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Microspheric Aluminosilicate Sorbents for Solidification of Liquid Radioactive Wastes in the Mineral-Like Form

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Abstract

The use of the products formed in combustion of the mineral part of coal (cenospheres) that are close in the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ to crystalline aluminosilicates of the structural type of rock-forming granitoid minerals, in processing and burying radioactive wastes (RAW) allows one to solve the problems of waste minimization both in nuclear and fuel power engineering. Due to the application of microspheric zeolites and porous materials based on cenospheres of the ash from the combustion of the Kuznetsk coal for solidification of liquid RAW containing cesium and strontium radionuclides, it becomes possible to obtain glass crystal compounds under rather soft conditions (750–900 °C). Under these conditions, mineral-like phases of feldspar and feldspathoids fixing radionuclides in their lattice are formed. The target phases content reaches 66–80 %.

Key words: cenospheres, solidification of liquid radioactive wastes, porous materials, microspheric sorbents, glass-ceramic compounds

INTRODUCTION

The development of nuclear power engineering, the activities of the enterprises of defence industry and research institutes have lead to the accumulation of a large amount of radioactive wastes (RAW) with different degrees of activity. About 5 million m^3 of liquid RAW with the total activity of $2.85 \cdot 10^{18}$ Bq is formed every year at the enterprises of the nuclear branch in Russia alone [1] while the volume of accumulated liquid waste exceeds $4.13 \cdot 10^8 \text{ m}^3$ [2]. The problem of processing liquid RAW is especially urgent for highly active wastes (HAW) containing both relatively short-lived but exclusively toxic and heat-generating elements of cesium-strontium group, and long-lived elements of the transuranium group. These wastes are characterized by the highest ecological danger during long-term storage in view of the risk of seal failure in the storage and the evolution of radionuclides into the

biosphere. Liquid RAW is formed mainly at radiochemical plants dealing with the regeneration of spent nuclear fuel (SNF).

The concept of SNF handling that formulates ecologically safe strategy for the nuclear branch in Russia concerning the final stage of the nuclear fuel cycle provides the isolation of transuranium elements (lanthanoid and actinoid fraction) and the fraction containing radionuclides ^{137}Cs and ^{90}Sr from HAW [3]; these elements are to be finally isolated from the environment in deep-lying geological storages after they are transformed into a stable solid form. The ecological safety of such storage is determined by the system of engineering barriers and is provided by the correspondence of the physicochemical properties of the solidified material and enclosing strata at the storage site.

In the majority of the countries that are members of the International Atomic Energy Agency, granitoids are considered as the prop-

er geological environment to bury RAW. According to the principle of the close position of RAW burying places to the places of their formation, accepted and realized in Russia, practical works aiming at the evaluation of the suitability of geological conditions for burying HAW and SNF were carried out at the territory of Krasnoyarsk Territory (Nizhnekansk granitoid body, the region of the Mining and Chemical Combine) and in the Chelyabinsk Region (RT-1 Plant, PO Mayak).

On the basis of the integrated analysis of the geological, geophysical, seismological and topographic materials, aero- and space photographs, granitoids of the Nizhnekansk body were accepted as the most promising geological ground for burying liquid RAW. This fact defines the urgent character of research aimed at the development of mineral-like matrices similar in structure and properties to the aluminosilicate rock-forming minerals of granitoids. A detailed analysis of the geological aspects of burying, the mineral composition of enclosing rocks, rock-forming minerals to form solid solutions into the structure of which cesium and strontium radionuclides may be incorporated, as well as mineral-like matrices with similar structures, the methods of obtaining them and their stability to leaching was carried out in [4, 5].

The direct synthesis of aluminosilicates, especially from mixtures containing radioactive isotopes, requires complicated and expensive technology. In this connection, the development of energy-saving and relatively cheap methods to include Cs–Sr fractions of HAW into aluminosilicate mineral-like matrices is urgent. The arrangement of these matrices in stable blocks of the Earth's crust, provided that the geochemical equilibrium between the matrix material and the enclosing rocks is conserved, will ensure their chemical stability for a long time and as a consequence this will ensure the ecological safety of the burying system [6].

