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FERRIC TITANOUS HOLLANDITE ANALOGUES – MATRICES FOR IMMOBILIZATION OF Cs-CONTAINING RADIOACTIVE WASTE: SYNTHESIS AND PROPERTIES

The fundamental regularities of (Fe, Ti)-hollandite analogues synthesis from nanodimensional amorphous systems of coprecipitated hydroxycarbonates are established by the methods of DTG, XRD, IR-spectroscopy, SE microscopy, electron diffraction, and energy dispersive analysis of X-rays. Its formation is demonstrated to proceed through the one-step mechanism by "explosive" crystallization. The synthesis optimum parameters of highly-dispersed powders by application of coprecipitated hydroxycarbonates and hard-sintered ceramic are defined to be much lower in temperature and time of thermal treatment with application of initial oxides mixture. The feasibility of Cs effective bonding in composition of (Fe, Ti)-hollandite analogues is ascertained. The normalized speed of Cs leaching from Cs-containing ceramic of $Ba_{0.9}Cs_{0.2}Fe_{2.0}Ti_{6.0}O_{16}$ composition is determined.

Keywords: hollandite, radioactive waste, immobilization of caesium.

Introduction. Heat-generating high-level waste with a high content of Cs isotopes has a significant place within the context of problems solution for radioactive waste (RW). Caesium belongs to such radionuclides which immobilization into the matrices waste form meets certain difficulties. These problems arise, first of all due to ^{134}Cs and ^{137}Cs high activity and an presence of long-living ^{135}Cs isotope ($T_{1/2} = 2.3 \cdot 10^6$ yr), the second — volatility of isotopes Cs at high temperatures and its ability to form its own water soluble compounds during the synthesis of Cs-bearing matrices. The decay of Cs radioactive isotopes is followed by emission of β -particles ($0.51 \leq \text{energy } E \leq 1.17$ Mev), γ -rays ($E \sim 0.6$ Mev) and Cs isotope transmutation into the stable Ba ($^{137}Cs \rightarrow ^{137m}Ba \rightarrow$

$\rightarrow ^{137}Ba_{\text{stable}}$). That is why the Cs-bearing matrices must be stable to (β , γ)-irradiation and leaching, also the transmutation processes, which follow Cs-bearing isotopes decay, should be taken into account. Technological probability of Cs or (Cs, Sr)-fraction emission from liquid high level waste (HLW) during the process of spent nuclear fuel reprocessing stimulates the performance of investigations on elaboration of new crystal matrices with improved isolation properties rather than glass ones (borosilicate or alumophosphate), which are now used for immobilization of non-separated liquid HLW [5]. (Fe, Ti)-hollandite analogues for Cs immobilization are expected to be the most perspective among such matrices. Their choice is conditioned by high isomorphic capacity to alkaline metals [3], radiation [1] and geochemical stability of natural hollandite [7].

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The given work sets out the findings of investigations on synthesis conditions and isolation properties of ceramic materials on the basis of (Fe, Ti)-hollandite analogues for Cs immobilization.

Procedure. In order to obtain Cs-containing (Ba, Fe, Ti)-containing ceramics it were preliminary synthesized polycrystalline finely dispersed powders (precursor) with the help of hydroxycarbonates coprecipitation method (HCCP). Main point of the method is coprecipitation of elements hydroxycarbonates from mixture of water solutions of their salts (see Fig. 1). Coprecipitation of (Ba, Fe, Ti)-containing compositions was conducted using $\text{NH}_4\text{OH} + \text{NH}_4\text{HCO}_3$ aqueous buffer solution with pH 8–9 as precipitant. In the case of partial colloidalization of precipitate, its coagulation was carried out by heating of "mother liquor-precipitate" system. Completeness of components precipitation was checked with the help of corresponding qualitative reactions. The precipitates resulted from the coprecipitation were separated from the mother liquor solution by filtration, then dried at the temperature of 100–130 °C, after which, pulverized in mortar and exposed to thermal treatment in the muffle furnace. Insertion of stable cesium (imitation of Cs radioactive isotopes) to the composition of precursors was performed in accordance with ceramic technology by mechanical mixing of appropriate quantities precursor and thermally instable Cs_2CO_3 . Further, the charge obtained in such a manner from polycrystalline powders, was pressed to pellets at ~120 MPa pressure during 2–3 s. The pellet diameter is 10–12 mm and height is 3–4 mm. Pellets were heat-

