

The mechanism of transformation of hydrophosphates (Na,Ce) and (Na,Sr) in reactions of metasomatic replacement under the scheme of "wet process» immobilization radionuclides

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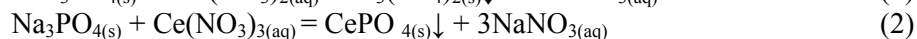
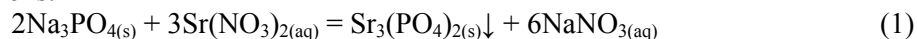
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Results of research of interaction are given in system: phosphate - containing mineral composition – Sr or Ce nitrate – Sr or Ce phosphate. Methods element, X-ray and AAS analyses investigated conditions at which practically all phosphate of sodium entering into initial mineral composition, it is possible to replace with insoluble phosphates of the corresponding radionuclides (Sr or Ce). In such a way received phosphates are those phases in the synthesized mineral matrixes which hold radionuclides.

Key words: radioactive waste, mineral matrixes, speeds of processes, immobilization of radionuclides of Sr and Ce

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Ceramic materials based on titanates, zirconates, and complex phosphates are produced for the immobilization of rare-earth and actinide radionuclides by the methods of hot pressing and sintering [Ringwood *et al.*, 1988, Martynov *et al.*, 1993]. In work [Suvorova *et al.*, 2009] the method of matrix material synthesis on the basis of metasomatic replacement reactions according to the scheme of «wet process» [Kotelnikov *et al.*, 2005] is described. Process of replacement can be carried out at room temperature and atmospheric pressure. Strontium and cerium phosphates were synthesized using the following reactions:



The essence of these reactions is the replacement of the crystalline phase of sodium phosphate by slightly soluble strontium (cerium) phosphate and the removal of a soluble compound (sodium nitrate) into aqueous solution. In work interaction processes phosphate - containing mineral compositions with Sr or Ce nitrates, and also pure Na phosphate with the same nitrates are investigated.

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In order to carry out the replacement reaction, strontium (cerium) nitrate solutions were filtered through columns filled with a model or natural granite and grains of crystalline sodium orthophosphate.

Behavior of Sr and Ce at interaction with calcinated Na_3PO_4

Starting materials. Anhydrous sodium orthophosphate was obtained by drying and annealing at 1100°C of $\text{Na}_3\text{PO}_4 \times 12\text{H}_2\text{O}$ reagent was attained, which resulted in the sintering of individual crystallites into polycrystalline aggregates. In columns with fraction of a starting mix 0.40–0.63 mm speed of solution infiltration provided course of exchange reactions in phosphates therefore this fraction was chosen for carrying out reactions of metasomatic replacement.

In order to carry out the replacement reaction in a initial series of experiences solutions of nitrates of strontium were filtered through the columns filled with a model granite and grains of crystal

orthophosphate of sodium (25 mas.% from mix weight). To receiving a model granite applied mixes of grains albite (90 mas.%) or a microwedge (85 mas.%) and quartz (10 ÷ 15 mas.%).

In preliminary experiences through columns with mixes it is flowed within 5 days by portions of 6.86 ml 1M Sr(NO₃)₂ solution. After the first portion (1.5 ml of solution) replacement was sharply broken since the stopper from the formed jellylike hydrophosphate of strontium – SrH(PO₄) - didn't pass the next portion of solution. In every portion of the proceed filtrate defined the composition of Sr. In a filtrate from a column with Mic of strontium isn't present, it replaced all in Sr₃(PO₄)₂ and NaSrPO₄ which have settled in a column. In a column with Ab there was an insignificant quantity of Sr.

For comparison in static conditions (without a channel of new portions of solution) experiments on interaction of phosphate of sodium with the distilled water, with 1M Sr(NO₃)₂ solution and with Mic+Qz mix + Na₃PO₄ + 1M Sr(NO₃)₂ were made. The composition of Sr and Na defined, separating a solution share. Results of these experiences are presented in table 1.

