_2O$ uranyl is bonded with one hydroxyl (the distance between uranium and surface oxygen O4 is equal to 2.49, 3.86 Å respectively, and the distance between uranium and surface oxygen O3 is almost equal for these complexes and is equal to 2.5 Å). At adsorption uranyl becomes bent ($\angle$O1-U- O2 $\sim$ 176 - 178 $^\circ$), the distance between uranium and oxygen atoms increases. Uranium charge is almost constant, uranyl oxygen charge is more negative, thus uranyl charge decreases (free uranyl charge $Q(UO_2)=2$, adsorbed uranyl charge $Q(UO_2) \sim 1.5 - 1.6$). At adsorption surface hydroxyls O3,4-H approach uranyl (but the surface does not destroy), bond order between Si1 and O3,4 and between U and O1,O2 decreases. Bond order between U and O3,4 $\sim$0.16, for the case of $Si_3O_4H_8UO_24H_2O$ complex (fig.7) bond order between U and O4 is very low ($<$0.05).

Let us find energies of reactions (in some approximation they can be considered as adsorption energies, but it is clear to calculate real adsorption energy we should not limit ourselves to consideration of hydration sphere only)
dE(1) = $E(Si_3O_4H_8UO_24H_2O) - E(Si_3O_4H_8) - E(UO_25H_2O) + E(H_2O)$ = -0.045 hartree (-1.2 ev)
dE(2) = $E(Si_3O_4H_8UO_23H_2O) - E(Si_3O_4H_8) - E(UO_25H_2O) + E(2H_2O)$ = -0.006 hartree (-0.16 ev),
here we take into account the fact that non adsorbed uranyl (hydrolysis is not taken into account) is surrounded by five water molecules [18].

Comparing with reaction energy, which was founded for the case of adsorption of uranyl on SiO_2 (when we do not take into account hydration shell [35], in this case reaction energy dE=-0.231 hartree), we can see, that presence of hydration shell influenced the value of reaction energy. Besides of this, presence of hydration shell influenced the charge distribution and distances: uranium charge increased, module of uranyl oxygen O1,2 charge increased; the distance between uranium and surface oxygen O3 increased, the bond between uranium and surface oxygen decreased.

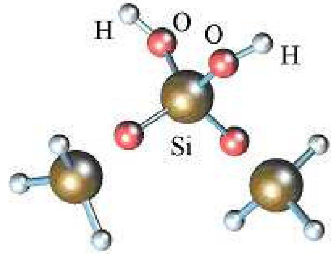

Fig. 1. Model cluster $Si_3O_4H_8$

Tab.1. Equilibrium geometry and charges of atoms of cluster $Si_3O_4H_8$

D(Si-O$\vert_{OH}$) = 1.68	Q(H) = 0.54
D(O-H) = 0.94	Q(O$\vert_{OH}$) = -0.98
$\angle$O$\vert_{OH}$-Si-O$\vert_{OH}$ = 110.6 $^\circ$	Q(Si) = 2.21
	bond O-Si $\sim$ 0.74
	bond order O-H = 0.75

Tab.2. Free uranyl UO_2^{2+}

Optymized bond distance, Å	Charge, $\vert e\vert$
D(U-O$_{ax}$) = 1.66	Q(UO_2) = 2
$\angle$O$_{ax}$-U- O$_{ax}$= 180 $^\circ$	Q(U) = 2.22
	bond order U-O $\sim$ 2.25

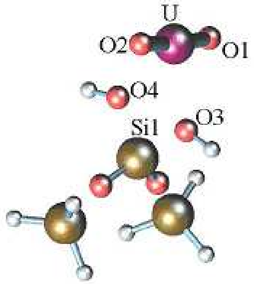

Fig. 2. Complex $Si_3O_4H_8$ UO_2, coordination of uranyl is 2

Tab.3. Equilibrium geometry and charges of atoms of complex $Si_3O_4H_8$ UO_2

D(U-O1,2) = 1.69	Q(U) = 2.217
D(U-O3,4) = 2.39	Q(O1,2) = -0.25
D(U-Si1) = 3.38	Q(O3,4) = -1.11
$\angle$O3-Si1-O4 = 84.9 $^\circ$	Q($H\|_{O3,4}$) = 0.54
D(Si1-O3,4) = 1.77	Q(Si1) = 2.29
D(O3,4-H) = 0.96	bond order Si1-O3,4 $\sim$ 0.44
$\angle$O1-U- O2= 174.1 $^\circ$	bond order H-O3,4 $\sim$ 0.69
	bond order U-O3,4 $\sim$ 0.24
	bond order U-O1,2 $\sim$ 2.13

