

SYNTHESIS OF MATRIX MATERIALS FOR RADIONUCLIDES IMMOBILIZATION BY THE «WET PROCESS» METHOD

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The problem of neutralization of high level waste is necessary for the further development of nuclear power. Existing methods of immobilization of radioactive waste (RAW) in matrix materials are far from optimum.

The conception of phase and chemical conformity developed by us has allowed optimizing matrix materials. According to the conception the best matrixes for immobilization of RAW are solid solutions of rock-forming and accessory minerals.

Isomorphic replacements in natural minerals, as a rule take place within the groups of periodic system of elements; therefore it is necessary to separate a mix of radioactive waste on groups of elements. Methods of such separation are developed on the radiochemical plants of Russia (specifically at PA «Mayak») and quite really can provide preliminary separation of high level waste products. Our researches are focused on such preliminary separation of RAW elements and synthesis of the corresponding mineral solid solutions, capable to include and immobilize groups of elements.

There is the general rule, known by any experimenter - the more stable is the mineral, it is more difficult to synthesize it. We used the idea of possible much simplification of process of matrix materials synthesis to lower parameters of synthesis, in an ideal - up to room. As a result of our theoretical studies, for synthesis of matrix materials we have decided to use the scheme of «wet process»:

Water solution of RAW	⇒	Separation of RAW on groups of elements	⇒	Sorption from water solutions, reaction of sedimentation, reaction of replacement	⇒	Phase transformation	⇒	Mineral matrix for disposal in rocks
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For synthesis of minerals by this scheme it is necessary to carry out primary fixing of elements on a sorbent, or a water mineral - these reactions proceed at room temperatures in water solutions, and then to carry out phase transformation of this material (heating up to ~ 1000°C) for its reduction into a stable mineral matrix.

Such substituted sorbents during heating turn into a stable matrixes. This scheme was approved on the following elements: Cs, Sr, Rb, REE, Ag, Pd, Rh, I.

In the work we used the following principles and techniques: 1) phase and chemical conformity; 2) sorption (normal and ion-exchange); 3) chemical reactions in solutions; 4) metasomatic reactions; 5) phase transformations.

1. Method of sorption (normal and ion-exchange)

For immobilization of radionuclides of alkaline-earth elements (Sr and Cs) synthesis of ceramic materials from the different zeolites preliminary impregnated with simulators of elements by sorption from solutions of corresponding nitrates on ion-exchange columns was executed. These zeolites are practically isochemical to feldspars and feldspathoids.

Phase transformation of strontium and cesium forms of zeolites was carried out by the next methods: 1) annealing of samples preliminary pressed in tablets at room temperature under pressure about 100 kg/sm² in a high-temperature furnaces during 3 days at 1000°C; 2) hot pressing of similar samples on original laboratory installation at 800-900°C and axial pressure of 150-500 kg/sm² during 1-2 hours.

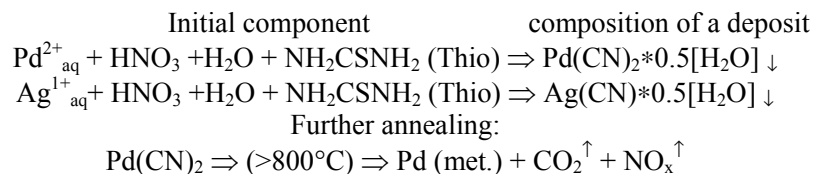
Strontium leaching rate from a matrix synthesized by phase transformation of strontium form of zeolite NaX is comparable with leaching rate of Sr from matrix Synroc-C (most stable matrix material developed

on today). Leaching rate of Cs-containing feldspathoids relatively to cesium at first days are comparable with Cs leaching rate from borosilicate glasses, but in time leaching rate is reduced and in 29 day becomes for feldspathoids up to 20 times less, than in glasses.

2. Method of chemical reactions in solutions. Sedimentation of precious metals

Selective extraction of palladium and silver from nitrate (6M HNO₃) solution of radionuclides was produced with the thiourea (Thio) which is oxidized up to cyanide-iones ore nitrilic groups [-C≡N] (during interaction with nitric acid), settling Pd and Ag as almost insoluble residual matter. Solubility of a residual matter of a palladium is equal $2 \cdot 10^{-7}$ mol/l. After annealing of this material at 800°C, metal Pd and Ag can be obtained.

The reactions schemes:

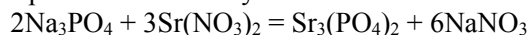


In distinction from method of extraction of Pd and Ag, Rh sedimentation was carried out in 2 stages. Sedimentation of the basic amount of rhodium was carried out from the concentrated solutions (C Rh(III) = 1-5 mg/ml on 3M HNO₃), adding to studying solution Thio nitrate solution with ratio Rh(III): Thio = 1:6. However the composition of a filtrate from a residual matter specified presence of Rh(III), that denote incomplete deposition of rhodium from a studied solution. Residual Rh was extracted from thinned solutions with the support of S-dioxide Thio - formamidinsulfine (NH₂)₂CSO₂, obtained from Thio by hydrogen peroxide using technique [1]. Thus, it is possible to extract Rh, Pd, Ag and other precious metals for their application in various industrial technologies.

3. Method of metasomatic reactions

Method based on metasomatic reactions of replacement is developed for immobilization of radionuclides from groups of alkaline-earth elements and actinides. This method is tested for synthesis of phosphates of Sr and Ce.

Synthesis of strontium phosphate carried out by method of metasomatic replacement on reaction:



For its realization through Na₃PO₄, placed in a modeling «granite» matrix (a mix of grains albite and quartz, or a microcline and quartz), filtered 1M solution Sr(NO₃)₂.

The circuit of process of synthesis of phosphate of cerium is similar. For its realization through Na₃PO₄, placed in a modeling «granite» matrix (a mix of grains albite and quartz, or a microcline and quartz) or river sand, filtered 1M solution Ce(NO₃)₃.

As a result of experiments the «pseudo-granite» ceramic materials including minerals of (NaSr)PO₄ and (Na_{1.36}Ce_{0.48})P_{0.98}O_{3.89} compositions, probably being the analogues of natural minerals olgite (NaSr_{0.55}Ba_{0.45}[PO₄]) and vitusite (Na₃Ce[PO₄]₂) were synthesized. The density of matrixes is about 60% from theoretical.

Conclusions

I. Techniques for fixing of RAW elements are developed and experimentally tested on the basis of the scheme of «wet process».

II. The method has the following advantages (in comparison with other methods):

- (1) Room conditions of reactions carrying out;
- (2) Possibility of carrying out of continuous process;
- (3) Techniques allow to carry out synthesis in «wet» conditions, avoiding of load powdering and constantly to supervise the composition of solution;
- (4) Simple scheme of phase transformation of transitional products into a stable mono- and polymineral matrixes.

III. Matrix materials for immobilization of radionuclides Cs, Sr, Rb, REE, Ag, Pd, Rh, I were synthesized using scheme of «wet process».

Reference

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