

## MODIFIED NATURAL SORBENTS AS RADIONUCLIDES ABSORBERS

**Razvorotneva L.I., Gilinskaya L.G., Markovich T.I.** (IGM SB RAS)

mark@uiggm.nsc.ru; fax: (383) 333-27-92; tel.: (383) 333-31-12

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Geochemical barriers are extensively used in the last decade for the purpose of the environmental protection from uncontrollable radionuclide migration. Not only existent natural geochemical barriers are used, but also anthropogenic barriers are built-up. The natural materials (soil, rock and etc.) can be the components to constitute depending on pollutants these barriers. For example the clay minerals (montmorillonites and kaolin) are used for bonding and long-term confinement of radionuclides.

To generate modified sorbents for the purpose of absorptive capacity increasing, the method of modification of clay minerals by organic components, specifically by humic acids escaped from peat.

Humic acids (HA) from the lowdown and upper peat were segregated by several techniques: peat decalcification by hydrochloric acid, by alkaline extraction at different temperatures (40-70°C), precipitation by concentrated hydrochloric and sulfuric acids [1]. The Dragunova's method defined the content of acid functional groups (from 0.67 to 1.00 mg-eq /g HA). According to the NMR<sup>13</sup>C data the proportion between different functional groups in HA was determined. Thus, the carboxyl groups (110-200 mkD) showed the proportion of 10.1 – 12.7, the aromatic (110-160 mkD) were over the range 35.3 to 43.8 and etc.

The montmorillonite Ca- of the Kamalinsky deposit of Krasnoyarsk Territory was used as a matrix, and also the kaolin and illite of the Troshkovsky deposit of Irkutsk region were. The patterns were subjected to some prior operations before the modification: water swell, converting in soda forms in some cases, pH changing, pretreatment by buffer solutions. After the modification the sediment was washed away from foreign ions, focused on filters or by means of three methods: centrifuging at 5-8·10<sup>3</sup> R.P.M., micro filtration (through the cellulose-acetate filter with filtration rating 0.45 mkD) and ultra filtration (through the filter with filtration rating fitting the molecular mass of 10 kD).

The effectiveness of the modification of clay minerals by organic components was shown by the results of the X-ray diffraction analyses; they displayed that the treatment of aluminosilicates described above was accompanied by the introduction of the organic compounds into their interplanar spacing. The X-ray patterns of the examined samples were obtained by the powder method at the diffractometer ДРОН-3М with the copper anathode. Immediately before the recording the samples were heated at 105°C for removing the absorbed moisture that affected the interval between packets of the given and modified montmorillonite. The received diffraction patterns reveal that the first diffraction maximum of montmorillonite in comparison with the natural clay was shifted to the smaller angles, it fitted to larger interlayer spacing. The difference between the interlayer intervals  $d_{001}$  of modified (17-28 Å) and given (12.8 Å) samples is a quantitative indicator of changing in the crystal structure of a mineral. It indicates the introduction of organic cations into interpacket spacing of clay. While organic molecules are introduced in the kaolin structure, the first interplanar basal spacing is increasing subjected to the size of the introduced molecules from 7,12 to 10,8- 14 Å.

The amount of organic matters adsorbed by the clay during the developing of a modified organic-mineral sorbent was determined from the termogravimetry of given and modified samples according to the TG and DTG curves. The research was carried out by termogravymetr of the F. Paulik, E. Paulik, L. Erdey system with the heating rate 10 d/min, the temperature range of 20 to 1000°C, the TG sensitivity – 200 mg; inaccuracy of 0.1%. The loss of mass of the modified pattern is made up from the loss of moisture in the given clay and the organic matter burning. The calculations showed that the amount of organic compounds introduced into the structure of clay minerals makes up 75-90 mg-eq/100 gr of the clay.

The area of the specific surface of the obtained samples and the textural analysis were defined by the nitrogen adsorption at 77°K. The adsorption isotherms were studied by the BAT method. The size of the specific surface vary from 80-95 m<sup>2</sup>/gr for the samples modified by amines and 132-147 m<sup>2</sup>/gr for the samples modified by humic components from peat. It should be noted that the modified sorbents have considerable pore space (the filtration rating over the range 45 to 320Å), that provides free volume diffusion of the solution molecules. While the ions implanted during the sorption and the additional layers of water are interposed, the volume of micropores increases from 0.12sm<sup>3</sup>/gr to 0.24-0.56 sm<sup>3</sup>/gr and its diameter increases from 97 to 256 Å.

