

solid concentration on exhaustion. *Environmental Science and Pollution Research*. 2011. Vol. 18. pp. 386–395.

3. Bhat S. C., Goswami S., Palchaudhury S., Ghosh U. C. Pb(II) sorption performance of hydrated titanium(IV) oxide from aqueous solution. *Indian Chemical Society*. 2005. Vol. 82. pp. 632–636.

4. Debnath S., Ghosh U. C. Kinetics, isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide. *Chemical Thermodynamics*. 2008. Vol. 40 (1). pp. 67–77.

5. Nitoi I., Oancea P., Raileanu M., Crisan M., Lucian Constantin L., Cristea I. UV–VIS photocatalytic degradation of nitrobenzene from water using heavy metal doped titania. *Industrial and Engineering Chemistry*. 2015. Vol. 21. pp. 677–682.

6. Herregods S., Mertens M., Van Havenbergh K., Van Tendeloo G., Cool P., Buekenhoudt A., Meynen V. Controlling pore size and uniformity of mesoporous titania by early stage low temperature stabilization. *Colloid and Interface Science*. 2013. Vol. 391. pp. 36–44.

7. Seck E. L., Doña-Rodríguez J. M., Melián E., Fernández-Rodríguez C., González-Díaz O. M., Portillo-Carrizo D., Pérez-Peña J. Comparative study of nanocrystalline titanium dioxide

obtained through sol-gel and sol-gel-hydrothermal synthesis. *Colloid and Interface Science*. 2013. Vol. 400. pp. 31–40.

8. Jolivet J.-P., Cassaignon S. Design of oxide nanoparticles by aqueous chemistry. *Sol-Gel Science and Technology*. 2008. Vol. 46 (3). pp. 299–305.

9. Pal M., Serrano J. G., Santian P., Pal U. Size-controlled synthesis of spherical TiO₂ nanoparticles: morphology, crystallization, and phase transition. *Journal of Physical Chemistry C*. 2007. Vol. 111 (1). pp. 96–102.

10. Maslova M. V., Gerasimova L. G., Knyazeva A. I. Synthesis of sorbent based on hydrated hydroxooxotitane. *Zhurnal Neorganicheskoy khimii*. 2015. Vol. 60, No. 4. pp. 1–7.

11. Gerasimova L. G., Maslova M. V., Matveev V. A., Mayorov D. V., Kobgunov N. N. Titanium-phosphate sorbents for purification of liquid flows from radioactive, non-ferrous and heavy metals. *Tsvetnye Metally*. 2005. No. 3. pp. 87–91.

12. Kokotov Yu. A., Zolotarev P. P., El'kin G. E. Theoretical foundations of ion exchanging: Complex ion-exchanging systems. Leningrad: Khimiya, 1986. 280 p.

13. Ho Y. S., MacKay G. A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Transition metal chemistry*. 1998. Vol. 78. pp. 332–340. NFM

Synthesis of a titanium (IV)-based sorbent and potentialities of its usage for extracting cations of non-ferrous metals

UDC 661.183.124:548.3

L. G. Gerasimova, Chief Research Assistant¹, e-mail: gerasimova@chemy.kolasc.net.ru

A. I. Nikolaev, Head of Laboratory¹

M. V. Maslova, Leading Research Assistant¹

E. S. Shchukina, Research Assistant¹

¹ Establishment of the Russian Academy of Sciences I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science Centre of the Russian Academy of Sciences, Apatity, Russia.

Studied are conditions of synthesizing frame-structured titanium-containing exchanger with a structure similar to ivanyukite out of (NH₄)₂TiO(SO₄)₂·H₂O salt. To increase hydrolysis stability, partial reduction of initial solution has been fulfilled by electrochemical method with Ti⁴⁺ conversion to Ti³⁺. This expedient allows avoiding an amorphous phase generation and directing the process to creation of crystalline ivanyukite in a form of two structural modifications: trigonal (Na₄(TiO)₄(SiO₄)_{3.6}H₂O) and cubic (Na₃H(TiO)₄(SiO₄)₃·4H₂O); the precipitate crystallinity degree is 90–95%. Crystallization proceeds under five times system oversaturation by sodium silicate. Determined have been optimal conditions for titanium-siliceous precursor sol-gel obtaining and consequent hydrothermal transformation of the obtained gel to crystalline phase: content of Ti₂O₃ in the solution after reduction is 30–45 g/l, molar ratio TiO₂:SiO₂ = 1:4.

