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Method of synthesis of ceramic matrices for the radionuclides immobilization and its optimization

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Method of synthesis of matrix materials for radionuclides of rare-earth and alcaline-earth elements immobilization based on metasomatic replacement reactions using the scheme of «wet process» is presented in the work, the possibilities of its optimization are consider . This method allows spending process of radionuclides fixation on phosphate-containing mineral compositions at room temperature and atmospheric pressure under wet conditions. The results of synthesis of mineral matrices containing of binary (Sr, Na)- and (Ce, Na)- phosphates and also simple strontium and cerium orthophosphates are presented in the work.

Deficiency of solutions of Sr- or Ce- nitrates leads formation of mineral phases similar by composition to natural minerals olgite $NaSrPO_4$ or vitusite $Na_3Ce(PO_4)_2$. Simple orthophosphates of Sr and Ce were synthesized using of super quantities of nitrates solutions. For the further optimization of mineral matrice synthesis - decrease in temperature and increase of matrice density, the addition of Na- silicate in the form of liquid glass to solid mineral composition was used. As a result of experiments the polymineral ceramics consisting of feldspars, quartz, phosphates of strontium and cerium and small amount of Sr-containing glass have been received.

Key words: radionuclides immobilization, crystalline matrix materials, matrices synthesis

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The conception of phase and chemical correspondence in system matrix – solution – wallrock [*Kotelnikov et. al*., 1994] allow to optimize matrix materials for immobilization of the radionuclides of nuclear fuel cycle and suggest solid solutions of rock-forming and accessory minerals as stable matrices. Our experiments on investigation of leaching velocities of elements from natural minerals [*Kotelnikov et. al., 1999*] show that it is possible to recommend application of ceramic matrices based on accessory minerals of groups of phosphates, titanates and zirconates for fixing of rare earth and transuranium radionuclides. The techniques of hot pressing and sintering [*Ringwood et al.,* 1988, *Martynov et al.,* 1993] are usually used for synthesis of ceramic mineral matrices. However in this synthesis there is an unresolved problem of an initial material dispersion during mixing of matrice components. For its decision we used the scheme of «wet process» [*Kotelnikov et. al., 2005, Suvorova et. al., 2006, Suvorova et. al., 2012*].

Synthesis of phosphates was carried out using the metasomatic replacement reactions:

$$2Na_3PO_{4(s)} + 3Sr(NO_3)_{2(aq)} = Sr_3(PO_4)_{2(s)}\downarrow + 6NaNO_{3(aq)} \quad (1)$$

$$Na_3PO_{4(s)} + Ce(NO_3)_{3(aq)} = CePO_{4(s)}\downarrow + 3NaNO_{3(aq)} \quad (2)$$

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 order to carry out the replacement reaction, strontium (cerium) nitrate solutions were filtered through columns from quartz glass filled with a model or natural granite and grains of crystalline sodium orthophosphate. The filtrate was collected in flasks and analyzed for strontium (cerium) and sodium. The mixtures of grains of natural feldspars (microcline, albite) and quartz (quartz sand in some experiments) were used as starting materials in the experiments on synthesis of granite matrix.

The filtrate was analyzed on containing of strontium (cerium) after the metasomatic replacement in columns. The matrices bringing from the columns were annealed at temperatures of 1100–1250°C during two hours. This resulted in the complete dehydration of aqueous phosphate and sintering of materials into massive aggregates. Products of experiments were investigated by the X-ray method; for an estimation of compositions of synthesized solid phases the microbeam method was applied.

Only up to 50 wt % of $Sr(NO_3)_2$ or $Ce(NO_3)_3$ water solutions were passed through the columns in the first experimental series. Then the columns were blocked up and the solution flow was completely passed off. After drying at 400°C and annealing at 1100°C, binary orthophosphates of Na and Sr or Na and Ce were diagnosed in columns.

Thus, the deficit of Sr- and Ce- nitrate solutions resulted in formation of mineral phases similar in composition to the natural minerals olgite $NaSrPO_4$ (Fig. 1) or vitusite $Na_3Ce[PO_4]_2$) (Fig. 2) in the column.