The special attention was paid to the role of water in successful operation of the geochemical barriers based on natural and modified materials. To characterize the fraction of the bound water, the strength of its bonding with the lattice ions, the differential-thermal curves (DTC) of kaolin and montmorillonite in dry and hydrated forms were obtained. The DTC curves show three endoeffects: the first – clear, drastic, corresponding to the removal of adsorbed water (up to 140°C); the second – very stretched and non-intensive, appearing as a result of the step-by-step loss of OH<sup>-</sup> mineral groups (up to 210°C); the third one (850°C) can be explained by the partial destruction of the mineral crystal lattice. The montmorillonite structure the most actively interacts with the water molecules, during this interaction the amount of retained water and the interlaminar water of a mineral increase from 13 % to 20 % and from 1.1 to 2.75 % respectively. Such interaction of the surface with the water causes the twofold growth of the quantity of hydroxyl groups which participate in the elements' bonding.

The sorbents quality was determined by the meaning of the capacity index of cation exchange (CCE) which is calculated according to the experimental results of sorption isotherm. Thus the CCE value for the samples modified by the humic components accounts for 3156 mg-eq UO<sub>2</sub><sup>2+</sup> or 15.6 mg-eq Sr<sup>2+</sup> or 78.9 mg-eq Cs<sup>+</sup> /for 100gr of the sorbent dry substance. The aminomodified montmorillonite gives the highest degree of saturation towards strontium - when pH 8.5 about 1800 mg-eq/100gr of the sorbent (the experiments were carried out using stable isotopes with 0.5 mol/l concentration and radioactive solutions of 10<sup>4</sup> Bk/l order). The solution flow through the columns filled with the modified sorbent during 15-20 days. To characterize the degree of extraction of the radionuclide by the sorbent the distribution coefficient (K<sub>d</sub>) was counted, K<sub>d</sub> does not depend on the ion concentration in the solution. It is noticed that K<sub>d</sub> considerably increases with the lapse of time for <sup>90</sup>Sr and <sup>137</sup>Cs. After the equilibrium in the sorbate-sorbent system has been established, the K<sub>d</sub> values become equal. However, the matrix selectivity towards the double-charge cations in comparison with the single-charge cations shows that the distribution coefficient for strontium is higher than for cesium. The experiments in the flowing conditions displayed that at the first hours the concentration of strontium falls to 92-98% in the eluates depending on the type of the process water. The sorption rate <sup>85</sup>Sr during the first hour was 456312 Bk/kg a minute. The difference between the sorption rates subjected to the water contents made up 6-8%. At the same time 60% Ca, 74.3% Na were washing from the composition of anthropogenic waters. The K<sub>d</sub> value was changing from 2.1\*10<sup>2</sup> to 6.7\*10<sup>3</sup> ml/gr. When the technical solution with the specific activity of <sup>137</sup>Cs 5.2 kBk/kg was running through the columns with the sorbent, the <sup>137</sup>Cs content achieved the level of the tolerable specific activity for the drinking water (96 Bk/kg). The K<sub>d</sub> indices were changing from 1.5\*10<sup>2</sup> to 2.2\*10<sup>3</sup> ml/gr. The experiment reveals that the effectiveness of the cesium absorption depends on the solution ionic strength, and the regularity is K<sup>+</sup>>>Na<sup>+</sup>>Ca<sup>2+</sup>.

It is generally accepted that the absorption of the dissolved forms of the liquid radionuclides occurs by the cation exchange. To make the exchange properties of clay minerals more considerable, they were treated by the inorganic acids which effectiveness was the following: H<sub>2</sub>SO<sub>4</sub> ≤ HNO<sub>3</sub>~HCl ≤ H<sub>3</sub>PO<sub>4</sub>. The most significant effect can be observed during the modification of the surface by the orthophosphoric acid almost for all types of clay and in short time. It can be explained by the fact that the phosphate containing surfaces tend to produce strong complex bonds with the rare earth and transuranium elements. Besides, the stability of such complexes is so high that they do not break even at 800°C. According to the preliminary results the clays which have been treated by the phosphoric acid possess the larger ion-exchange capacity than the natural phosphate minerals. It is proved by the comparison of experimental data of the treated and natural clay analyzed by the method of infrared spectroscopy. The cation of ammonium is of particular interest, being introduced into the aluminosilicate matrix it easily gives the proton. The clays which have been pretreated by bicarbonate of ammonium better sorb the elements in comparison with the given samples treated by sodium chloride. To make the structure imperfection of the crystal lattice and, consequently, its capacity more significant the following method was applied: the mechanical activation in the centrifugal planetary-type mill EG 2\*150 and M-3 into the nephrite drum with nephrite balls during 5, 10, 20 and 30 minutes. Judging by the changes of the fine structure characteristics (the decrease of ACD and microdeformations) during 10 minutes of the mechanical activation meso- and microflaws appear, that lead to the pickup of intrusion ions. The number of such disturbances rises at the time of the particle size reducing, at the same time the EPR method shows up that the uncompensated paramagnetic states emerge. The formation of the centers like O<sup>-</sup>, O<sub>2</sub><sup>3-</sup>, OH<sup>0</sup>, Si-O<sup>-</sup> was recorded in the studied samples; they actively participate in bonding of adsorbed ions.

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