

ION-EXCHANGE MATERIALS BASED ON HYDROXOOXOTITANE FOR WASTE WATER PURIFICATION

Marina V. Maslova, Lidia G. Gerasimova

Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials,
Kola Science Center, Russian Academy of Sciences, Apatity, Murmansk region, 184209 Russia

Abstract

The present investigation deals with preparation of a stable titanium (IV) colloid solution from ammonium oxysulfotitanate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and oxysulfotitanate $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ solutions. The colloid precursor was used in the synthesis of spherical TiO_2 particles with ion-exchange properties. A relationship between the nature of the initial solution, the number of terminal and bridging OH groups in resulting sol, and the sorption properties of hydroxooxotitane prepared by sol–gel method has been established. Studies of the exchange behavior of different cations have confirmed the dominant role of bridged OH groups.

Key words: *hydroxooxotitane, ion-exchange material, sorption properties, radioactive and water waste purification*

1. INTRODUCTION

Ways to the synthesis of hydrated hydroxooxotitane (HOT) are being actively explored due to its unique physical and chemical properties that open wide opportunities for practical application. Special attention has been paid to HOT as a sorbent for air and water purification. Works on the waste water treatment to remove arsenic, chromium, heavy metals, fluorine, phenolic compounds, and organic dyes are known. Due to its high thermal stability, resistance to oxidation, very low solubility in both acidic and alkaline solutions and ability to have its ion-exchange properties tailored HOT can be used for deactivation and purification of waste water containing radioactive isotopes, heavy and toxic metals (Shabana and El-Dessouky, 2002; Ho, et al., 2004; Zhijun, et al., 2005).

There are many publications dealing with preparation and studying of the properties of hydrated hydroxooxotitane (Goroshchenko, 1972; Dobrovolskii, 1988; Miliordos, et al., 2011; Pletnev, et al., 1986; Godneva and Motov, 2006), where the authors note that the HOT structure and functional properties are strongly dependent on the synthetic conditions used: the nature of initial solution, concentration parameters, methods and modes of precursor and final product precipitation. The methods for the HOT precipitation are essentially two: thermal hydrolysis and alkaline neutralization of titanium(IV) solutions. During the thermal hydrolysis of titanium(IV) salts, the protons are gradually removed from the initial titanium hexaaquacomplexes to yield the polynuclear forms further transforming to macromolecular structures (Gerasimova and Maslova, 2011, 2012). It is very difficult to control the phase formation because the system is unstable, as a rule. The stages of primary species transformation proceed competitively rather than consecutively. Uncontrolled synthesis without regulation of the solid phase coagulation rate leads to inhomogeneity of its phase and dispersed composition and therefore deteriorates the technical characteristics of final products. During the alkaline neutralization of titanium(IV) solutions, the process of precipitate formation is conducted with the use of gel and sol–gel methods. The gel approach is based on precipitating of HOT from a titanium salt solution followed by washing and drying of the gel-like precipitate (Makarova and Belinskaya, 1986; Amflet, 1966; Boichinova, 1984). The sol–gel process consists of the following main stages: preparation of a metal hydroxide sol, gelation of sol drops in the precipitant solution, and washing and drying of gel spheres (Sharygin, et al., 1980; Strekalovskii, et al., 1987; Reinten, 1973). In the sol–gel process, the stages of sol and gel formation are separated in time, therefore the gel spheres are made up from initially formed sol particles, which provides the preparation of HOT as mechanically strong granules of prescribed size with reproducible properties. The best known sol–gel synthesis consists in preparation of metal alkoxide sols followed by the formation of spherical particles upon dropwise into

organic solutions (Sugimoto and Kojima, 2008; Eiden-Assmann, 2004; Mine, et al., 2005; Pal, et al., 2007). The drawbacks to this method are the use of expensive organometallic compounds and complex instrumentation.

In this work, we consider the possibility of using new, cheap reagents for the synthesis of spheroidal granulated HOT and substantiate some original techniques for preparing a sorbent with high ion-exchange characteristics.

