Removal of radionuclides and toxic metal ions from water with use of new highly effective sorbiting material

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Abstract. The adsorption of radionuclides of strontium, rubidium, cesium, uranium and some toxic metal ions from water streams using flasks has been experimentally and theoretically studied. When studying the adsorption of a number of metal ions on them, it was found that in a wide range of pH many cations are durably adsorbed, and in some cases irreversible sorption is observed. Ammonium, potassium, rubidium, cesium, iron, cobalt, nickel, manganese (II), chromium (III), zinc, cadmium, lead, mercury, copper and rare earth ions are durably adsorbed. At the same time, sodium, aluminum, gallium, zirconium, and molybdenum (VI) ions are captured during adsorption from solutions. These ions can be desorbed not only by acidification of the eluting solution, but also by washing the sorbent with water. An analysis of the results obtained in the study of the adsorption of cations made it possible to draw an initial conclusion: those ions that contain vacant d or f orbitals form strong adsorption complexes with flasks. Flasks are used to extract potassium, rubidium, cesium, calcium, strontium and barium ions from water of varying degrees of salinity.

1. Introduction

Natural sorbents, such as mordenite, diatomites, tripoli, synthetic and natural zeolites are very rarely used to remove potassium, rubidium, cesium and strontium ions from natural objects, in particular, from water.

Quantum-chemical calculations of the adsorption of cations on the surface of aluminosilicates are performed using a cluster approach with semi-empirical methods based on the so-called NDDO approximation (Neglect of Diatomic Differential Overlap).

Most of the calculations were performed using the PM3 method; for comparison, some AK models are calculated using the MNDO and AM1 methods [1-4]. The calculations were carried out using the MNDO-90 program. Some models were also calculated using ab initio GAMESS. The clusters contained the following active centers of the surface of aluminosilicates: an incompletely coordinated Al atom (Lewis Acid Center, LAC), =SiOH silanol group, adsorbed water molecules, a bridging OH group (Brönsted Acid centers, BAC) [5].

2. Materials and methods

The boundary conditions for the clusters, i.e. the effect of atoms in the bulk of a solid on the atoms of the surface group included in the cluster was taken into account with the help of a model of an orbital-
The selected fragment is a crystalline pseudocell, the orbital, electronic, and core composition (OSC) simulating a volume fragment of an ideal crystal must correspond to the stoichiometry of the modeled object. The basic set of OSC includes all valence atomic orbitals and electrons of internal atoms, and from boundary atoms, only those HLOs that correspond to σ-bonds with internal atoms. The number of electrons and the charge of the core introduced into the OSC from the BA (which in the general case can be fractional) correspond to the fraction of HLO participating in the OSC basis.

The total number of electrons for all atoms, the number of basic orbitals and the total charge of the core must be equal or multiple of those integer values that correspond to the formula unit of the simulated structure [6]. The transition from the OSC, which simulates the bulk structure of a solid, to cluster models of surface centers is carried out by dividing the “volume” OSC into its component parts corresponding to the simulated surface centers [9]. The boundary connections of the sorbent clusters closed on the BA silicon Si*. Each Si* atom introduces one sp3-hybrid orbital oriented towards the adjacent intracluster oxygen atom, one electron and the core charge 1 into the OSC basis. This means that silicon BAs do not participate in the OSC entirely, but only by “part” (one-quarter) corresponding to the share of its participation in the chemical bond with the neighboring oxygen atom.

Tables 1 and 2 show the electronic and energy characteristics of the structure of cluster models of aluminosilicates and silica by various methods. Separate designations: q is the charge of an atom; W is the Weiberg bond index; EVBMO is the energy of the valence band of the molecular orbital; ENVMO is the energy of the non-valent band of the molecular orbital [10-12].

By the example of these clusters, it is also seen that with an increase in the angle \( \angle \text{SiOH} \), the absolute values of the charges on the H, O, and Si atoms of the silanol group increase slightly, and the Weiberg indices of the corresponding bands remain almost unchanged [13].
When studying the adsorption of a number of metal ions on aluminosilicates, it was found that in a wide pH range many cations are durably adsorbed on aluminosilicates, and in some cases irreversible sorption is observed. Ammonium, potassium, rubidium, cesium, iron, cobalt, nickel, manganese (II), chromium (III), zinc, cadmium, lead, mercury, copper and rare earth ions are strongly adsorbed. At the same time, sodium, aluminum, gallium, zirconium, and molybdenum (VI) ions are captured during adsorption from solutions [14-16]. These ions can be desorbed not only by acidification of the eluting solution, but also by washing the sorbent with water.