treated in air environment at the temperature of 1000–1100 °C with isothermal heating during 2–3 h and cooling to room temperature together with the furnace. Computational composition of samples foresees that Fe is in trivalent state, as it was previously determined by Mossbauer spectroscopy for (Fe, Ti)-hollandite analogues [8].

Analytical techniques. The study of obtained polycrystalline powders and ceramic pellets were performed using DTG (NETZSCH STA 449F1, alunde cups, air environment, mass of samples — 0.02 g, heating rate 5° per minute, optional cooling, standard — Al_2O_3), X-ray diffraction was done on a DRON-3 diffractometer (with Cu $K\alpha$ -irradiation and Ni-filter). The IR-spectroscopy was done on the UR-20 spectrometr (range 400–4000 cm^{-1}), and Mossbauer spectroscopy was done using NGRS-4M spectrometer at room temperature with $^{57}\text{Co}(\text{Cr})$ source. Obtaining of SEM-images and chemical composition determination were performed with the help of JSM-6700F scanning electronic microscope, equipped with 20 kV energy disperse system for microanalysis JED-2300 ("JEOL", Japan) with probe diameter 1–2 micrometers. Chemical stability (leaching) of ceramic samples was determined with respect to international standard (test MCC-2) [4].

Results and discussion. Thermogravimetric investigation of HCCP air-dry charge (precursor) of (Ba, Fe, Ti)-containing compositions have demonstrated the presence of three clear thermal effects on the DTA records. For the HCCP charge with ratio Ba : Fe : Ti = 1.0 : 2.0 : 6.0 the endothermic effect in the temperature interval between

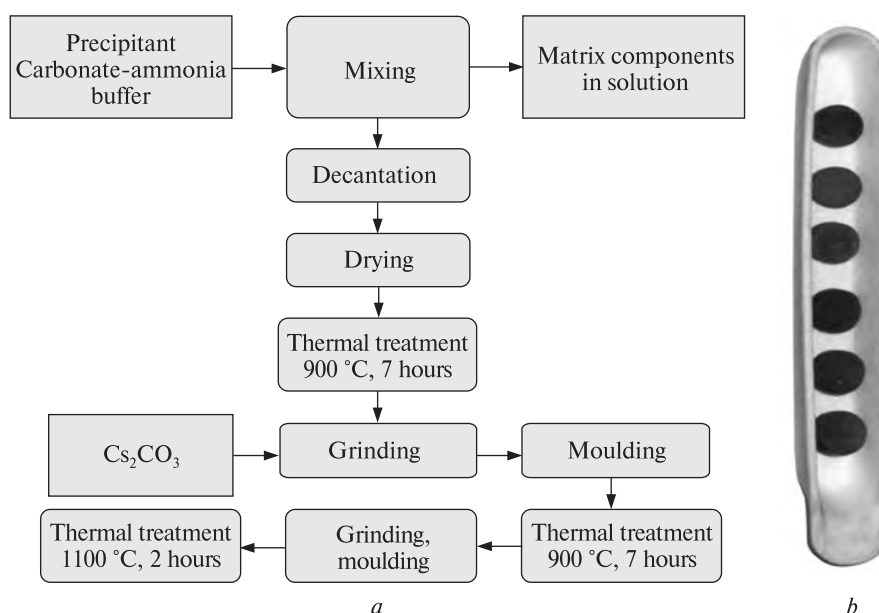


Fig. 1. Scheme of synthesis main stages of Cs-containing (Ba, Fe, Ti)-containing ceramics (a) and visual appearance of pellets after sintering on air at temperature of 1100 °C during 2 hours (b)