2. EXPERIMENTAL

The titanium-containing sol was obtained from titanium salts: oxotitanium sulfate $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ (OTS) and ammonium oxotitanium sulfate $(\text{NH}_4)_2\text{Ti}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (AOTS), which are byproducts of integrated processing of titanium-containing mineral and technogenic raw materials (Gerasimova et al., 2011). The titanium concentration in initial solution varied from 54 to 110 g/L of TiO_2 . The sol was obtained using a 10% ammonia solution, which was gradually added on stirring to the titanium solution until the $\text{H}_2\text{SO}_4/\text{TiO}_2$ weight ratio reached 0.1–0.5, which corresponds to pH 2.0–3.5. The resultant colloidal system mainly consisted of a titanium sol of variable composition $\text{TiO}_{1+x}(\text{OH})_{2(1-x)}$ ($x < 1$) with a particle size of 1–100 nm (Miliordos, et al., 2011; Chernykh and Boichinova, 1971). To obtain a narrow fractional composition, the sol was peptized by slow heating to 65–70°C for 1 h; the prepared colloidal solution was stabilized by keeping for 2 h, whereupon it was quickly cooled to ambient temperature. These conditions promote the polycondensation reactions between molecular precursors followed by titanium-oxo-polymer network formation (Gerasimova and Maslova, 2011). The content of disperse phase in the sol (%) was determined by adding of strong HCl to the sol aliquot until the volume ratio of the components was equal 1:1. The resultant suspension was filtered to remove precipitate, and the residual titanium(IV) concentration in the liquid phase was determined. The concentration was calculated by the formula (Gerasimova, et al., 2011)

$$A = (C_f/C_0) \times 100,$$

where A is the amount of titanium disperse phase in sol, %; C_0 is TiO_2 concentration in initial titanium solution, g/L; C_f is TiO_2 concentration in filtrate, g/L.

Highly spherical particles were produced from the sol solution by slowly adding into concentrated ammonia solution at room temperature. The precipitate was separated from the liquid phase, the mother liquor was removed by washing, first with a 5% NH_4OH solution, next with water, and then the precipitate was dried in air yielding a product, which was HOT. The ion-exchange ability of prepared samples was determined by the known procedure (Chernykh and Boichinova, 1971). The metal salt solutions at a concentration of 0.6–1 g/L towards the metal were used as samples for purification. The ion-exchange capacity for the metals was calculated after 24 h of gentle agitation of the gel and solution by the batch method. The concentration of OH^- groups in HOT was determined by the fluoride procedure (Gerasimova, et al., 2002). The specific surface and total pore volume were determined by BET analysis from nitrogen adsorption–desorption isotherms. The pore size distribution was determined by nitrogen thermal desorption (BJH method); the structure microporosity was determined from the dependence of adsorbed nitrogen volume on the adsorbate film thickness (t-plot method).

3. RESULTS AND DISCUSSION

The titanium(IV) concentration in initial solution plays an important role for the formation of structure and ion-exchange properties of HOT. Stable colloidal systems were obtained as sols from OTS and AOTS solutions with different titanium(IV) concentrations and colloidal portion concentration that varied within 50–80%. The titanium-containing colloidal particles in the studied sols were polynuclear complexes where bonding results from hydroxo or oxo bridges. Drop-wise addition of such a sol into an ammonia solution results in neutralization of residual acidity and the formation of a gel network

Accompanied by the development of hydrogen bonding among the monomer units whose composition is dependent on the content of colloidal titanium(IV) in the sol.

Table 1 shows that the TiO_2 content in HOT decreases while the NH_4^+ and water contents increase in response to rising titanium(IV) concentration in initial solution. These HOT are formed by small associates with a minimal degree of crosslinking between the neighboring titanium atoms, which leads to the growth of content of terminal OH^- groups in precipitate. The degree of ammonium adsorption depends on the structure of colloidal particles. The higher colloidal titanium content in sol, the larger associates resulting from oxo-complexes and, correspondingly, the smaller the number of terminal OH^- groups capable of binding to ammonium. These particles have a less branched structure, hence they are less hydrated. The HOT obtained from ammonium salt of AOTS was found to contain more ammonium ions compared to the HOT prepared from OTS.