One of the versions to transform water-soluble ^{90}Sr and ^{137}Cs forms into water-insoluble mineral-like aluminosilicate materials can be implemented within the framework of sorption-mineralogical approach. This approach is based on the sorption of cesium and strontium radionuclides on aluminosilicate precursors and their subsequent solid-phase transformation into feld-

spar and feldspathoids that are able to fix cesium and strontium radionuclides in the framework cavities on the basis of isomorphous substitution [7–9]. Precursors may be thermodynamically metastable systems (amorphous and crystalline) that undergo phase transition under relatively soft conditions (temperature, pressure) with the fixation of the necessary amount of radionuclides in the form of insoluble compounds (mineral-like ceramics) with the low rate of leaching radioactive elements.

Hollow aluminosilicate microspheres of volatile energy ash – cenospheres – can serve as these precursors. These cenospheres are formed from the mineral part of coal during combustion in the form of dust. They are formed either as the direct semi-products of the fine separation of heterogeneous concentrates or as the products of their modification – microspherical zeolites and porous materials [5]. With this approach, the cycle of RAW processing and burying in fact involves the products of the combustion of the mineral part of coal close in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio to the predicted RAW solidification products (feldspars and feldspathoids) [5], which provides a simultaneous solution to the problems of waste minimization but in nuclear and in fuel power engineering.

The goal of the present work was to evaluate quantitatively the phase composition of vitreous crystalline compounds incorporating ^{137}Cs and ^{90}Sr radionuclides and prepared using the microspherical aluminosilicate sorbents based on cenospheres of ash from power engineering facilities.

EXPERIMENTAL

Two types of microspherical aluminosilicate sorbents were used in the work: porous aluminosilicate matrices of block type (PM) and microspherical zeolite sorbents (MZS) containing the phase of zeolite belonging to the structural type of NaP1 (NaP1-MZS). The latter sorbents were obtained on the basis of narrow fractions of cenospheres isolated according to the procedure described in [10] from the concentrates of volatile ash formed as a result of combustion of coal from the Kuznetsk Basin at the Tom-Usinsk Heat and Electric Power Plant (fraction (+0.08–0.18) mm, packed density $(0.40 \pm 0.01) \text{ g/cm}^3$).

Porous aluminosilicate matrices of the block type were obtained through consolidation of cenospheres in the form of blocks by molding a mixture of cenospheres having the stabilized composition with the silicate binder (at a ratio of 1 : 0.15), followed by annealing at 950 °C [11]. They are characterized by open pores, the porosity of (63.6±1.3) %, and specific surface of (0.21±0.02) m²/g [11]. Porous matrices have the following phase composition, mass %: vitreous phase 86.3, quartz 4.7, mullite 4.7, cristobalite 2.5, and hematite 2.0. The chemical composition of PM determined according to State Standard GOST 5382–91 is presented in Table 1.

Zeolitization of cenospheres was carried out through hydrothermal treatment in 1.5 M NaOH solution (the volume ratio of liquid to solid was 5 : 1) in the autoclave at a temperature of 120–125 °C and autogenic pressure for 72 h [9]. As a result of treatment, cenospheres are transformed into zeolite in which the content of the zeolite phase with NaP1 structural type is 64 % (according to XPA data). After the reaction, the resulting sorbent was separated from the liquid, washed with distilled water to the weakly alkaline pH of rinsing water, and dried at 110 °C for 24 h. Sorption of cesium and strontium cations was carried out from nitrate solutions with Cs⁺ (Sr²⁺) content 250 mg/L at room temperature for 3 h. The specific surface of MZS was measured by means of the thermal desorption of argon using a Gasometr GKk-1 instrument (TU 25-0585.001–85); it was equal to 33 m²/g. The chemical composition of MZS determined according to GOST 5382–91 is shown in Table 1.

The structure and qualitative phase composition of the samples were determined by means of powder X-ray phase analysis using the Rietveld method [12] and minimization of the difference derivative [13]. The XPA spectra were recorded with a PANalytical X'Pert PRO MPD diffractometer with the solid pixel detector and the secondary graphite monochromator for CuK_α radiation.