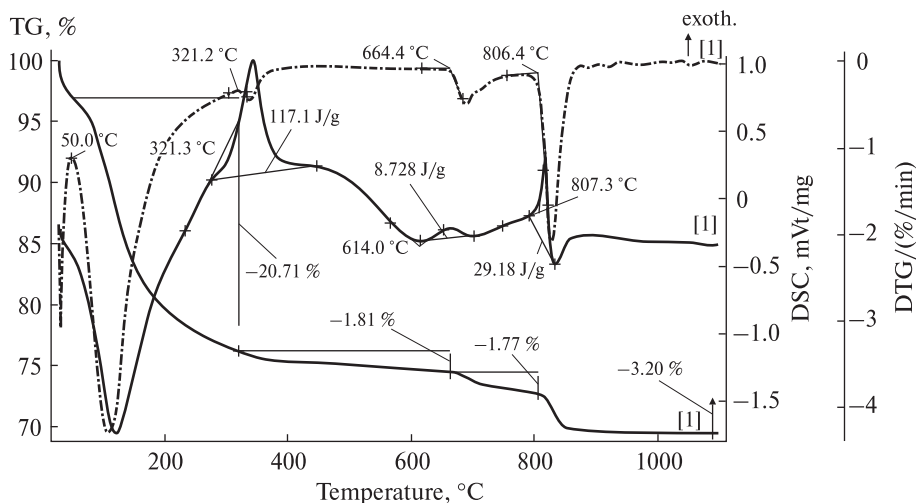


Fig. 2. DTG record of air-dry charge of coprecipitated hydroxycarbonates with ratio: Ba : Fe : Ti = 1.0 : 2.0 : 6.0

50 and 321 °C with maximum at 123 °C is accompanied with mass loss of 20.7 % and caused by removal of water (Fig. 2). The stepwise water exuding with further splitting out of hydroxyl groups, as it is observed with the individual hydroxides is not fixed. Exothermal effect (117.1 J/g) with mass loss beginning at 321.2 °C and maximum at 359 °C is caused by disintegration of ammonium nitrate caught by precipitate. Till 806 °C the dynamic mode product of thermal treatment of HCCP charge is X-ray amorphous, and the strong exothermal effect (29.2 J/g) with maximum at 828 °C is caused by crystallization of thermal treatment product, which is typical for explosive mechanism of crystallization, evidenced by appearance of XRD pattern on the diffractograms. Insignificant ((3.2 %), but sharp sample mass loss (rate of mass loss of 2 %/min), which accompanies this exothermal effect (29.18 J/g), is caused by extraction of non-structural impurities from the sample as the crystalline structure is being formed. The general loss of sample mass makes about 28 %.

Thermogravimetric data and X-ray amorphous character of dynamic mode thermal treatment products of HCCP at $T < 806$ °C suggest that charge is not just a mixture of separate hydroxides and carbonates (or hydroxycarbonates), but it is a product of components' chemical interaction during the process of their precipitation. This also testifies that crystalline compounds formation during HCCP (Ba, Fe and Ti) heating, takes place without the stage of free oxide release.

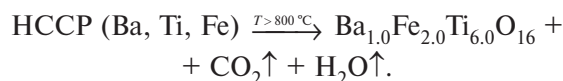
The results of X-ray investigation of HCCP charge samples with ratio Ba : Fe : Ti = 1.0 : 2.0 : 6.0, which had passed consequent isothermal heat treatment within the temperature range from 300 to 900 °C, have demonstrated that $Ba_{1.0}Fe_{2.0}Ti_{6.0} \times$

$\times O_{16}$ ferrotitanate hollandite is the first crystalline product of thermal treatment, and the mechanism of its formation has a one-stage character. A slightly lower temperature of formation $Ba_{1.0} \times Fe_{2.0}Ti_{6.0}O_{16}$ (800 °C) than crystallization exothermal effect (806 °C, Fig. 2), is explained by considerably longer heating of HCCP sample during isothermal mode of thermal treatment.