Analysis of the results obtained in the study of the adsorption of cations made it possible to draw an initial conclusion: those ions that contain vacant d or f orbitals form durable adsorption complexes with aluminosilicates. The calculations were carried out taking into account the effect on the interaction energy with the silonal and siloxane groups of the sorbent s-, p-, d- and f-orbitals of cations (table 3).

| Sorbate | CL-1 | CL-2 | CL-3 | CL-4 | -ΔE_theor | -ΔE_exper |
|---------|------|------|------|------|-----------|-----------|
| NH₄⁺    | 7,1  | 7,5  | 7,8  | 12,1 | 11,9      |           |
| Na⁺     | 4,3  | 4,3  | 4,5  | 5,5  | 4,5       |           |
| K⁺      | 6,5  | 6,5  | 6,7  | 12,5 | 12,1      |           |
| Rb⁺     | 7,1  | 7,1  | 7,3  | 17,5 | 16,1      |           |
| Cs⁺     | 8,5  | 9,1  | 9,5  | 21,5 | 20,5      |           |
| Ca²⁺    | 7,5  | 7,5  | 7,5  | 8,3  | 8,1       |           |
| Sr²⁺    | 7,2  | 7,2  | 7,2  | 8,1  | 8,0       |           |
| Ba²⁺    | 6,3  | 6,2  | 6,3  | 7,5  | 6,3       |           |
| Fe³⁺    | 15,1 | 15,2 | 15,5 | 23,5 | 22,9      |           |
| Zn²⁺    | 5,8  | 5,8  | 5,8  | 7,5  | 6,8       |           |
| Cd²⁺    | 6,1  | 6,3  | 6,5  | 10,5 | 7,6       |           |
| Pb²⁺    | 8,5  | 9,1  | 9,8  | 26,5 | 23,2      |           |
| Hg²⁺    | 12,5 | 13,1 | 14,5 | 21,5 | 23,7      |           |
| Cr³⁺    | 10,5 | 10,5 | 10,5 | 16,5 | 13,7      |           |
| Mn²⁺    | 17,1 | 18,5 | 19,5 | 27,5 | 25,4      |           |
| Ti⁴⁺    | 17,1 | 17,5 | 20,5 | 28,5 | 25,1      |           |
| Pr³⁺    | 16,5 | 16,5 | 17,1 | 22,5 | 21,5      |           |
| Nd³⁺    | 16,5 | 16,7 | 17,5 | 22,5 | 22,1      |           |
| Gd³⁺    | 17,5 | 17,5 | 18,1 | 29,5 | 25,3      |           |

As shown by the results of the calculations of ΔE_exper and ΔE_theor (for clusters 1-4), it is possible with a high degree of probability to make a prediction of the mechanism of the capture of cations by clusters of different structure. Now it can be considered proven that cations having vacant d and f orbitals form AKs with the participation of cluster 4 [17]. Proof that this particular cluster configuration is most likely is also due to the fact that sorbents C and CB from solutions in which the most different ratio is taken (for example, 1: 10,000) K: Na or Rb: Na or Cs: Na selectively sorbs K, Rb and Cs, and Na remains in solution [18].

Flasks of the Astrakhan region, are used to extract from water of varying degrees of salinity of potassium, rubidium, cesium, calcium, strontium and barium ions. For this purpose, the adsorption of the listed ions from specially prepared solutions, as well as from the water of natural reservoirs and brines, which filled the tanks for storing gas condensate and liquid hydrocarbons, which were created by a special ‘Vega’ project, was studied.

The content of all considered ions was determined by flame photometry and atomic absorption spectroscopy. The adsorption in the dynamic mode. The flow system was loaded with 2 kg of sorbent -
crushed flasks with a particle diameter of from 20 to 50 mm. Water was passed through this sorbent at a rate of 1 cm³/s until the content of the studied ions in the flowing water reached 10% of the content of these ions in the initial water [19]. The results of the experiments are shown in table 4.

Table 4. Changes in the content of metal ions in aqueous media depending on time. Sorbent - flask crumb diameter of 20-50mm.