It has been shown that the pore system (total volume of pores) of crystalline ivanyukite particles is approximately 1.5 times larger than that of X-ray amorphous samples and that it is mainly represented by mesopores of medium size, which are characterized by the most activity in sorption processes. Sodium and potassium ions situated in the ivanyukite frame space along with water provide high exchange velocity of cations absorption in sorption processes due to minimal diffusive obstacles. The reported preliminary data on sorption allow to describe the frame-structured crystalline alkaline titanosilicates as effective sorbents of cations of non-ferrous metals, strontium, as well as univalent cations, caesium in particular.

Key words: titanium-containing sorbents, titanosilicates, synthesis, sol-gel process, crystallization, surface behaviour, sorption kinetics, uni- and bivalent cations.

DOI: 10.17580/nfm.2017.02.06

Actual economic circumstances in Russia connected with the needs of domestic market in import-substituting production, brings to the fore the question of developing new functional materials. At present, demand for them is considerable, but their manufacturing in Russia is almost lacking. Among these materials are titanium-containing sorbents, which are represented by wide class of compounds with different composition and structure — amorphous and crystalline titanium phosphates, framework titanosilicates, titanium oxyhydroxides and so on. Investigations in the area of synthesis and study on the properties of such sorbents are carried out quite intensively. Titanic reagents in the form of sulphate and fluoride salts of titanium (IV), tetrachlorated titanium [1–3], titanium hydroxide [4] as well as titanium-containing industrial waste products arising, for example, as a result of apatite-nepheline ores processing [5, 6] are used as a raw material for producing such sorbents. In the latter case cost of the sorbents significantly comes down. Advantages of synthetic titanium-containing sorbents over traditional ion exchange resins consists in higher temperature and radiation steadiness, and in a number of cases, selectivity as well, which is especially important during liquid radioactive waste processing and subsequent reagentless utilization of spent sorbents in the form of mineral-like ceramics [7]. Preliminary estimation of titanium-containing sorbents appropriateness for extracting toxic cations of heavy non-ferrous metals is also of practical interest.

The problem of wastewater treatment at enterprises of non-ferrous metallurgy is especially acute, since toxicity of these wastes is injurious to animate nature. Usage of such inorganic sorbents as titanium phosphates and hydroxides for purification is well known. Their synthesis and properties are clearly understood in contrast to the sorbents based on framework titanosilicates. The investigations, implemented in the latest years, has showed that sorptive activity of titanium phosphates is stipulated by functional groups with complexing properties, presented in them. In other words, sorption of cations proceeds due to exchange for gegenions, which neutralize a charge of phosphate groups [8]. As it is shown by crystallographic research, framework titanosilicates, ivanyukite-group minerals in particular, form an open microcellular framework $[\text{Ti}_4\text{O}_3(\text{OH})(\text{SiO}_4)_3]^{3-}$ with a system of three groups of mutually perpendicular channels, defined by 8-membered rings with an effective channel width of 3.5 Å, in which Na^+ , K^+ extra framework cations and H_2O molecules are localizing [7].