Relative expansion peaks of X-ray diffraction patterns of thermal treated (at 800 °C) samples of Ba, Fe and Ti (Ba : Fe : Ti = 1.0 : 2.0 : 6.0) HCCP charge, indicates the fine-dispersion of produced $Ba_{1.0}Fe_{2.0}Ti_{6.0}O_{16}$, and also does not exclude the existence of substantial tensions in its structure.

Increase in heating time (7 h) at 900 °C does not change the sample phase composition, improves its crystallinity and reduces the lattice parameter "a" of hollandite phase ($a = 10.160$ (3) Å). The lattice parameter "c" does not vary practically. As the temperature of thermal treatment increases till 1100 °C (heating for 2 h) the "a" parameter comes to 10.125 (9) Å, $c = 2.998$ (5) Å, unit cell: $V = 307.4$ (1) Å³, that is probably due to hollandite structure ordering.

On the basis of above-mentioned data analysis, the process of $Ba_{1.0}Fe_{2.0}Ti_{6.0}O_{16}$ formation from the HCCP charge can be illustrated by the following scheme:



SEM-investigation of the thermal treatment products of HCCP charge showed that the charge of $Ba_{1.0}Fe_{2.0}Ti_{6.0}O_{16}$ composition dried at room temperature is represented as fibres with diameter of about 0.5–0.6 μm (Fig. 3), consisting of highly agglomerated microcrystallines of undetermined

Fig. 3. SEM images of air-dry charge fibres of coprecipitated hydroxycarbonates with ratio Ba : Fe : Ti = 1.0 : 2.0 : 6.0 (*a* – $\times 11000$, *b* – $\times 40000$)

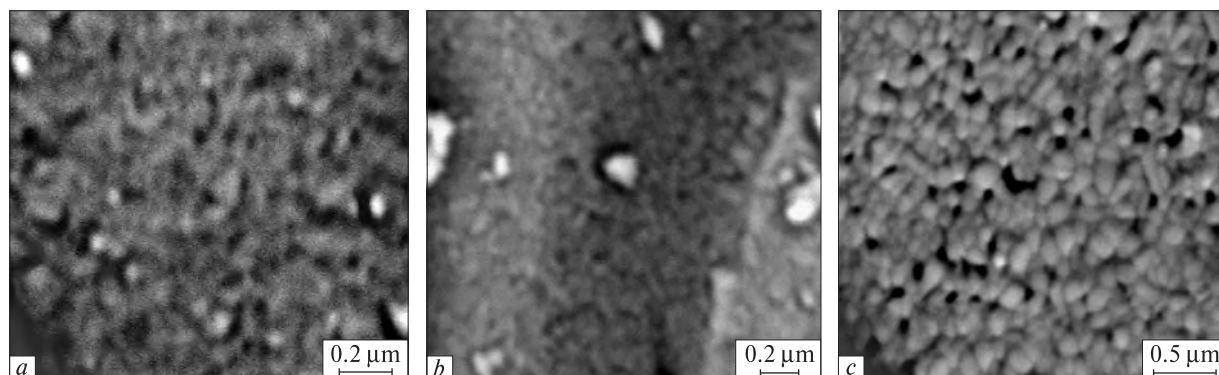
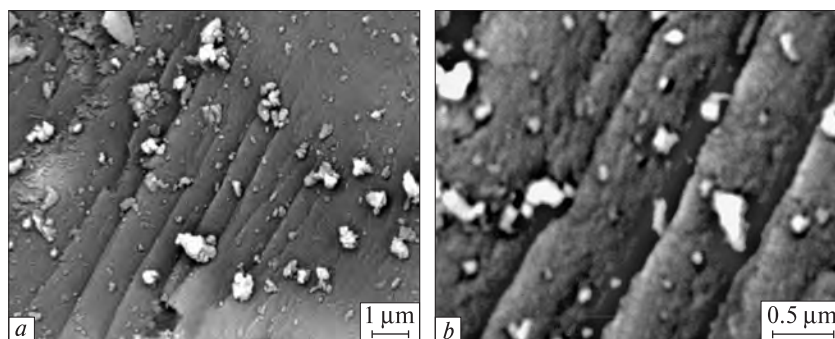