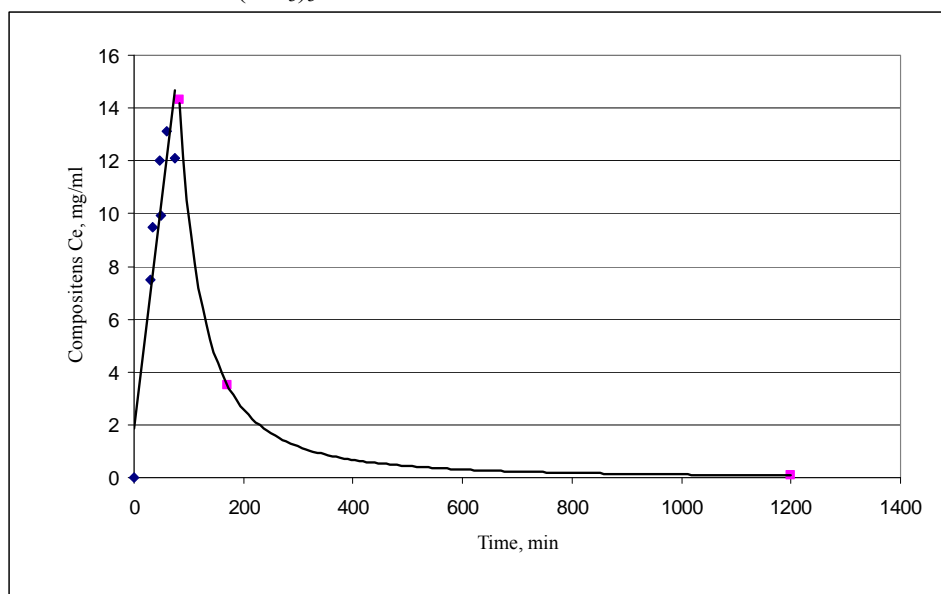
Table 1. Change of composition of Sr and Na during exchange reactions with phosphate Na₃PO₄.

Composition	Duration of contact	[Na], mg/ml	[Sr], mg/ml
Mic+Qz + Na ₃ PO ₄ + Sr(NO ₃) ₂	5 days, column N 4	1.06	0.0
Ab+Qz + Na ₃ PO ₄ + Sr(NO ₃) ₂	5 days, column N 2	145.0	0.012
Na ₃ PO ₄ + 6.86 ml H ₂ O	2 hour, static	315.0	-
Na ₃ PO ₄ + 6.86 ml Sr(NO ₃) ₂	2 hour, static	21.6	51.0
Mic+Qz + Na ₃ PO ₄ + Sr(NO ₃) ₂	2 hour, static	46.0	23.0

In the composition of the solid phase which has remained in reactionary capacity, except Mic+Qz, there is Sr₃(PO₄)₂ and NaSrPO₄. Experiments on interaction of sodium phosphate mixed with Mic+Qz or Ab+Qz in static conditions were carried out also with 1M Ce(NO₃)₃ solution. In the composition of the solid phase in both experiences, except Mic+Qz or Ab+Qz, there is CePO₄ and Na₃Ce(PO₄)₂.

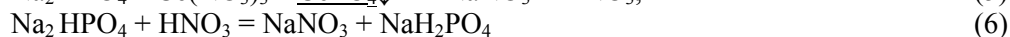
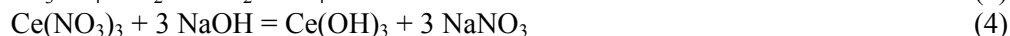
The interaction kinetics in a column of Ce(NO₃)₃ solution of the various concentration with various model granite mixes is investigated, is the most detailed - filtration kinetics 0.1M Ce(NO₃)₃ solution through a column filled with a granite-phosphatic mix. Composition of Ce defined in portions of the replaced filtrate. The salt which slipped into a filtrate - rabdofonite CePO₄·nH₂O, where n = 0,5-1,5. Results of this experience are presented on fig. 1.

Fig. 1. Kinetics of change of he Ce contents in a product of reaction of a granite - phosphatic mix with 0.1M Ce(NO₃)₃ solution.



As appears from fig. 1 in process of intake of solution the maintenance of Ce grows as solution is spent for Na phosphate moistening. that leads to its hydrolysis. Emergence of NaOH leads to formation of a hydroxide of Ce – Ce (OH)₃. Gradually hydrolysis chokes with the additives of Ce (NO₃)₃ solution leading to growth of concentration of Ce. Eventually, accumulation of badly soluble hydroxide leads to obstruction of a column and reduction of filtrate exit.