Exchange of these cations for cations of non-ferrous metals should determine sorptive behaviour of titanosilicates. Model procedure of synthesizing alkaline titanosilicates (Ti – Si) with a structure similar to that of natural minerals consists in mixing silicate and titanium-containing solutions with formation of a gel, which is held in autoclave at high temperature. Various technological and physicochemical aspects of synthesis are discussed in

the literature: selection of initial structure-forming titanate and silicon reagents, their molar ratio and pH indicator of a reaction blend, temperature and time behaviour of technological stages [9, 10]. At the same time, it is noticed that the phase content of crystalline products being formed in a process of hydrothermal synthesis depends upon velocity of silicon and titanium compounds hydrolysis at a sol-gel stage of the titanosilicate gel-like precursor formation. Uncontrolled hydrolysis may cause formation of the phases, enriched in silicon or titanium. This corrects the solid phase structure formation, in particular, causes arising a multiphases precipitate which crucially affects technical properties of the final product. The most widespread way of adjusting the process of titanosilicates structure formation is adding into a reaction mass the inorganic compounds, which suppress or accelerate reaction activity of the structure-forming components of the blend [11].

Materials of the present article contain results of the investigations of synthesizing Ti – Si with an ivanyukite-type structure [12]. For directional ivanyukite synthesis it is necessary to suppress reaction ability of titanium component. Authors of the papers [15] add hydrogen peroxide into titanium chloride (IV) solution in order to form a hydrolysis-resistant titanium peroxycomplex (IV), which allows to control a solid phase formation rate. Adding an organic complexon, acetylacetonate for example, pursues the same goals. Process of the solid phase formation (sol particles) during sol-gel synthesis can be slowed down by metal powders (zinc, iron) addition into acid titanium liquor as well. Hydrogen arising with this going on reduces titanium (IV) to more hydrolysis-resistant titanium (III). In a sol-gel process, cations-dopants take part in generating the colloid titanosilicate particles, and on consequent hydrothermal action they penetrate into a solid titanosilicate phase structure, provoking its deformation, which doesn't allow getting stability of the final product sorption behaviour. In this connection search of new reagentless technoschemes of titanium (IV) stabilization, which guarantee a directional synthesis of titanosilicate with ivanyukite-type structure is interesting as scientific and practical matters.

Subject and method of inquiry

To implement the experiments there has been used a titanium salt - ammonium titanyl sulphate, out of which a solution has been prepared. Further, partial Ti^{4+} reduction until Ti^{3+} has been carried out by electrochemical technique. The reduction plant is depicted below (in section).

Experimental procedure involves the following sequential operations:

– preparing titanium (IV) solution of titanium salt with composition $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ by its dilution in water without forced heating with the salt consumption in an amount so that the solution with concentration of

80 g/l by TiO_2 would be obtained. Acidic factor, or ratio of H_2SO_4 concentration in the solution to TiO_2 corresponds to 1.45–1.5.

– electrochemical reduction of titanium (IV) to trivalent state at current density on electrodes of 0.1 A/cm^2 . Time of reduction processes has been controlled by achieving the given Ti^{3+} concentration in a solution.

– preparing a titanium-silicate mixture (gel) for hydrothermal synthesis. For this purpose, sodium silicate solution has been gradually introduced into the reduced titanium solution until achieving the ratio $\text{TiO}_2:\text{SiO}_2 = 1:0.75-4$, then potassium fluoride has been added as $\text{TiO}_2:\text{KF} = 1:0.25$, and then a sodium alkali solution has been added to a ratio of $\text{TiO}_2:\text{Na}_2\text{O} = 1:3.8$ (a pH indicator is 12.5–13.5). The blend has been mixed for 0.5–1 h and kept at rest for 2 h.

– conducting the gel-like mass hydrothermal synthesis in autoclave during 5 days at the temperature of 200°C .

– the obtained suspension filtering under vacuum.

– the precipitate abluion of mother waters on a filter.

– the washed precipitate drying at the temperature of $70-75^\circ\text{C}$.

Solid phases has been studied by a Siemens/Bruker D5000 *X*-ray Diffractometer with monochrome $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), UR-20 Carl Zeiss Jena spectrophotometer, Cameca MS-46 electron microanalyzer and Carl Zeiss LEO-1450VP Scanning Electron Microscope with a QUANTAX Energy-dispersive *X*-ray spectrometer. To characterize a surface behaviour of synthesized titanositates a Micromeritics TriStar 3020 surface area and porosity analyzer has been used. The secific surface area and total volume of pores has been determined by a BET method through the nitrogen sorption/desorption isotherms. Size distribution of pores has been calculated by nitrogen thermal desorption method (BJH-method), the structure porosity has been determined by the adsorbed nitrogen volume dependence on adsorbate film thickness (*t*-plot method).