Fig. 4. SEM images of charge coprecipitated hydroxycarbonate of $\text{Ba}_{1.0}\text{Fe}^{3+}_{2.0}\text{Ti}_{6.0}\text{O}_{16}$ composition thermal treated during one hour (at *a* – 500 °C, *b* – 700 °C, *c* – 900 °C of temperature)

habitus with size of 10–15 nm. Increase in temperature of thermal treatment up to 700 °C enlarges the size of grains to 40–50 nm (Fig. 4).

Thermal treatment of charge at 900 °C during 1 hour results in formation end products with sharp increase in grains average size to 150 nm. With increase of thermal treatment duration at 900 °C the average size of charge grows and comes to about 200 nm (3 hours of heating), 250 nm (5 h), 300–400 nm (7 h).

The absorption bands, which correspond to oscillations of CO_3^{2-} -ions and OH^- groups are observed on the IR spectra of air-dry charge. The triplet of 1385, 1515 и 1630 cm^{-1} bands being peculiar to CO_3^{2-} -ions oscillations is present in the interval of 1350–1700 cm^{-1} . A wide intensive

band with maximum about 3350 cm^{-1} is within the range of OH-group (2800–3600 cm^{-1}) valence oscillation observed. During the time of charge thermal treatment the intensity of valence oscillation of water and CO_3^{2-} -ions decreases gradually. The samples, which are thermal treated at temperature of 900 °C and over, observed substantial difference in IR spectra: by absence of bands which are peculiar to oscillations of CO_3^{2-} -ions and OH-groups, and also by the presence of band of 780 cm^{-1} .

On the Mössbauer spectra of hollandites observed approximated by one duplet, which parameters are represented in Table. The value of isomeric shift corresponds to trivalent iron ions in octahedron oxygen environment.

The parameters of Mössbauer spectra of hydroxycarbonate charge with ratio Ba : Fe : Ti = 1.0 : 2.0 : 6.0

| Number of sample | $T, ^\circ\text{C}$ (heating time) | I_s | Q_s | W | LG | Xi_2 |
|------------------|---------------------------------------|-----------|----------|----------|----------|---------------|
| 1 | 300 (1) | 0.595(2) | 0.896(3) | 0.606(5) | 0.77(2) | 1.396 |
| 2 | 500 (1) | 0.590(1) | 0.951(2) | 0.633(3) | 0.74(2) | 2.693 |
| 3 | 900 (1) | 0.634(1) | 0.522(1) | 0.368(2) | 0.985(3) | 1.21 |
| 4 | 900 (3) | 0.626(1) | 0.516(1) | 0.357(2) | 0.985(3) | 1.38 |
| 5 | 900 (5) | 0.593(1) | 0.482(1) | 0.335(2) | 0.983(3) | 1.44 |
| 6 | 900 (7) | 0.589(1)8 | 0.478(1) | 0.329(2) | 0.989(3) | 1.422 |