In 2 hours in plum CePO₄ salt loss - a product of interaction of the arrived Ce (NO₃)₃ solution with neogenic Na hydrophosphate was observed. Reduction of concentration of Ce began. The filtrate went very slowly. The mechanism of this interaction can be described the following scheme:



This mechanism proves to be true also other columnar experiences with Sr and Ce nitrates. Results of these experiences are presented in table 2 and in drawing 2.

A) **Table 2.** Change of Sr and Na contents during experience with 1M Sr (NO₃)₂ solution

Duration of interaction, min	37	42	47	67	80	122
Content Sr, mg/ml	32	27.3	25.5	30	34	8.5
Content Na, mg/ml	3	-	-	-	-	22.5

B)

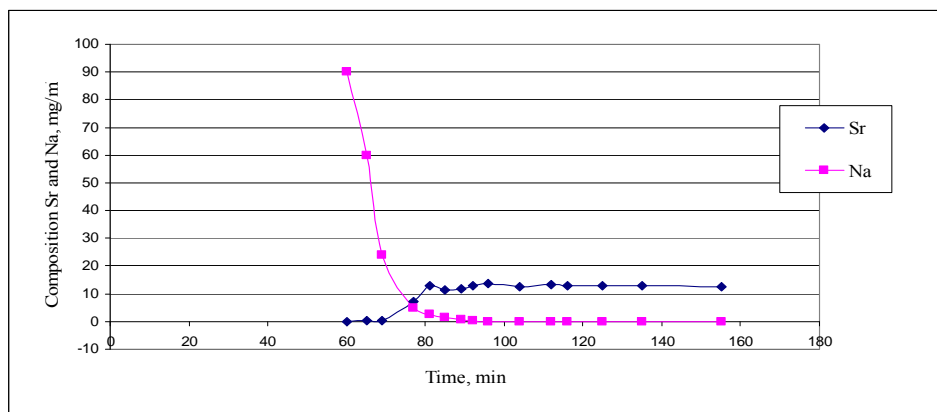


Fig. 2. Kinetics of change of Sr and Na contents in a reaction product phosphate - containing composition with 0.2M Sr(NO₃)₂ solution

C) Similar experiences with 1M Ce (NO₃)₃ solution too show a small amount of sodium in a filtrate (17 mg/ml) - solution of nitrate is spent for Na phosphate hydrolysis.

So, in all columnar experiences similar nature of interaction – formation of the connection interfering course of settlement amount of nitrate solutions that leads to the premature termination of reagents interaction is observed. To define optimum parameters of «wet process» immobilization of radionuclides, a series of experiments on interaction of nitrates of these nuclides with a pure reactant of Na₃PO₄·12H₂O was carried out.

Behavior of Ce and Sr at interaction with Na₃PO₄·12H₂O

1. Static conditions

Ce: In each of 6 capacities it is placed on 250 mg of Na₃PO₄·12H₂O and it is flowed on 6,6 ml 0.2M Ce(NO₃)₃ solution. By the expiration of chosen time determined the conten of Ce in solution from the next capacity. It practically didn't change, as it is presented in table 3.

Table 3. Change of Ce content in reaction products with 0.2M Ce(NO₃)₃ solution.

Duration of interaction, min	50	130	220	1200	2460	3880
[Ce], mg/ml	20.3	20.5	21.5	22.7	18.9	18.2

Sr: The similar technique was used in experiences with 0.2M Sr(NO₃)₂ solution. Results are presented on fig. 3.

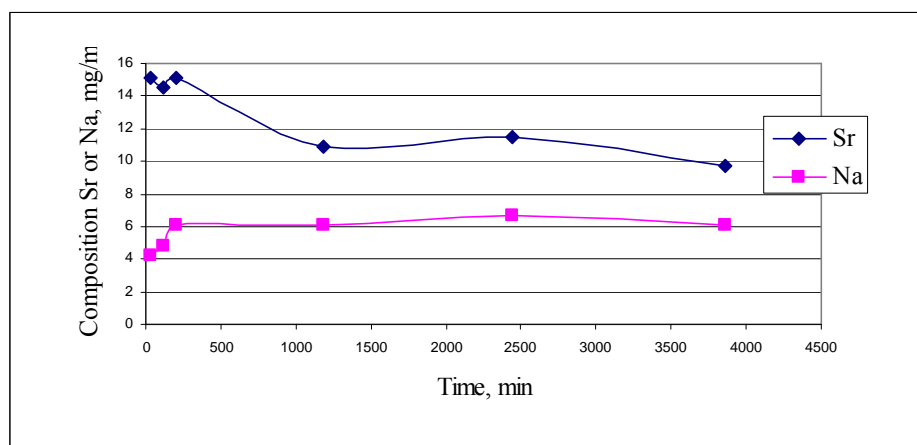


Fig. 3. Dependence on duration of interaction with 0.2M $\text{Sr}(\text{NO}_3)_2$ solution of Sr and Na contents in a reaction product with $\text{Na}_3\text{PO}_4 \times 12\text{H}_2\text{O}$