Sorptive capacity of obtained materials with respect to some uni- and bivalent cations has been established in static conditions at a solid to liquid phase ratio of 1:200 and a sorbent and sorbate contacting time of 24 hours. The cations concentration in solutions has been determined by mass-spectrometry with inductive-connected plasma (MS-ICP) on a PerkinElmer Elan 9000 quadrupole ICP-mass spectrometer (Perkin Elmer, USA) [13].

Results and their discussion

Two sulphate-ammonium solutions with a trivalent titanium concentration of 30 and 45 g/l by Ti_2O_3 respectively have been used for research. When implementing the experiments by the procedure outlined above, precipitates have been obtained, the phase composition of which according to *X*-ray phase analysis is aggregated in Table 1.

Nucleation for structuring titanositate has started in a multicomponent sol-gel system. During the consequent high-temperature hydrothermal reaction on a gel-like mass under autoclave conditions, regulating the solid phase particles structural order takes place. In experiments with stoichiometric for ivanyukite molar titanium to silicon ratio $\text{TiO}_2:\text{SiO}_2 = 1:0.75$, an *X*-ray amorphous precipitate with crystallinity degree is forming (experiment 1 and 3 in Table 1). This is because the Ti_2O_3 presence in an initial solution slows down a Ti^{4+} hydrolysis, initiating by this the silicon hydrolysis with formation of amorphous silica. Titanium hydrolysis with an *X*-ray amorphous phase formation as well is beginning at significant shortage of silicon in dissolved state. The following hydrothermal process leads to structure consolidation and appearing of the phase (anatase) with low crystallinity degree. In a case of the heightened silicon consumption $\text{TiO}_2:\text{SiO}_2 = 1:4$, in other words, on the system satiety by silicon-containing reagent in analogous experiment conditions, two structurally close crystalline phases of ivanyukite are forming: trigonal — $\text{Na}_4(\text{TiO})_4(\text{SiO}_4)_3 \cdot 6\text{H}_2\text{O}$ (*T*) and cubic — $\text{Na}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3 \cdot 4\text{H}_2\text{O}$ (*C*) (experiments 2 и 4). The excess silicon content provides keeping the stoichiometric ratio of the components over the course of both stages of the titanositate structure formation and promotes production of crystalline precipitate — ivanyukite (crystallinity degree is 90–95%). The initial Ti^{3+} concentration on Ti_2O_3 in titanium solution in either case have insignificant effect on the precipitate structure.

Since TiSi (samples of experiments 2 and 4) have approximately similar phase content, the authors cite data only on one of them (Fig. 1). An intensive peak of the synthetical ivanyukite main phase on the *X*-ray photograph has coordinates $2\theta - 11.31$ (Ref. Code 01-078-3450). Low-intensity refelexes with coordinates $2\theta - 24.40, 32.14, 48.38, 62.84$ have been attributed to a titanium phase $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (Code 00-047-0124). Low sensitivity of *X*-ray phase analysis and presence of *X*-ray amorphous phase don't permit to completely describe composition of synthesized products. Presence of *X*-ray amorphous phase (silica) is attested by unclearness of peaks at 2θ more than 35.