Table 1. Synthesis conditions and composition of HOT

Sample no.	Synthesis conditions		Chemical composition, mol			Terminal OH ⁻ groups	Bridged OH groups
	TiO ₂ init, g/L	Colloidal particles, %	TiO ₂	NH ₄ ⁺	H ₂ O	mol/mol TiO ₂	mol/mol TiO ₂
AOTS							
1	54	50	0.96	0.21	1.22	0.107	0.826
2		60	0.97	0.16	1.21	0.097	0.718
3		80	0.97	0.12	1.17	0.091	0.646
4	84	50	0.93	0.24	1.33	0.138	0.790
5		60	0.93	0.17	1.32	0.106	0.711
6		80	0.93	0.13	1.29	0.097	0.613
7	110	50	0.80	0.27	1.72	0.207	0.752
8		60	0.81	0.19	1.72	0.172	0.675
9		80	0.83	0.13	1.75	0.099	0.541
OTS							
10	54	50	0.95	0.19	1.11	0.062	0.841
11		60	0.96	0.15	1.12	0.055	0.823
12		80	0.99	0.13	1.08	0.054	0.814
13	84	50	0.94	0.20	1.16	0.053	0.853
14		60	0.95	0.16	1.14	0.049	0.841
15		80	0.96	0.13	1.12	0.042	0.836
16	110	50	0.92	0.22	1.25	0.040	0.869
17		60	0.92	0.17	1.23	0.038	0.867
18		80	0.92	0.12	1.21	0.037	0.843

The effect of ammonium concentration in initial solution on the amount of terminal and bridging OH^- groups bound to titanium. According to our findings, the total amount of OH^- groups in HOT decreases due to the formation of high molecular oxo complexes that produce colloidal particles via bridging Ti-O-Ti bonds with increasing of colloidal titanium(IV) content in the sol.

The growth of titanium(IV) concentration in initial solution leads to increase in the quantity of OH^- groups in HOT due to proliferation of the number of terminal hydroxyl groups upon synthesis from AOTS solutions and bridged OH^- groups upon synthesis from OTS solutions (Fig. 1). This is caused by the presence of ammonium ion in the sol obtained from AOTS solution, which prevents the condensation of complexes promoting the formation of hydroxide bridged bonds (Sugimoto and Kojima, 2008).

The sorption capacity of HOT as an ion-exchange material is determined by the surface properties of its particles and the number of OH^- groups, which in turn depends on the content of colloidal titanium in the sol. Structures containing titanium(IV) atoms bound via bridging OH^- groups should display a better acid-type dissociation (due to the labile proton). Terminal Ti-OH groups exhibit a lower protonation ability and could be predominantly basic and exchangeable with other anions.

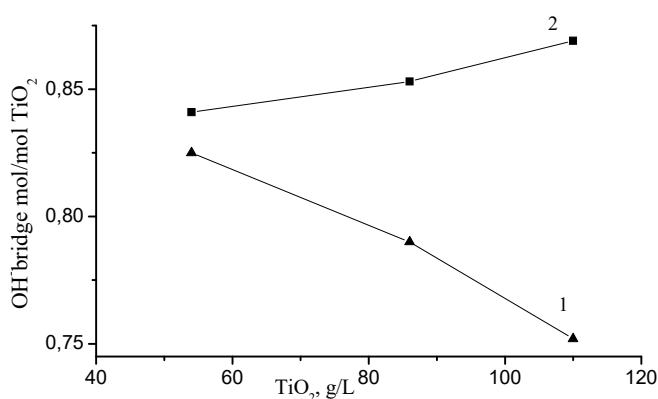


Fig. 1. Variation of content of bridging OH^- groups in HHOT depending on titanium(IV) concentration in initial solution: 1, AOTS; 2, OTS.

Figure 2 shows diagrams built in composition vs property coordinates, demonstrating the dependence of the sorption properties of HOT on the OH^- group nature. According to our findings, the sorption capacity toward Sr^{2+} of the HOT samples obtained from OTS is higher than that for the samples prepared from AOTS, which is caused by the nature of OH^- groups. The products obtained from OTS contain a larger amount of bridged groups. Bonding with oxygen in these groups is weakened because of strong polarization by titanium(IV) cations, which enhances their protolytic properties and hence the ion-exchange ability. Moreover, the sorption ability decreases for all samples when colloidal titanium content in sol rises in spite of the growth of passive OH^- groups concentration.