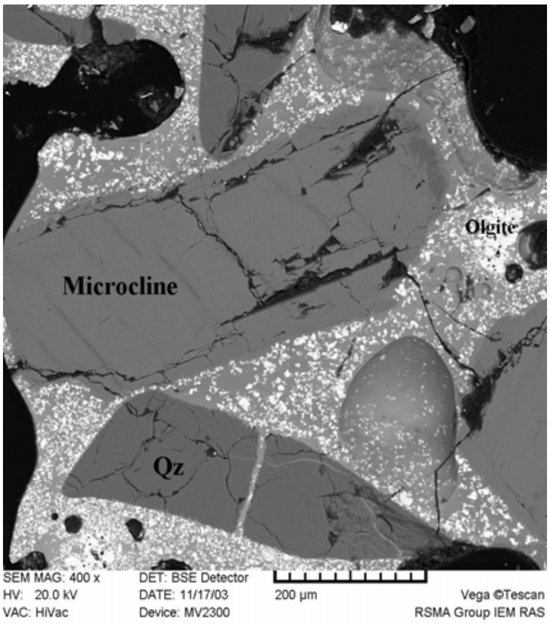

Fig. 1. Polymineral matrix on the basis of model granite for Sr immobilization in phosphate form. The small light grains on photo – phosphate Sr olgite ($NaSrPO_4$).

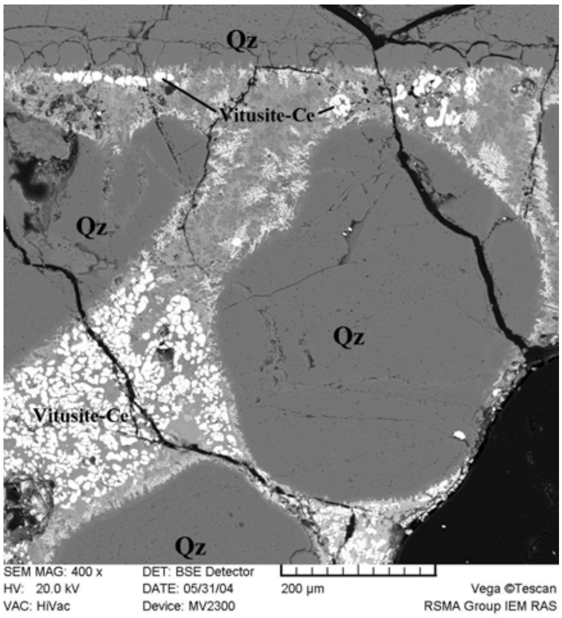

Fig. 2. Polymineral matrice on the basis of quartz sand for Ce immobilization in phosphate form. Light grains on photo – phosphate Ce vitusite ($Na_3Ce[PO_4]_2$).

Simple strontium and cerium orthophosphates were synthesized with excess amount of nitrate solutions. In order to decrease the temperature of matrix sintering and increase its density the leucogranite of the Spokoininskoe deposit of Eastern Transbaikalia was used as a starting material instead of separate feldspar and quartz grains. Synthesis of mineral matrices was carried out by the method described above under the same optimal conditions. In these experiments, compulsory depression was created at the output of the column, which accelerated the solution flow and provided the completeness of its infiltration trough the leucogranite – Na phosphate mixture.

The experiments on metasomatic replacement with subsequent drying and annealing produced polymineral ceramic composites consisting of feldspar, quartz and strontium phosphate (Fig. 3) or cerium phosphate (Fig. 4). Phosphate of strontium is close by its structure to α- $Sr_3(PO_4)_2$ and cerium phosphate – to a mineral monazite-Ce ($CePO_4$).

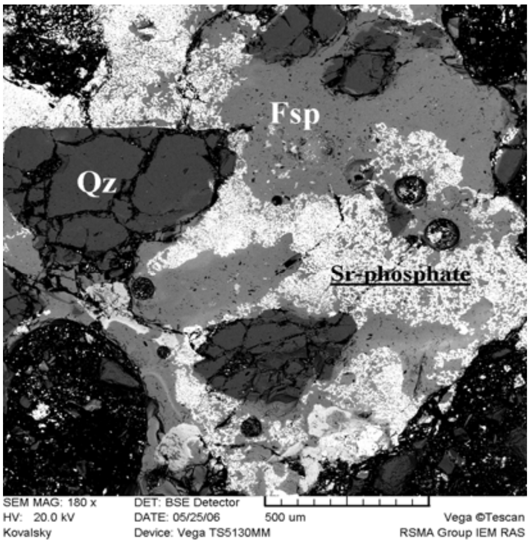

Fig. 3. Mineral matrice for Sr immobilization based on granite from the Spokoininskoe deposit containing strontium α-phosphate, $Sr_3(PO_4)_2$.