Table 1
Conditions of experiments and phase composition of the synthesized precipitates

The solid phase characteristics, % (wt.)	Experiment 1 30 g/l Ti_2O_3	Experiment 2 30 g/l Ti_2O_3	Experiment 3 45 g/l Ti_2O_3	Experiment 4 45 g/l Ti_2O_3
	$\text{TiO}_2:\text{SiO}_2 = 1:0.75$	$\text{TiO}_2:\text{SiO}_2 = 1:4$	$\text{TiO}_2:\text{SiO}_2 = 1:0.75$	$\text{TiO}_2:\text{SiO}_2 = 1:4$
Amorphous phase	65	5	65	10
Anatase with low crystallinity degree	35	–	35	–
Ivanyukite – C + Ivanyukite – T	–	95	–	90

Nuclear magnetic resonance data of the sample study (for ^{29}Si) has showed that principal peaks at -94.3 and -97.5 ppm refer to $3\text{Si}1\text{Ti}$ environment (Fig. 2). This implies that three silicon are bounded with titanium and SiO_4 tetrahedron are perpendicular to $\text{Ti} - \text{O} - \text{Ti}$ chains. Small peak at -104.5 ppm corresponds to $4\text{Si}0\text{Ti}$ environment, in which the central atom of silicon is tetrahedrally connected with 4 other structural blocks of silicon. Frequencies in a zone around -87.5 ppm witness about presence of a small number of free groups = $\text{Si}(\text{OH})_2$ in the analyzed assay.

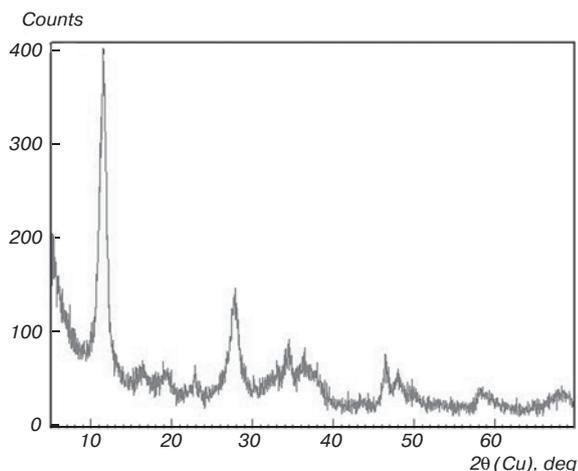


Fig. 1. An X-ray photograph of the sample 2

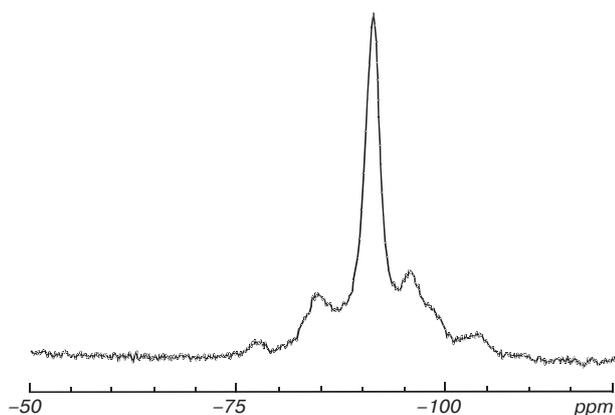


Fig. 2. An NMR spectrum of the sample 2

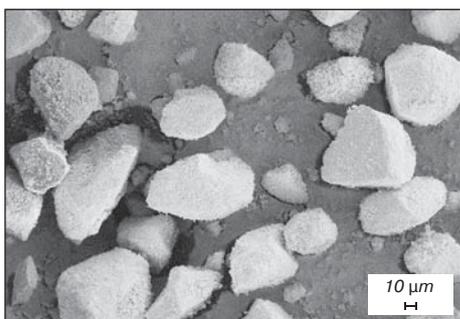


Fig. 3. A SEM image of the synthetic ivanyukite particles (sample 2)

Particles of ivanyukite in a sample are predominantly represented by fraction of $5-20 \mu\text{m}$. Individual crystals of size up to $100 \mu\text{m}$ are also contained (Fig. 3).

The ivanyukite mineral crystalline structure is inherited for its synthetic analogue as well. Values of specific surface area and average pore size of the particles of investigated samples are given in Table 2.