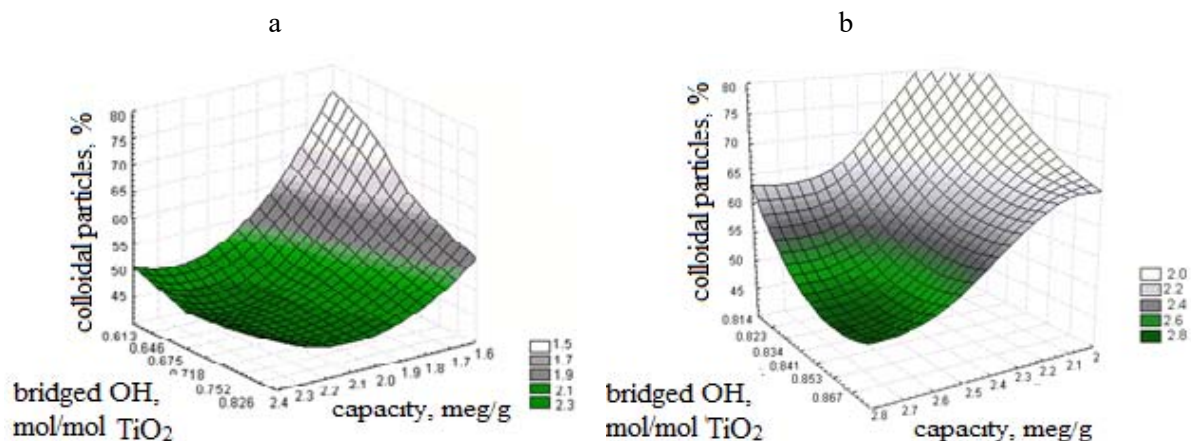


Fig. 2. Effect of the content of bridged OH^- groups in sol on the ion-exchange properties of HOT obtained using AOTS (a) and OTS (b) in initial solution: (a) AOTS, (b) OTS.

Obviously, this is caused by changing of the sample porosity. Analysis of porosity of the obtained samples (Table 2) displays that the growing titanium(IV) concentration in initial solution and the colloidal titanium content in sol are accompanied by increase in the surface area of the samples. Obviously, the composition of initial solution has a determining effect on the surface properties of HOT. The porous system begins to form already during the process of sol preparation in initial solution, which is manifested by the formation of hydroxo-oxo bonds between the neighboring titanium(IV) atoms. Thus, the resultant associates consist of hydrolyzed species with different crosslinking extents. It was noted that both the surface area and micropore volume of the samples increase with increasing of the content of colloidal titanium in sol due to the formation of a rigid framework of the gel by growing $-\text{Ti}-\text{O}-\text{Ti}-$ polymeric units. A part of the exchange groups proves to be in an energetically unfavorable position that decreases the HOT sorption capacity.

Table 2. Surface properties of HOT

Sample no.	S, m^2/g	V_{pore} , cm^3/g	$V_{\text{micropore}}$, cm^3/g	D_{av} , Å
AOTS				
1	147.1	0.0801	0.0067	26.9
2	254.3	0.1029	0.0107	25.9
3	267.1	0.1054	0.0126	24.9
7	236.9	0.0822	0.0118	27.4
8	272.9	0.1045	0.0159	26.2
9	281.3	0.1066	0.0174	24.4
OTS				
10	163.1	0.0781	0.0043	28.2
11	169.4	0.0806	0.0056	26.9
12	175.8	0.1015	0.0066	25.1
16	167.1	0.0685	0.0107	29.0
17	173.2	0.0829	0.0094	28.1
18	251.8	0.0841	0.0104	27.6

The surface area of HOT particles also increases with increasing of the content of titanium(IV) in the initial solution in sol. The average pore size slightly rises due to increasing of the mesopore size, which favors the elevation of the HOT sorption capacity. The adsorption–desorption isotherms (Fig. 3a) refer the obtained samples to type IV with an E-type hysteresis loop that characterizes mesoporous samples. This means that the porous system is mainly formed by cylindrical pores with necks (ink-bottle pores). Hysteresis in the region $0.5 p/p_0$ indicates the presence of transition pores. All synthesized samples have a narrow pore distribution range of 18–40 Å (Fig. 3b), which promotes the development of selective properties of the material toward ions of a particular size. The volume of micropores in the precipitates obtained from OTS solutions is smaller, which is indicative of the presence of a greater part of narrow mesopores in the porous system.