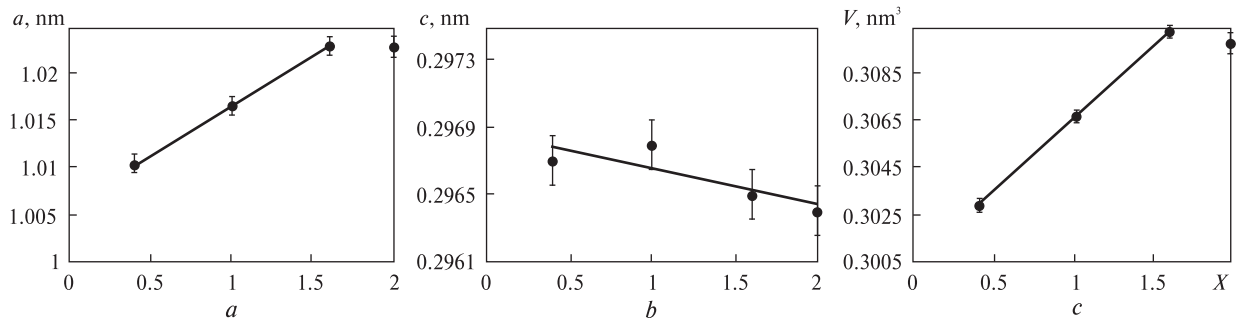


Fig. 5. Unit cell parameters of $Ba_{2-x/2}Cs_xFe_2Ti_6O_{16}$ series and cesium molar part dependence; legend — $BaFe_2Ti_6O_{16}$

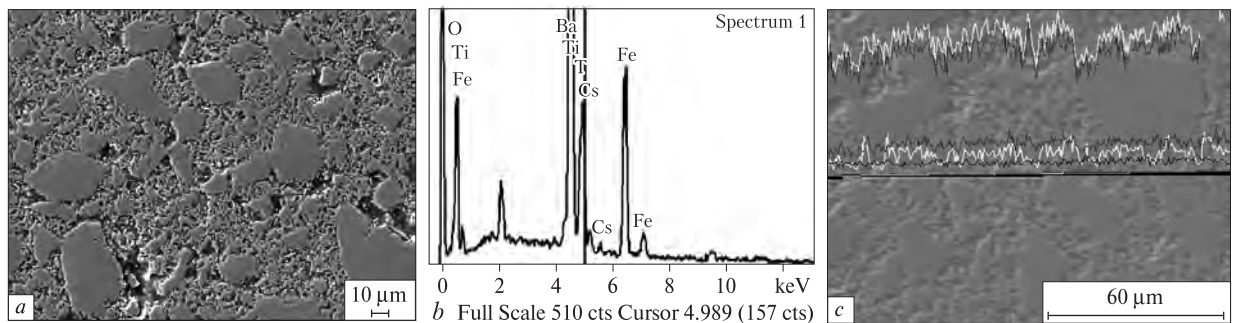


Fig. 6. SEM-image (a), EDS-spectrum of Cs-containing (Ba, Fe, Ti)-containing ceramics of $Ba_{0.9}Cs_{0.2}Fe_{2.0}Ti_{6.0}O_{16}$ composition (b) and distribution of elements over the sample (c): 1 — titanium, 2 — barium, 3 — iron, 4 — oxygen, 5 — cesium

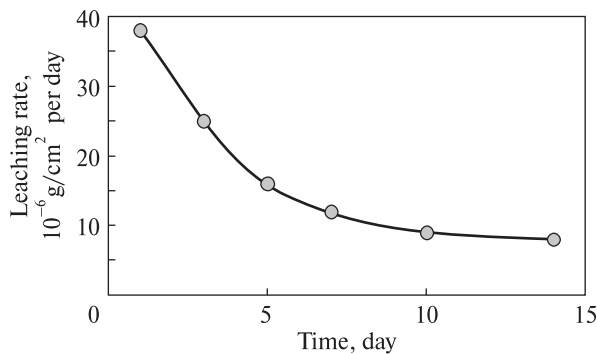


Fig. 7. Cs leaching rate in deionized water at 150 °C from ceramics of $Ba_{0.9}Cs_{0.2}Fe_{2.0}Ti_{6.0}O_{16}$ composition

It follows from these data, that with increase in temperature of calcination of HCCP charge from 300 to 900 °C the width of band absorption diminishes and the value of quadrupole splitting that corresponds to the stages of hollandite structure formation during the process of thermal treatment of hydroxycarbonate charge.

The diffraction patterns of ceramic samples are found to be analogous to polycrystalline powders, and monophasic character of ceramics is confirmed by results of SEM/EDS analysis. Chemical composition of hollandite phase almost does not differ from the target one ($Ba_{1.0}Fe_{2.0}Ti_{6.0}O_{16}$). A difference is only 0.03–0.05 per formula unit.