Values of a specific surface area of the powder particles, mainly consisting of X-ray amorphous phase and anatase phase with low crystallinity degree, significantly exceed that of the samples with dominating content of crystalline ivanyukite (about 1.5 times). On the contrary, total pore volume of ivanyukite particles is 1.5 times higher. Since pore diameter in that case is essentially smaller than that of the samples of experiments 1 and 3, it can be assumed that the pore system of ivanyukite particles is represented by narrow but deep mesopores, which can guarantee transportation of ions deep into the particles thus rising sorptive ability. This assumption is confirmed by the data given in Table 3.

Sorptive behaviour of $\text{Ti} - \text{Si}$ products have been determined in static conditions with the proviso that sorbent:sorbate = 1:200 [14]. Model solutions have been used as sorbates. Origin concentration of cations (CMe, g/l) and pH of model solutions corresponds to the following values: $\text{CCo} - 0.45$, $\text{pH} - 6.3$; $\text{CNi} - 0.83$, $\text{pH} - 6.5$; $\text{CCu} - 0.89$, $\text{pH} - 5.15$; $\text{CSr} - 1.17$, $\text{pH} - 6.59$; $\text{CCs} - 2.06$, $\text{pH} - 6.94$.

Thus, it can be stated that ivanyukite samples have higher sorptive capacity over cations of caesium and strontium in comparison with X-ray amorphous or weakly crystalline anatase samples. Distinction of the investigated samples sorptive capacity over cations of non-ferrous metals becomes apparent to a lesser degree.

Absorption of cations by sorbents proceeds according to different mechanisms. For X-ray amorphous samples

Table 2
Surface behaviour of the synthesized samples

Experiment	$S_{sp}, \text{m}^2/\text{g}$	$V_{pore}, \text{cm}^3/\text{g}$	D_{pore}, nm (average)
1	216.9	0.445	11,4
2	197.3	0.619	4,2
3	281.27	0.405	14.2
4	187.57	0.625	4.9

Table 3
Sorptive capacity of the samples over univalent and bivalent cations, mg/g

Sample number	E_{Co}	E_{Ni}	E_{Cu}	E_{Sr}	E_{Cs}
1	47.4	52.6	62.3	72.1	166.0
3	28.0	34.7	46.0	62.5	144.8
2	68.9	101.1	144.6	152.0	450.6
4	67.0	94.8	140.9	160.3	438.5

and the ones with low crystalline degree (1 and 3), which practically don't contain ivanyukite, a cation absorption mechanism is based on surface complexing for the most part and on ion exchange to a smaller extent. For ivanyukite (experiments 2 and 4) with crystalline frame structure of the particles, filled by cations of sodium and potassium, the sorption mechanism is based on ion exchange.

Conclusions

The conditions of synthesizing frame-structured titanosilicate with a structure similar to ivanyukite with the use of a solution, prepared of ammonium titanil sulphate have been investigated. To increase titanium (IV) hydrolysis stability, partial reduction of initial solution has been fulfilled by electrochemical method with Ti^{4+} conversion to Ti^{3+} . This expedient allows one to avoid an amorphous phase generation and to direct the process to creation of crystalline ivanyukite in a form of two structural modifications: trigonal ($Na_4(TiO)_4(SiO_4)_3 \cdot 6H_2O$) and cubic ($Na_3H(TiO)_4(SiO_4)_3 \cdot 4H_2O$); the precipitate crystallinity degree is 90–95%.

Crystallization proceeds under five times system oversaturation by sodium silicate. Determined have been optimum conditions for titanium-silicon precursor sol-gel synthesis and consequent hydrothermal transformation of the obtained gel to crystalline phase: content of Ti_2O_3 in the solution after reduction is 30–45 g/l, molar ratio $TiO_2:SiO_2 = 1:4$.

It has been shown that total volume of pores of the crystalline ivanyukite particles is approximately 1.5 times larger than that of X-ray amorphous samples and that the pore system is represented by mesopores of medium size, which are characterized by the most activity in sorption processes.

The reported preliminary data on sorption allow one to describe the frame-structured crystalline alkaline titanosilicates as effective sorbents of non-ferrous metals, strontium and caesium ions.

The research has been implemented thanks to the grant of the Russian Science Foundation (project No. 17-19-01522).