| Water source or solution | Initial content of ions, mg/dm³ | Content of ions, mg/dm³ depending on transmission time (min) |
|-------------------------|---------------------------------|----------------------------------------------------------|
|                         | 1 | 10 | 60 | 600 | 6000 | 1 | 10 | 60 | 600 | 6000 |
| The solution prepared by dissolving salts in dist. water. | Ca²⁺ | 100 | 0.01 | 0.01 | 0.01 | 0.10 | 5.00 | 10.00 |
|                         | Sr²⁺ | 50 | 0.01 | 0.01 | 0.01 | 0.10 | 0.25 | 5.00 |
|                         | Ba²⁺ | 10 | 0.01 | 0.01 | 0.01 | 0.10 | 0.25 | 5.00 |
|                         | K⁺ | 100 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
|                         | Rb⁺ | 20 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
|                         | Cs⁺ | 10 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| er. Bereket, 1000 m to the S-E from the Astrakhan Gas Processing Plant | Ca²⁺ | 20 | 0.005 | 0.005 | 0.005 | 0.01 | 1.0 | 2.0 |
|                         | Sr²⁺ | 5 | 0.001 | 0.001 | 0.001 | 0.005 | 0.005 | 0.008 |
| Brines from hydrocarbon storage tanks | Ba²⁺ | - | - | - | - | - | - | - |
|                         | K⁺ | 20 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
|                         | Rb⁺ | 0.5 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
|                         | Cs⁺ | 0.1 | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. | не обн. |
| Brines from hydrocarbon storage tanks | Ca²⁺ | 50 | 0.01 | 0.01 | 0.01 | 0.05 | 0.5 | 5.0 |
|                         | Sr²⁺ | 10 | 0.01 | 0.01 | 0.01 | 0.02 | 0.05 | 1.0 |
|                         | Ba²⁺ | - | - | - | - | - | - | - |
|                         | K⁺ | 250 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.10 | 10.0 |
|                         | Rb⁺ | 0.5 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
|                         | Cs⁺ | 0.5 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| "AKSOL". Prepared 20% aqueous solution | Ca²⁺ | 20 | 0.005 | 0.005 | 0.005 | 0.01 | 0.01 | 5.0 |
|                         | Sr²⁺ | 20 | 0.005 | 0.005 | 0.005 | 0.01 | 0.01 | 5.0 |
|                         | Ba²⁺ | - | - | - | - | - | - |
|                         | K⁺ | 500 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 5.0 |
|                         | Rb⁺ | 15 | 0.001 | 0.001 | 0.001 | 0.001 | 0.1 | 2.0 |
|                         | Cs⁺ | 15 | 0.001 | 0.001 | 0.001 | 0.001 | 0.1 | 2.0 |

*Salt of the enterprise "AKSOL".*

Static adsorption. At the bottom of three steel tanks (St-3) (1 × 1 × 0.5) m³, a layer of 50 mm of flasks with a diameter of 20-50mm was poured, river sand, or a platform were not specially created. 250 dm³ of the investigated water were poured into each tank and the content of ions in this water was determined at certain intervals [20-21]. The results of the experiments are shown in table 5.

4. Conclusions

As can be seen from the results given in table. 4 and 5, the grains from the flasks can be effectively used to purify water from calcium, strontium, barium, potassium, rubidium and cesium ions. If the reservoir contains a significant amount of these elements, so the best option is to cover the bottom of this reservoir with a layer of crushed flasks, and after a certain time the concentration of these elements in the water will sharply decrease. The elements themselves are not desorbed (Table 5) for a long time.
Table 5. Water purification from metal ions in a static mode with a crumb of flasks with a particle diameter from 20 to 50 mm.

| Water source or solution | Initial content of ions, mg/dm³ | Content of ions, mg/dm³ depending on transmission time (days) |
|--------------------------|--------------------------------|----------------------------------------------------------|
|                          |                                | 1   | 10  | 30  | 60  | 300 |
| The solution prepared by dissolving salts in dist. water. | Ca²⁺ | 100 | 10,0 | 0,1 | 0,01 | 0,01 | 0,01 |
|                          | Sr²⁺ | 50  | 10,0 | 0,1 | 0,01 | 0,01 | 0,01 |
|                          | Ba²⁺ | 10  | 5,0  | 1,0 | 0,10 | 0,05 | 0,01 |
|                          | K⁺  | 100 | 0,01 | 0,001 | 0,001 | 0,001 | 0,005 |
|                          | Rb⁺ | 20  | 0,01 | 0,001 | 0,001 | 0,001 | 0,005 |
|                          | Cs⁺ | 10  | 0,01 | 0,001 | 0,001 | 0,001 | 0,005 |
| er. Bereket, 1000 m to the S-E from the Astrakhan Gas Processing Plant | Ca²⁺ | 20  | 0,05 | 0,01 | 0,01 | 0,01 | 0,01 |
|                          | Sr²⁺ | 5   | 0,05 | 0,01 | 0,01 | 0,01 | 0,01 |
| Brines from hydrocarbon storage tanks | K⁺  | 20  | 0,01 | 0,001 | 0,001 | 0,001 | 0,002 |
|                          | Rb⁺ | 0,5 | 0,005 | 0,001 | 0,001 | 0,001 | 0,002 |
|                          | Cs⁺ | 0,1 | <0,001 | <0,001 | <0,001 | <0,001 | <0,001 |
| * Salt of the enterprise "AKSOL". Prepared 20% aqueous solution | Ca²⁺ | 20  | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 |
|                          | Sr²⁺ | 10  | 0,01 | 0,01 | 0,01 | 0,01 | 0,01 |
|                          | Ba²⁺ | -   | -    | -    | -    | -    | -    |
|                          | K⁺  | 250 | 0,01 | 0,001 | 0,001 | 0,001 | 0,005 |
|                          | Rb⁺ | 0,5 | 0,005 | <0,001 | <0,001 | <0,001 | <0,001 |
|                          | Cs⁺ | 0,5 | 0,005 | <0,001 | <0,001 | <0,001 | <0,001 |

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