Thus, the results of investigations had been carried out, made it possible to determine the conditions of chemical diffusion-free synthesis, and to specify phase transformation sequence during the synthesis of (Ba, Fe)-titanate hollandites from systems of coprecipitated hydroxycarbonates.

For the Cs bonding to (Ba, Fe)-titanate hollandites the precursors were used with such a type of crystalline structure, where some part of Ba atom positions was vacant and can be filled with Cs with generation of Cs-containing hollandites. Obtained X-ray data completely confirmed such possibility and proved Cs-containing (Ba, Fe)-titanate hollandites generation at 900 °C.

Substitution of Ba to Cs in the $Ba_{2-x/2} \times Cs_xFe_2Ti_6O_{16}$ ($0.2 \leq x \leq 1.6$) series keeps the structural type of the basic phase — hollandite. Several additional to hollandite reflections, which belong to phases of other structural types, appear on X-ray diffraction patterns of the samples. With Cs content increase from 3 to 25 mass % (by Cs_2O) the hollandite phase unit cell volume also increases, mainly due to increase of lattice parameter "a" (see Fig. 5). The lattice parameter "c" slightly decreases, that is the most probably caused by large cations (Cs, Ba) ordering in the channel positions of hollandite structure. The nature of cell parameter change suggests the possibility of

effective Cs bonding by (Ba, Fe)-titanate hollandite up to ~25–26 mass % by Cs₂O (see Fig. 5).

The findings of X-ray and electron microprobe analysis of ceramics on the base of Cs-containing (Ba, Fe)-titanate hollandites of Ba_{2-x/2}Cs_xFe₂Ti₆O₁₆ (0.2 ≤ x ≤ 1.6) series have demonstrated the adequate convergence between aimed and experimentally determined compositions (see Fig. 6). According to SEM/EDS analyses, the Cs-containing samples (with x = 1.0; 1.6) together with basic Cs-containing hollandite phase are characterized by presence of insignificant quantities of arizonite and rutile phase (<10 relative %).

Arizonite phases contain almost no Cs and Ba (<1 mass %) and their composition is close to ferrous titanate (2Fe₂O₃ · 3TiO₂). Rutile phases contain 98–99 % of TiO₂ with Fe (1.1–1.20 % Fe₂O₃) impurity that is typical for natural rutile. Thus, Cs in the Cs-containing hollandite samples is hosted in the hollandite phase. Its content in arizonite and rutile phases does not exceed a determination error.

In order to determine the chemical stability of Cs-containing (Fe, Ti)-hollandite analogue of Ba_{0.9} × Cs_{0.2}Fe_{2.0}Ti_{6.0}O₁₆ composition a non-polished ceramic pellet of this composition was placed into titanium alloy autoclave with fluoroplastic inserts for leaching and was covered with contact solution – distilled water under 150 °C during 1, 3, 7, 10, and 14 days (test MCC2). The temperature was supported with an accuracy of ± 3 °C. The pressure corresponded to saturated steam pressure (~20 MPa) and it was set by coefficient of autoclave filling.

After some certain time interval the autoclaves were exposed to water hardening in cold water, the samples were taken out and covered with fresh contact solution. The sample should not get dry during changing of contact solution. The analysis of elements in each contact solution was performed with the help of atom adsorption method (stable Cs sensitivity makes 0.8 mg/l, Ti – 2 mg/l), and rate of leaching was determined according to equation [4]. The surface of samples was determined without correction for ceramic porosity. Sample surface-leaching agent volume ratio was kept within the limits of 0.01 mm⁻¹.

Visual appearance of samples after experiments almost did not change. Discolorations, surface destruction, caverns and fractures were absent.

Time-dependent decrease of Cs leaching rate is shown on Fig. 7. After 10 days the cesium leaching rate from the matrix slows down, and is equal to

~10⁻⁵ g/cm² · day. These values are analogous to Cs leaching rates of from (Al, Ti)-titanate hollandite [2] and synroc hollandite ceramics [6], and is two orders less comparing to cesium leaching rate from phosphate or borosilicate glass, which is about 10⁻³ g/cm² · day [9].