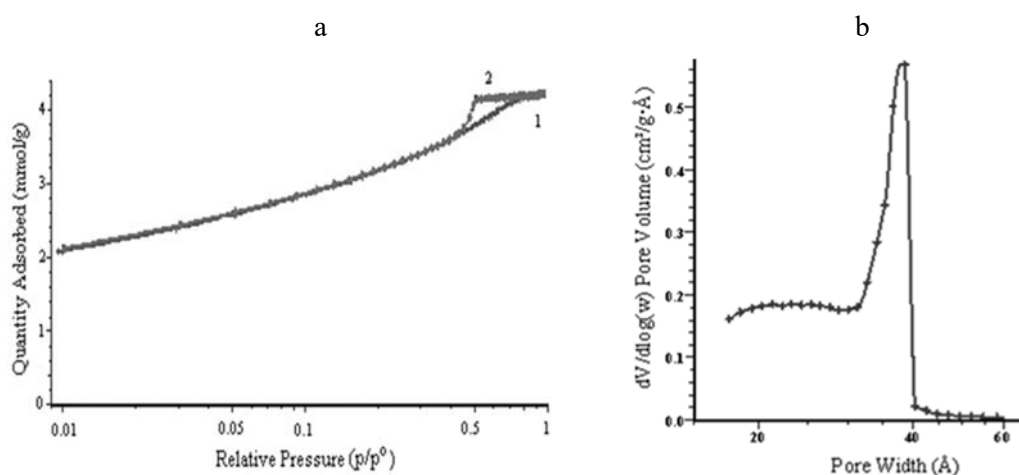


Fig. 3. Adsorption (1) and desorption (2) isotherms and pore size distribution curve (b) for a HOT sample.

The preferable sorption of bivalent metal cations (Sr^{2+}) in comparison with monovalent cations (Cs^+) is due to the cation size and, correspondingly, to the sterical hindrances emerging upon exchange of large cations. Thus, we have explored a new method of sol–gel synthesis of an ion-exchange material based on hydrated titanium dioxide from titanium salts: oxotitanium sulfate $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and ammonium oxotitanium sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The sorption capacity of the material was found to be determined by the concentration of bridging OH^- groups in HOT, which in turn depends on the content of colloidal titanium(IV) in the sol. Optimal concentration parameters for the synthesis were established (the colloidal titanium(IV) content in the sol should not enhance 50%), providing high sorption properties for HOT.

The ion-exchange capacity of titanium solids, synthesized from AOST (1) and OST solutions (2) with equilibrium pH are shown in Fig. 4 and 5. The samples were obtained from an initial solution with a titanium concentration about 54 g/L, and the contents of colloidal particles in the sol were about 80%. For both cations (Cs^+ and Sr^{2+}) the capacity continuously increases with a pH increase, which is characteristic of a weak acid exchanger. Increasing pH promotes ionization of the surface proton, which is expected to enhance the cation sorption.

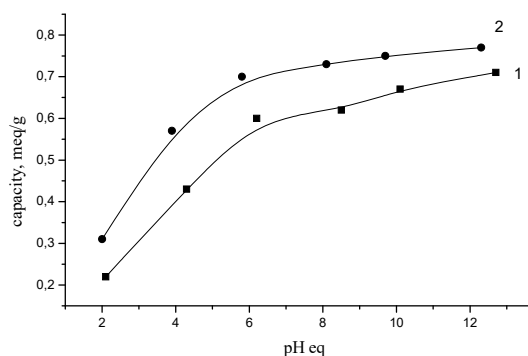


Fig. 4. Dependence of the Cs^+ uptake on the aqua pH.

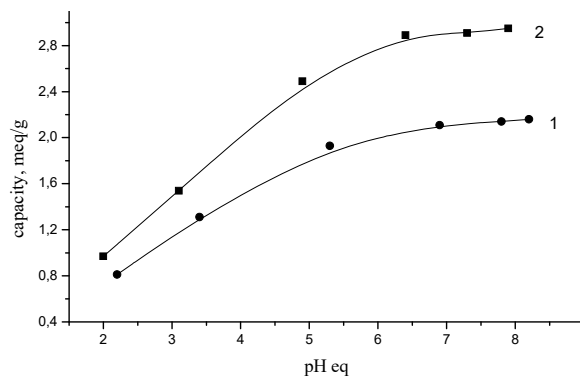


Fig. 5. Dependence of the Sr^{2+} uptake on the aqua pH.

The distribution coefficients (K_d) of Cs^+ and Sr^{2+} between the exchanger and their aqueous solutions were determined as a function of pH (Fig. 6). The plots of $\log K_d$ vs. equilibrium pH show that the hydrous titanium dioxide works efficiently in the alkaline pH range, K_d value for Sr^{2+} and Cs^+ cations reach 10^6 and 10^4 mg/L respectively.