RESULTS AND DISCUSSION

Aluminosilicate sorbents based on cenospheres as precursors of the mineral-like forms for burying cesium and strontium radionuclides

Developing the processes of RAW solidification for burying in granitoids involving the materials based on cenospheres and taking into account the features of storage arrangement over the RF territory, one should aim at the raw material from the territories located most closely to burying sites. Cenospheres from the combustion of coal from the Kuznetsk Basin, in particular cenospheres formed at the Tom-Usinsk power plant and Novosibirsk heat and electric power plant TETs-5, can be the necessary raw material. The coal from the Kuznetsk Basin is characterized by the highest yield of cenospheres during combustion (>1 %); in view of the predicted increase in the consumption of coal from the Kuznetsk Basin within the forthcoming decade, the amount of the formed cenospheres may increase by a factor of 2–2.5 [14].

One of the criteria of the applicability of cenospheres as the precursors of the mineral-like forms of burying cesium and strontium radionuclides is the ratio SiO₂/Al₂O₃; this ratio is the geochemical indicator of the mineral forms of coal responsible for the formation of cenospheres [15]. In addition, this indicator may be used to determine the concentrates of cenospheres for which the yield of narrow fractions of cenospheres with the prescribed ratio will be maximal. Figure 1 shows the dependence of SiO₂/Al₂O₃ ratio on Al₂O₃ content for the concentrates of cenospheres from the combustion of different kinds of coal [15, 16] and for narrow fractions isolated from the concentrates of volatile ash of Kuznetsk coal. The macro-component composition of the concentrates of cenospheres varies within the following ranges, mass %: SiO₂ 50–65, Al₂O₃ 20–36, Fe₂O₃ 2–10, and includes the particles with a size from

TABLE 1

Chemical composition of porous matrices (PM) and microspherical zeolite sorbents (NaP1-MZS), mass %

| Samples | Chemical composition | | | | | | | | SiO ₂ /Al ₂ O ₃ |
|----------|----------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|------------------|--|
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | TiO ₂ | |
| PM | 66.34 | 19.22 | 3.38 | 2.60 | 1.92 | 2.24 | 2.06 | 0.63 | 3.5 |
| NaP1-MZS | 42.16 | 23.08 | 3.43 | 1.26 | 2.0 | 9.92 | 0.36 | 0.05 | 1.8 |

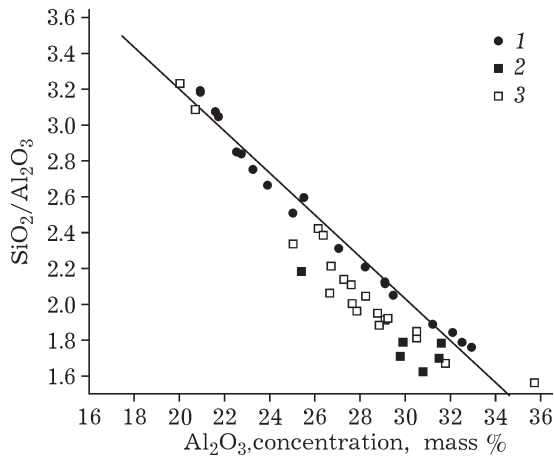


Fig. 1. Dependence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ on the content of aluminium oxide in cenospheres: 1 – narrow fractions of non-magnetic cenospheres from the combustion of Kuznetsk coal ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.54 - 0.12[\text{Al}_2\text{O}_3]$; $r = -0.99$; 2, 3 – concentrates of cenospheres from the combustion of different kinds of coal, according to the data published in [15] and [16], respectively.

5 to 500 μm with the maximum of size distribution 50 to 250 μm for different sources [15]. The concentrates with low Fe_2O_3 content (<4 mass %) are composed mainly of the globules of different morphological types formed from high-silicon melts.

On the basis of the fundamental principle of the physicochemical analysis of functional materials that determines the interconnection between composition, morphology (structure) and properties, we chose the technological stages for the separation of narrow size fractions of cenospheres with constant composition with the predominance of one or two morphological types from the concentrations of undetermined composition formed from the combustion of coal from the Kuznetsk Basin. The data presented here indicate that the narrow fractions of cenospheres under examination overlap almost the whole range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios for the concentrates [15, 16] (see Fig. 1).