Conclusions. 1. Main regularities of (Fe, Ti)-hollandite analogue synthesis from nanodimensional amorphous systems of coprecipitated hydroxycarbonates are determined. It is shown that generation of these compositions occurs by single-stage mechanism through the "explosive" crystallization at considerably less temperatures (200–300 °C) and shorter heat-treatment time (one order less), than in case of initial oxides charge usage. Here also the Cs losses are eliminated or considerably decreased during the synthesis of Cs-containing samples.

2. It is elicited the possibility of effective Cs bonding in the (Fe, Ti)-hollandite analogue hollandite composition with generation of solutions limited hard series. Threshold value of Cs concentration reaches ~25–26 % by oxide.

3. It is determined normalized rate of Cs leaching from Cs-containing ceramic of Ba_{0.9}Cs_{0.2} × Fe_{2.0}Ti_{6.0}O₁₆ composition, which was two order lower comparing to leaching rate of alkaline elements from the industrial borosilicate glass.

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**ЗАЛІЗОТИТАНОВІ АНАЛОГИ ГОЛАНДИТУ —
МАТРИЦІ ДЛЯ ІММОБІЛІЗАЦІЇ Cs-ВМІСНИХ
РАДІОАКТИВНИХ ВІДХОДІВ:
СИНТЕЗ ТА ВЛАСТИВОСТІ**

За допомогою методів термогравіметрії, рентгенографії, ІЧ-спектроскопії, рентгеноспектрального електронно-зондового аналізу та сканувальної електронної мікроскопії встановлено основні закономірності синтезу (Fe, Ti)-аналогів голандиту із нанорозмірних аморфних систем спільноосаджених гідроксикарбонатів. Показано, що їх утворення відбувається за одностадійним механізмом шляхом "вибухової" кристалізації. Визначено оптимальні параметри синтезу високодисперсних порошоків з використанням спільноосаджених гідроксикарбонатів і щільноспеченої кераміки, які характеризуються значно меншими температурою і часом термообробки, порівняно з використанням шихти вихідних оксидів. Встановлено можливість ефективного зв'язування Cs у складі (Fe, Ti)-аналогів голандиту. Визначено нормалізовану швидкість вилуговування цезію з Cs-вмісної кераміки складу $Ba_{0,9}Cs_{0,2}Fe_{2,0}Ti_{6,0}O_{16}$.

Ключові слова: голандит, радіоактивні відходи, іммобілізація цезію.

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**ЖЕЛЕЗОТИТАНОВЫЕ АНАЛОГИ ГОЛЛАНДИТА —
МАТРИЦЫ ДЛЯ ИММОБИЛИЗАЦИИ
Cs-СОДЕРЖАЩИХ РАДИОАКТИВНЫХ
ОТХОДОВ: СИНТЕЗ И СВОЙСТВА**

С помощью методов термогравиметрии, рентгенографии, ИК-спектроскопии, рентгеноспектрального электронно-зондового анализа и сканирующей электронной микроскопии установлены основные закономерности синтеза (Fe, Ti)-аналогов голландита из наноразмерных аморфных систем совместноосажденных гидроксикарбонатов. Показано, что их образование происходит по одностадийному механизму путем "взрывной" кристаллизации. Определены оптимальные параметры синтеза высокодисперсных порошков с использованием совместноосажденных гидроксикарбонатов и плотноспеченной керамики, которые характеризуются значительно меньшими температурой и временем термообработки, по сравнению с использованием шихты исходных оксидов. Установлена возможность эффективного связывания Cs в составе (Fe, Ti)-аналогов голландита. Определена нормализованная скорость выщелачивания цезия из Cs-содержащей керамики состава $Ba_{0,9}Cs_{0,2}Fe_{2,0} \times Ti_{6,0}O_{16}$.

Ключевые слова: голландит, радиоактивные отходы, иммобилизация цезия.