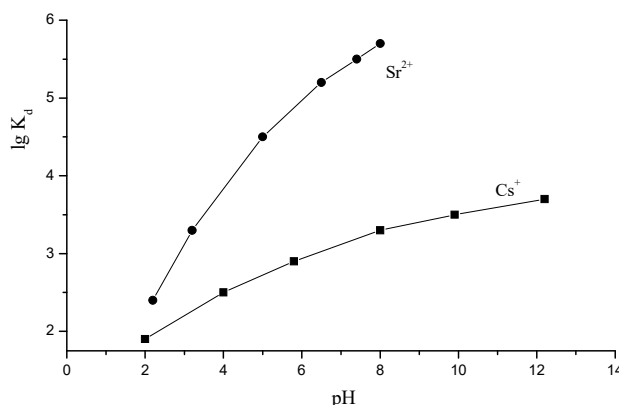


Fig. 6. Variation of K_d with pH on hydrous titanium oxide

As a rule, real LRW contain high levels of sodium and calcium ions competing for sorption centers with radionuclides. Separation of liquid wastes containing radioactive ions occurs under column operation. The distribution coefficient for a radionuclide allows to quantitatively estimate the maximum capacity that can be obtained in a dynamic mode based on the number of loaded sorption material and the volume of solution passed. The selectivity of HOT towards the Cs^+ and Sr^{2+} ions in the presence of Na^+ and Ca^{2+} ions at pH 6 was determined by the batch mode. Concentration of background ions were changed 0-2 mol/L, the amount of radionuclides was 10^{-3} mol/L.

As can be seen in Fig.7, the presence of non-radioactive competing ions decreases the sorption affinity to the ions of interest. For the Sr^{2+} - Ca^{2+} pair the distribution coefficient is about 10^4 ml/g until the concentration of the background salt reaches 0.15 mol/L; for Cs^+ - Na^+ under the same conditions the K_d value is 10^3 ml/g. Further increasing of the background salts content results in sharp decreasing in the sorption affinity towards the cations of interest, and when the concentration of Na^+ and Ca^{2+} ions reaches 2 mol/L, the K_d values are 35 and 180 for Cs^+ and Sr^{2+} , respectively.

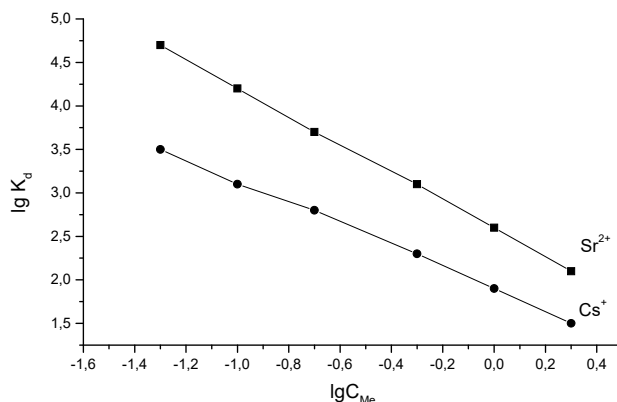


Fig. 7. Dependence of the distribution coefficient (K_d) in the systems Na^{+} - Cs^{+} and Ca^{2+} - Sr^{2+} on the background salts concentration

In neutral media, without a salt background, the uptake of strontium ions achieved 99.8% of the initial Sr^{2+} content in solution (fig.8). With $Ca(NO_3)_2$ as a background salt, the sorption level decreased abruptly to not higher than 65% at a sodium ions concentration in starting solution of 2 mol/L. Sodium ions also make up a considerable competition to strontium ions in the solution, and the sorption affinity of Cs^{+} sharply decreases from 89.7% in the absence of Na^{+} ions to 37% with a salt content of 2 mol/L. The results allow to predict the use of HOT in treatment of liquid radioactive wastes with low contents of background cations.

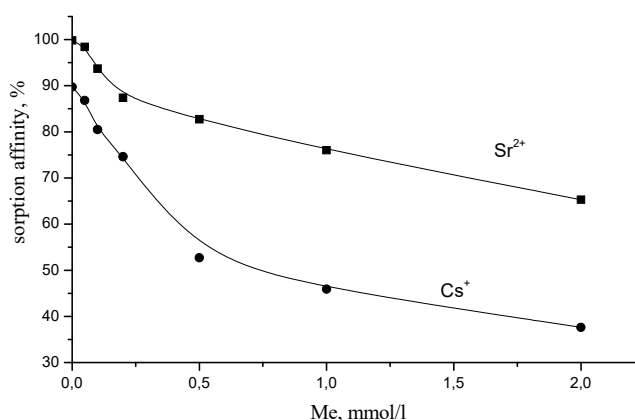


Fig. 8. Sorption affinity of Cs^{+} and Sr^{2+} ions in the presence of Na^{+} and Ca^{2+} ions.