The analysis of the chemical compositions of narrow fractions of cenospheres shows that in the aspect of obtaining monomineral products from the thermochemical transformations of cenospheres and sorbents based on them, the choice of the cenosphere composition depends on the ratio of the major framework-forming components SiO_2 and Al_2O_3 and the minimal content of the ballast components (for

example, less than 4 % Fe_2O_3) that do not participate in the formation of Cs- and Sr-containing aluminosilicate phases.

The compositions of the major rock-forming minerals of magmatic rocks (feldspars and feldspathoids), as well as zeolites, mica and clay that may develop over the rock-forming and coloured minerals as a result of metamorphic and other post-magmatic processes are shown in Fig. 2. The compositions of the narrow fractions of cenospheres formed in the combustion of coal from the Kuznetsk Basin, PM and MZS are shown there, too.

A comparison of the SiO_2 and Al_2O_3 content of cenospheres, PM and MZS with the compositions of rock-forming framework aluminosilicate minerals of magmatic rocks (see Fig. 2) showed that the introduction of the stoichiometric amount of alkaline oxides (Na_2O , Cs_2O , SrO) within the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio range from 1.2 to 3.5 can cause the transformation of the precursor material into the crystal phases of such framework aluminosilicate minerals as Na,Cs- and Na,Sr-feldspar ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.5$ and 1.2, respectively) and feldspathoids (pollucite and nepheline with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 2.4 and 1.2, respectively) that are able to incorporate cesium.

The possibility of the fixation of cesium and strontium in feldspar and feldspathoids with the help of zeolites was demonstrated in a number of Russian [8] and foreign publications [17, 18].

In the case of the use of zeolites of NaP, NaA, NaX structural types as the precursor (these can be obtained from cenospheres, too [19–21]), depending on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (see Fig. 2) and the affinity to Cs^+ and Sr^{2+} cations [22], one may expect their transformation into pollucite [23, 24] or Sr-feldspar [8, 25]. Zeolite structures of the NaP type with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.8-5.0$ [22] can serve as precursors for the transformation into the solid solutions of minerals for which the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio falls within the indicated range (for example for pollucite, nepheline and Sr-feldspar this index is equal to 2.4, 1.2 and 1.2, respectively). It follows from the analysis of the published data that MZS containing NaP1 zeolite with the framework structure of gismondine type appears to be the most promising sorbent for the simultaneous removal of Cs^+ and Sr^{2+} [26].