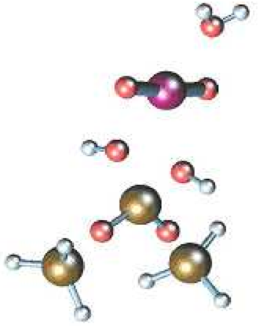

Fig. 3. Complex $Si_3O_4H_8$ UO_2 H_2O, uranyl coordination is 3

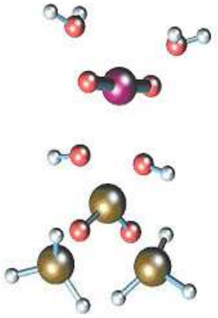

Fig. 4. Complex $Si_3O_4H_8$ UO_2 $2H_2O$, uranyl coordination is 4

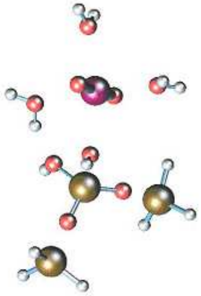

Fig. 5. Complex $Si_3O_4H_8$ UO_2 $3H_2O$, uranyl coordination is 4

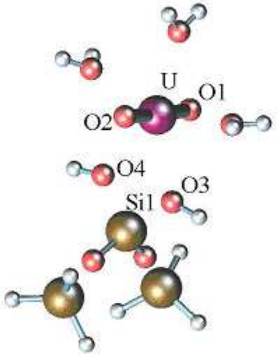

Fig. 6. Complex $Si_3O_4H_8$ UO_23H_2O, uranyl coordination is 5

Tab.4. Equilibrium geometry and charges of atoms of complex $Si_3O_4H_8$ UO_23H_2O

D(U-O1,2) = 1.72	Q(U) = 2.32
$\angle$O1-U- O2= 176.0 $^\circ$	Q(O1,2) = -0.39
D(U-O3,4) = 2.49	Q(O3,4) = -1.1
D(U-Si1) = 3.45	Q($H\|_{O3,4}$) = 0.51
$\angle$O3-Si1-O4 = 86.37 $^\circ$	Q(Si1) = 2.30
D(Si1-O3,4) = 1.74	bond order Si1-O3,4 $\sim$ 0.49
D(O3,4-H) = 0.95	bond order H-O3,4 $\sim$ 0.71
D($U-O\|_{H2O}$) = 2.49-2.495	bond order U-O3,4 $\sim$ 0.16
	bond order U-O1,2 $\sim$ 2.02

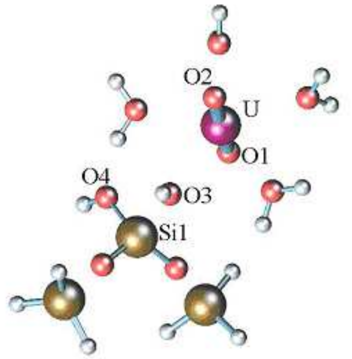

Fig. 7. Complex $Si_3O_4H_8$ UO_24H_2O, uranyl coordination is 5

Tab.5.Equilibrium geometry and charges of atoms of complex $Si_3O_4H_8$ UO_24H_2O

D(U-O1,2) = 1.72	Q(U) = 2.34
D(U-O$\|_{H2O}$) = 2.43-2.51	Q(O1,2) = -0.40
∠O1-U- O2= 178.0 °	Q(O3) = -1.12
D(U-O3) = 2.48	Q(O4) = -1.05
D(U-O4) = 3.86	Q(H$\|_{O4}$) = 0.5
D(U-Si1) = 3.85	Q(H$\|_{O3}$) = 0.51
∠O4-Si1-O3 = 97.6 °	Q(Si1) = 2.28
D(Si1-O4) = 1.7	bond order Si1-O3,4 ∼ 0.47,0.63
D(Si1-O3) = 1.76	bond order H-O3,4 ∼ 0.7,0.72
D(O4-H) = 0.95	bond order U-O3 ∼ 0.16
D(O3-H) = 0.96	bond order U-O4 < 0.05
	bond order U-O1,2 ∼ 2.01

3. Adsorption of Cs^+, Sr^{2+} on SiO_2 surface.

By analogy to the previous section, we calculate adsorption of Cs^+, Sr^{2+} on SiO_2 surface, the basis LANL2DZ ECP was used for atoms Cs, Sr. It was revealed that situation of Cs^+, Sr^{2+} ions on SiO_2 surface is more advantageous than the situation of these ions far from surface, the energy gain

$$dE = E(Si_3O_4H_8M) - E(Si_3O_4H_8) - E(M)\ ,\ M = Cs, Sr$$

at this is as follows:
dE = -0.043 hartree (-1.17 ev) for Cs,
dE(1) = -0.164 hartree (- 4.46 ev) , dE(2) = -0.157 hartree (- 4.27 ev) for Sr,
two possible positions of Sr were revealed at adsorption – see fig. 9,10. Comparing the data of tab. 6,7,8 with the one of tab. 1, we can see that at adsorption of Cs^+, Sr^{2+}(just as in the case of uranyl adsorption) the distance d(Si-O1,2) increased, module of charge of O1,O2 oxygen increased, charge of adsorbed Cs, Sr decreased, bond order between Si1 and O1,2 decreased. Bond order between Sr and O1,2 ∼ 0.06, for the Cs case bond order is less than 0.05.