According to the mass action law, the ion exchange in concentrated electrolyte solutions can be described by the following equation (Griessbach, 1963):

$\lg K_d = B - n \lg C$, where

C is the equilibrium concentration of electrolyte mol/L, B is a constant including the total exchange capacity of sorbent and exchange constant, n is the slope ratio of a straight line, numerically equaling the ratio between the charges of exchanging and macrocomponent ions.

In the case of ideal exchange, the distribution coefficient in changing electrolyte concentration should be expressed by a straight line with a slope $n=1$ when equal-charge ions exchange. We calculated the constant B and coefficient n by treating the data of the above equation (Fig.9). The values are given in Table 3.

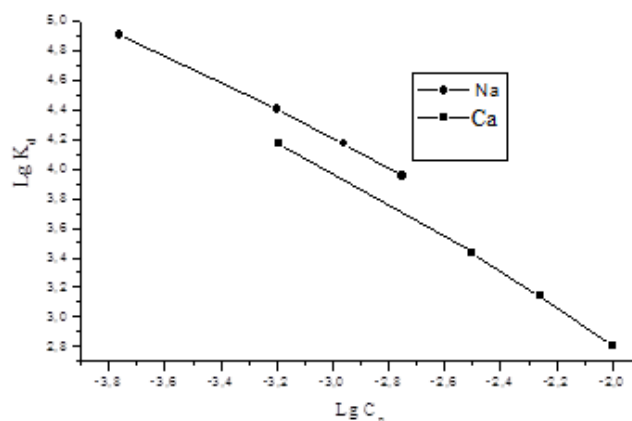


Fig. 9. Cs^+ and Sr^{2+} distribution coefficient (K_d) as a function of sodium and calcium concentrations in the solutions

Table 3. Approximation parameters for the $\lg K_d = B - n \lg C$ dependence and the exchange constant (K_{exch}); R is correlation coefficient

System	Parameter values			K_{exch}
	n	B	R	
Cs-Na	0.933	4.39	0.891	11.3
Sr-Ca	2.03	3.57	0.979	32.5

The B parameter was used to calculate the exchange constants according to the following equation (Incze, 1979):

$$\lg K_{\text{exch}} = B - \lg Q,$$

where Q is the sorbent total capacity, mmol/g

The obtained data are presented in Table 4. It is seen that the exchange constant in the presence of calcium ions is an order of magnitude greater than that with sodium ions.

CONCLUSIONS

Thus, we have explored a new method of sol-gel synthesis of an ion-exchange material based on hydrated titanium dioxide from the following titanium salts: oxotitanium sulfate $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and ammonium oxotitanium sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. The sorption capacity of the material was found to depend on the concentration of bridging OH^- groups in HOT, which in turn depends on the content of colloidal titanium(IV) in the sol. The optimal concentration parameters for the synthesis of HOT with high sorption properties have been determined: the colloidal titanium(IV) content in the sol should not enhance 50%.

It has been shown that HOT can be used for LRW with low concentrations of background salt. Sodium and calcium ions actively compete with cesium and strontium ions in solution. For the Sr^{2+} - Ca^{2+} pair, the distribution coefficient is about 10^4 ml/g until the background salt concentration reaches 0.15 mol/L; for Cs^+ - Na^+ under the same condition the K_d value is 10^3 ml/g. The ion-exchange constants for Cs and Sr ions were calculated, the constant values being 11.3 and 32.5, respectively.