References

1. Gerasimova L. G., Maslova M. V., Shchukina E. S. Sphe concentrate technology with titanium salts obtaining. *Khimicheskaya tekhnologiya*. 2008. No. 6. pp. 241–246.
2. Maslova M.V., Rusanova D., Naydenov V., Antzutkin O., Gerasimova L. G. Extended study on synthesis of amorphous ti-

tanium phosphates with tailored sorption properties. *Journal of Non-Crystalline Solids*. 2012. Vol. 358. pp. 2943–2950.

3. Gerasimova L. G., Nikolaev A. I., Maslova M. V., Yakovenchuk V. N., Ivanyuk G. Yu., Krivovichev S. V. Method of processing titanium-containing concentrate. Patent RF, No. 2467953, IPC C01G 23/00, C22B 3/08 (2006.01). Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials (Kola Science Center RAS). No. 2011127614/05. Applied: 05.07.11. Published: 27.11.12. Bulletin No. 33.

4. Gerasimova L. G., Maslova M. V. Titanium hydroxides and compositions on their basis. Obtaining and use. Moscow : LLC «Izdatel'stvo LKM-press». 2011. 86 p.

5. L. Gerasimova, M. Maslova, A. Nikolaev, E. Shchukina. Alkali titanosilicates from titanite. Production and properties. *AMAM-2015, Taranto, Italy, June 7–12, 2015 Scientific research abstracts*. 2015. Vol. 4. p.114.

6. Yanicheva N.Yu., Ganicheva Ya.Yu., Kalashnikova G. O. Prospects of use of titanium raw materials in Kola Peninsula for synthesis of microporous titanium silicates. *Materials of the XIX Inter-region scientific-technical conference «Scientific-practical problems in chemistry and chemical technologies»*. Apatity, 15–17 April 2015. Apatity: Izdatelstvo KNTs RAN, 2015. pp. 21–24.

7. Dimova L. M. Inorganic ion exchangers. Irkutsk: Izdatelstvo IGU, 2012. 62 p.

8. Maslova M. V., Chugunov A. S., Gerasimova L. G., Konovalova N.V. Acid-base and sorption properties of amorphous titanium phosphate. *Radiokhimiya*. 2013. No. 4. pp. 323–328.

9. Lu Lv, Fabing Su, X. S. Zhao. A reinforced study on the synthesis of microporous titanosilicate ETS-10. *Microporous and mesoporous materials*. 2004. Vol. 76. pp. 113–122.

10. Zhaoxia Ji, Bilge Yilmaz, Juliusz Warzywoda, Albert Sacco Jr. Hydrothermal synthesis of titanosilicate ETS-10 using $Ti(SO_4)_2$. *Microporous and mesoporous materials*. 2005. Vol. 81. pp. 1–10.

11. Hsuan-Fu Yu, Shenq-Min Wang. Effects of water content and pH on gel-derived TiO_2-SiO_2 . *Journal of Non-Crystalline Solids*. 2000. Vol. 261, Iss. 1–3. pp. 260–267.

12. Yakovenchuk V. N., Nikolaev A. I., Selivanova E. A., Pakhomovsky Ya. A., Korchak Yu. A., Spiridonova D. V., Zalkind O. A., Krivovichev S. V. Ivanyukite–Na–T, ivanyukite–Na–C, ivanyukite–K and ivanyukite–Cu: New microporous titanosilicates from the Khibiny massif (Kola Peninsula, Russia) and crystal structure of ivanyukite–Na–T. *American Mineralogist*. 2009. Vol. 94. pp. 1450–1458.

13. Yanicheva N. Yu., Kalashnikova G. O. Synthetic ivanyukite — perspective ion-exchange material. *Vestnik Murmanskogo GTU*. 2014. Vol. 17, No. 1. pp. 106–111.

14. Ludmany A., Nagy L. G. Preparation, characterization and application of titanium phosphate inorganic sorbents. *Radiochemical and Radioanalytical Letters*. 1982. Vol. 51, No. 5. pp. 301–310.