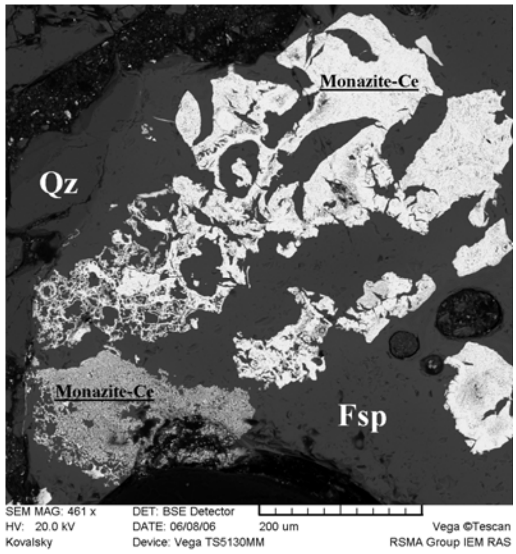

Fig. 4. Mineral matrice for Ce immobilization based on granite from the Spokoininskoe deposit containing Ce-monazite, $CePO_4$.

In details proven conditions of synthesis of mineral matrix materials allow to receive compact ceramics with the minimum surface for a leaching of components. Increase of density of the received crystal mineral composition for additional decrease of leaching velocities of matrix components may be reach by: 1) annealing of the received mineral composition in a column at the atmospheric pressure and temperature in an interval 900–1250ºC (depending on mineral composition of a silicate granite basis) or 2) hot pressing at the axial pressure of 700 kg/cm^2 and temperature in an interval 815–900ºC (depending on mineral composition of granite basis).

Method of synthesis of matrix material with addition of industrial liquid glass in composition was developed for optimization of process of ceramics synthesis (decrease in temperature of sintering and increase of matrix density). Na- silicate in the form of liquid glass with silica ratio equal 2 was added into a column after metasomatic replacement reaction. The increasing of speed of percolation of liquid glass through leicogranite grains was caused by assisted depression on an exit from a column. Further drying of ceramic composition without its unloading from a column was carried out at 110ºC within 24 hours. The cylindrical fragments of a column received as a result of hot pressing at 850ºC and axial pressure of 680 kg/sm^2. The products of experiments on synthesis of Sr- containing composition using such method consists of feldspar, quartz, strontium phosphate (white phases on fig. 5) and Sr-containing glass (small light-grey phases on fig. 5).

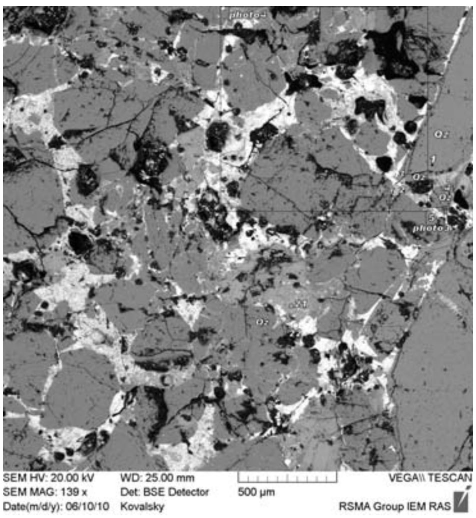

Fig. 5. Matrice for Sr immobilization in a mineral composition with addition of of liquid glass (Na- silicate).

In case of using of small-grained natural granite in experiences the eutectic melting on grain borders is reached at the minimum temperature. Such natural mineral composition can be recommended as an alumosilicate basis of a mineral matrice for immobilization of components of liquid high level waste of alcaline-earth and rare earth element groups in crystalline phosphate.

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