4. Conclusions

In this work using quantum-chemical calculations (ab-initio method) adsorption of uranyl with hydration shell on SiO_2 surface was investigated. It was revealed that the charge of adsorbed on the surface uranyl is positive. It was shown that presence of hydration shell influences the reaction energy (without hydration shell dE ∼ -6 ev, with hydration shell dE ∼ -1ev) and its influence on charge and distance distribution is not very strong. The adsorption of strontium and cesium on SiO_2 surface was investigated also, the reaction energy was founded: dE ∼-4ev and -1ev respectively (the presence of water molecules for the case of adsorption of strontium and cesium was not taking into account).

Thus, using quantum-chemical calculations we showed that silicate surface adsorbs UO_2^{2+}, Cs^+, Sr^{2+} and obtained a detail information about charge and distance distribution at adsorption, and bond forces between atoms.

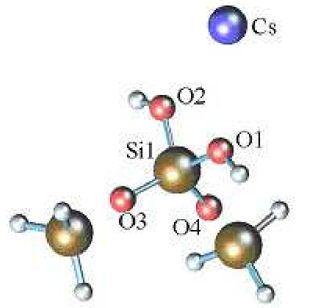

Fig.8. Complex $Si_3O_4H_8Cs$

Tab.6. Equilibrium geometry and charge of atoms of complex $Si_3O_4H_8Cs$

D(Cs-Si1) = 3.91
D(Cs-O1,2) = 3.085
D(Cs-O3,4) = 5.0
D(Si1- O1,2) = 1.70
$\angle$O1-Si1-O2 = 98.6 °
D(O1,2-H) = 0.95

Q(Cs) = 0.95
Q(O1,2) = -1.02
$Q(H|_{O1,2}) = 0.47$
Q(Si1) = 2.24
bond order Si1-O1,2 ∼ 0.67
bond order H-O1,2 ∼ 0.75
bond order Cs-O1,2 < 0.05

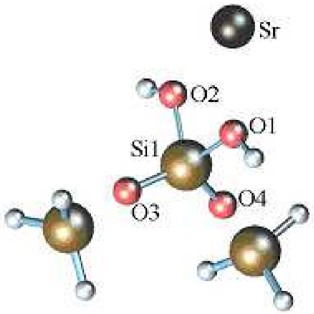

Fig.9. Complex $Si_3O_4H_8Sr$ (1)

Tab.7. Equilibrium geometry and charges of atoms of complex $Si_3O_4H_8Sr$(1)

D(Sr-Si1) = 3.37
D(Sr-O1,2) = 2.46
D(Sr-O3,4) = 4.40
D(Si1- O1,2) = 1.745
$\angle$O1-Si1-O2 = 89.23 °
D(O1,2-H) = 0.95

Q(Sr) = 1.92
Q(O1,2) = -1.13
$Q(H|_{O1,2}) = 0.51$
Q(Si1) = 2.24
Q(O3,4) = -1.2
bond order Si1-O1,2 ∼ 0.54
bond order H-O1,2 ∼ 0.72
bond order Sr-O1,2 ∼ 0.06

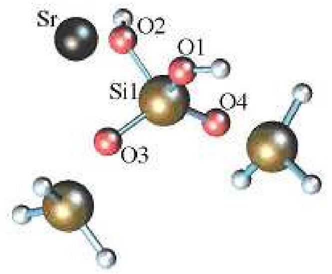

Fig.10. Complex $Si_3O_4H_8Sr$ (2)

Tab.8. Equilibrium geometry and charges of atoms of complex $Si_3O_4H_8Sr$ (2)

D(Sr-Si1) = 3.04	Q(Sr) = 1.87
D(Sr-O1) = 2.52	Q(O1,2) = -1.1
D(Sr-O2) = 2.53	$Q(H\|_{O1,2})$ = 0.52
D(Sr-O3) = 2.75	Q(Si1) = 2.24
D(Sr-O4) = 4.62	Q(O3) = -1.26
D(Si1- O1,2) = 1.72	Q(O4) = -1.18
∠O1-Si1-O2 = 93.25 °	bond order Si1-O1,2 ∼ 0.58,0.59
D(O1,2-H) = 0.95	bond order H-O1,2 ∼ 0.71
	bond order Sr-O1,2 ∼ 0.06

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