Apparently from drawing 3, Na_3PO_4 was hydrolyzed with formation of the soluble forms which have defined increase of sodium concentration within the first 20 hours. For this short period the content of strontium in solution only it was designated, and then began to fall since there passed reaction of replacement of $\text{Sr}(\text{NO}_3)_2$ to settling $\text{Sr}_3(\text{PO}_4)_2$. Concentration of both elements, as well as cerium (see tab. 3), remain after about 20 hours constants, despite long endurance.

2. Kinetic conditions

Ce: Through a column in which 1 g of $\text{Na}_3\text{PO}_4 \times 12\text{H}_2\text{O}$ is placed, it is flowed by portions of 18 ml 0.2M $\text{Ce}(\text{NO}_3)_3$ solution. Results of this experience are presented in table 4.

Table 4. Change of Ce content in a product of reaction of $\text{Na}_3\text{PO}_4 \times 12\text{H}_2\text{O}$ with 0.2M $\text{Ce}(\text{NO}_3)_3$ solution

Duration of interaction, min	15	960	970	1200	1220	1305
[Ce], mg/ml	0.034	0.440	0.466	0.510	-	0.910

Sr: The similar technique was used in experiences with 0.2M $\text{Sr}(\text{NO}_3)_2$ solution. Results are presented on fig. 4.

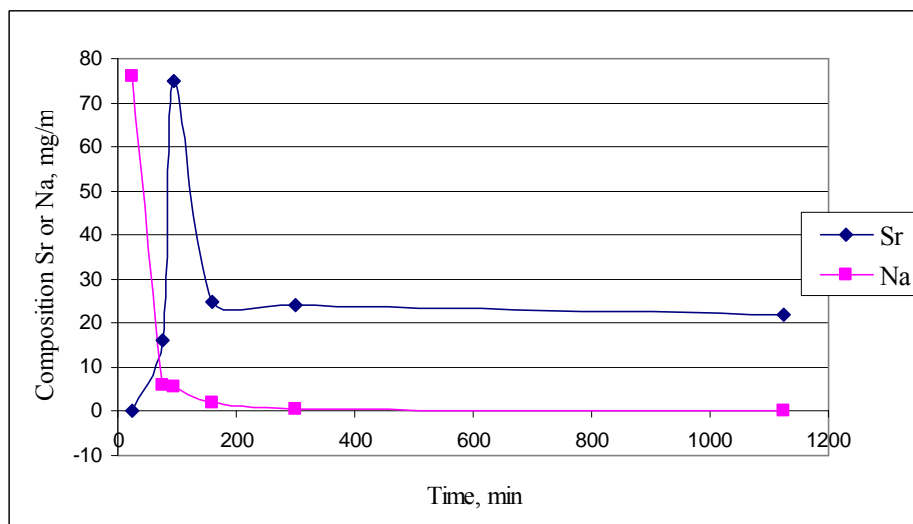


Fig. 4. Kinetics of change of Sr and Na contents in a product of reaction of $\text{Na}_3\text{PO}_4 \times 12\text{H}_2\text{O}$ with 0.2M $\text{Sr}(\text{NO}_3)_2$ solution

In these experiences – with participation few the concentrated solutions, as well as in all columnar experiences, it is possible to observe initial sharp growth of concentration of cerium and strontium though at cerium it comes later. Then concentration of both elements fall since there passes reaction of replacement of $\text{Sr}(\text{NO}_3)_2$ to settling $\text{Sr}_3(\text{PO}_4)_2(s)$ on reaction (1) or $\text{Ce}(\text{NO}_3)_3$ on settling $\text{CePO}_4(s)$ on reaction (2). Having sharply fallen, they remain constants, despite long endurance, i.e.

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further interaction doesn't occur owing to formation of the jellylike hydrophosphates interfering contact of reactants. Judging by amount of sodium in a filtrate, its replacement occurs actively, and it is spent up to the end.

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