REFERENCES

1. Amflet Ch. 1966, *Inorganic Ionites*, Mir, Moscow.
2. Boichinova E. S. 1984, "Anion-exchange properties of some of hydrated metal oxides" *Ion Exchange and Ionometry*, LGU, Leningrad, no. 4, pp. 76-82.
3. Chernykh O.A. and Boichinova E. S. 1971, "Effect of certain conditions on the ion-exchange properties of zirconium hydrated oxide", *Russian Journal of Applied Chemistry*, vol. 44, no.12, pp. 2628-2632.
4. Dobrovolskii I.P. 1988, *Chemistry and Technology of Titanium Oxides*, UPI, Sverdlovsk.
5. Eiden-Assmann S., Widoniak J., and Maret G. 2004, "Synthesis and characterization of porous and nonporous monodisperse colloidal TiO₂ particles," *Chemistry of Materials*, vol. 16, no. 1, pp. 6-11.
6. Gerasimova L. G., Okhrimenko R. F., and Zhdanova N. M. 2002, "Study of the composition of a solid phase isolated by thermohydrolysis of a titanium sulphate acidic solution", *Russian Journal of Applied Chemistry*, vol.75, no.6, pp. 895-897.
7. Gerasimova L.G. and Maslova M.V. 2011, *Titanium Hydroxides and titanium compositions: Preparation and Application*, LKM Press, Moscow.
8. Gerasimova L. G. and Maslova M. V. 2012, "Behavior of titanium sulphate (IV) solutions under hydrothermal conditions", *Russian Journal of Inorganic Chemistry*, vol. 57, no.3, pp.1-7.
9. Gerasimova L.G., Maslova M.V., and Nikolaev A.I. 2011, "Using colloidal titanium-containing precursor for synthesis of an ion-exchange material", *Russian Journal Glass physics and chemistry*, vol. 38, no.4, pp. 67-73.
10. Godneva M.M. and Motov D.L. 2006, *Titanium Subgroup Chemistry*, Nauka, St. Petersburg.
11. Goroshchenko Y.G, *Titanium Chemistry*, 1972, Naukova Dumka, Kiev.
12. Griessbach R. *Ion-exchange in theory and practices* 1963, Inostrannaya Literatur Publ., Moscow.
13. Ho L.N., Ishihara T., Ueshima S., Nishiguchi H. and Takita Y.2004, "Removal of fluoride from water through ion exchange by mesoporous Ti oxyhydroxide ", *Journal of Colloid and Interface Science*, vol. 272, pp. 399-403.
14. Inczedy J. 1979, *Analytical applications of complex equilibria*, Mir, Moscow.
15. Makarova E.D. and Belinskaya F.A. 1976, "About structure and ion-exchange properties of titanium hydroxide" in *Ion Exchange and Ionometry*, LGU, Leningrad, pp.3-16.
16. Miliordos E., Harrison J. F., and Hunt L. C.2011, "First principles calculations of the electronic and geometrical structures of neutral [Sc, O, H] molecules and the monocations, ScOH⁰⁺ and HScO⁰⁺", *Journal of Chemical Physics*, vol. 135, pp. 14411-14413.
17. Mine E., Hirose M., Nagao D. 2005, "Synthesis of submicrometer-sized titania spherical particles with a sol-gel method and their application to colloidal photonic crystals", *Journal of Colloid and Interface Science*, vol. 291, pp. 162-168.
18. Nikolaev A.I., Larichkin D.F., Gerasimova L.G., Maslova M.V. 2011 *Titanium and its compounds*, KSCRAS, Apatity.
19. Pal M., J. Serrano G., Santiano P., and Pal U. 2007, "Size-Controlled Synthesis of Spherical TiO₂ nanoparticles: Morphology, Crystallization, and Phase Transition," *The Journal of Physical Chemistry C*, vol. 111, no. 1, pp. 96-102.
20. Pletnev R.N., Ivakin A.A., Kleshchev D.G., Denisova T.A., and Burmistrov V.A. 1986, *Hydrated Oxides of Groups IV and V Elements*, Nauka, Moscow.
21. Reinten K.T. 1973, *Structure and Properties of Adsorbents and Catalysts*, Mir, Moscow.

22. Shabana E.I. and El-Dessouky M.I. 2002, "Sorption of cesium and strontium ions on hydrous titanium dioxide from chloride medium", *Journal of Radioanalytical Nuclear Chemistry*, vol. 253, no. 2, pp. 281-284.
23. Sharygin L.M., Malykh T.G., Loguntsev E.N., and Shtin A.P. 1980, "Investigation of hydrated titanium dioxide sol formation under the electrolysis of titanium tetrachloride solution", *Russian Journal of Applied Chemistry*, vol.53, no.6, pp.1277-1281.
24. Strekalovskii V.N., Polezhaev Yu.M. and Palguez S.F. 1987, *Oxides with Admixture Disordering*, Nauka, Moscow.
25. Sugimoto T. and Kojima T. 2008 , "Formation mechanism of amorphous TiO₂ in organic solvent. 1. Roles of ammonia", *Journal of Physical Chemistry*, vol. 112, pp. 18437-18444.
26. Sugimoto T. and Kojima T. 2008, "Formation mechanism of amorphous TiO₂ in organic solvent. 2. Kinetics of precipitation", vol. 112, pp. 18760-18771.
27. Zhijun G., Lijun N., and Zuyi T. 2005, "Sorption of Th(IV) ions onto TiO₂: Effects of contact time, ionic strength, thorium concentration and phosphate" , *J. Radioanalytical. Nuclear Chemistry*, vol. 266, no. 2, pp. 333-338.