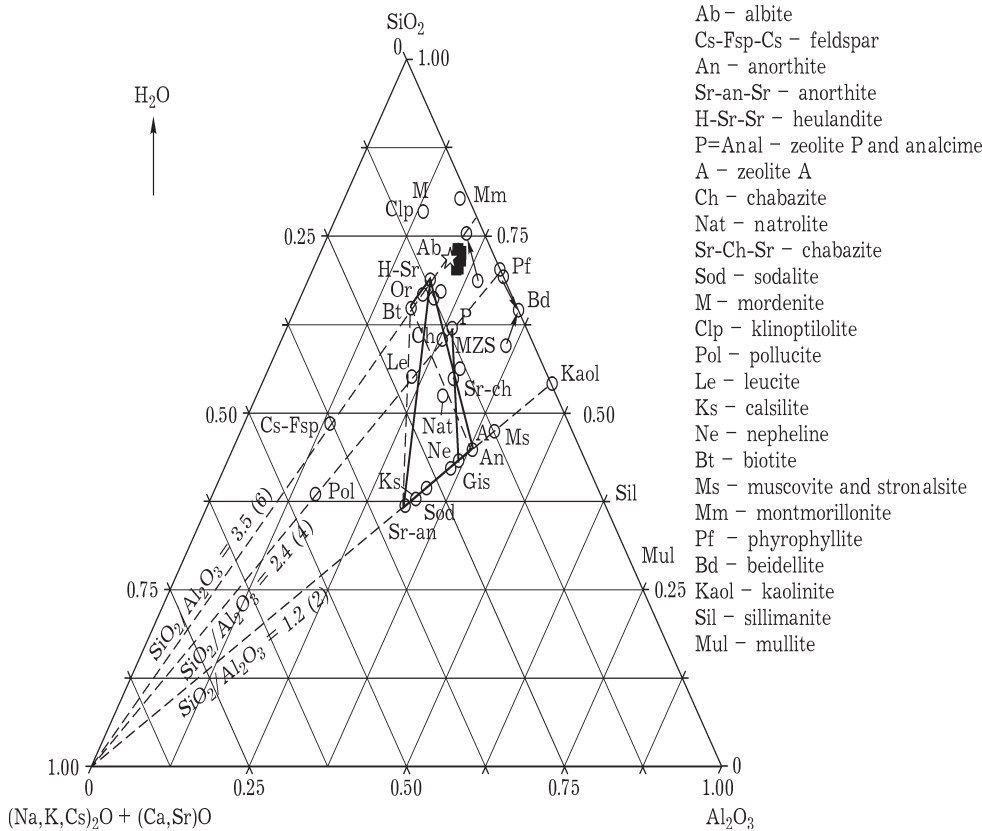


Fig. 2. Composition of minerals and cenospheres from the Tom-Usinsk heat and electric power plant. Asterisk marks the composition of PN; black squares mark the narrow fractions of cenospheres; unbroken lines mark the solid solutions between feldspar species; the lines of SiO₂/Al₂O₃ ratios contain the values of the ratio of mass and molar (in parentheses) content.

Solidification using porous matrices of block type based on cenospheres

The use of PM is most reasonable for solidification of the small volumes of liquid HAW and MAW and can be implemented in the mode of concentrating followed by calcinations stage at a temperature of 700–850 °C resulting in mineral-like compounds [27, 9].

For the quantitative evaluation of the phase composition of solidification products formed from Cs-containing solutions, crystal glass compounds based on PM were obtained in the following mode: 1) impregnation of the porous matrices with the solution of cesium nitrate during boiling; 2) drying at a temperature of 130 °C; 3) calcination of saturated matrices at a temperature of 750 or 900 °C for 24 h. The amount of CsO₂ was introduced taking into account aluminium present in the PM, aiming at obtaining the compound with the maximal possible pollucite content for this PM composition.

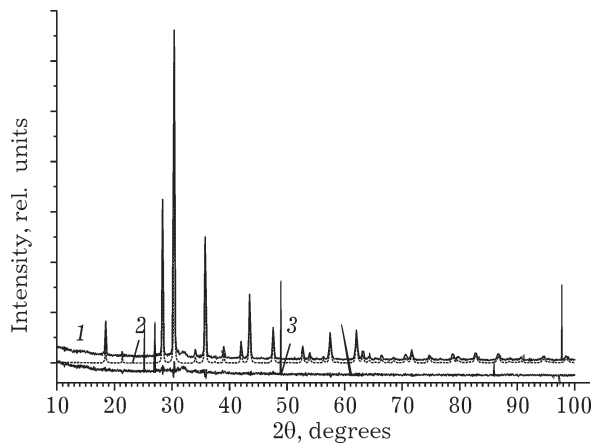


Fig. 3. Diffraction profile of the product of solid-phase transformation of the composition of porous aluminosilicate matrices with Cs₂O (33.8 % Cs₂O, 750 °C, 24 h): 1 – experimental, 2 – calculated, 3 – difference curve; the phase composition of the product, mass %: pollucite 65.8, quartz 0.1, residue 34.1.

It was established that thermal treatment of PM saturated with cesium salts for 24 h at 750 °C leads to the formation of the target pollucite phase $\text{CsAlSi}_2\text{O}_6$ with the mass fraction about 66 % (Fig. 3).

Solidification using microspherical zeolite sorbents NaP1

NaP1-MZS is composed of hollow spherical formations 80–160 μm in size; their walls are composed of the zeolite phase NaP1 (framework topology GIS) and aluminosilicate glass (Fig. 4). As it was demonstrated previously [7], NaP1-MZS is efficient in extracting the cations of cesium and strontium from solutions with low salt background (less than 10 g NaNO_3/L), for example, when purifying non-technological low-active wastes of nuclear plants.

The samples of MZS with sorbed cesium (200 mg Cs/g of sorbent) were annealed at a temperature of 900 °C for 24 h. In the case of MZS with sorbed cesium, the predicted target phases in the polyphase compound accounted for 58 % pollucite and 16 % nepheline, respectively. The transformation of Sr-containing MZS at 900 °C resulted in the formation of polyphase compound containing 62 % Sr-feldspar $\text{SrAl}_2\text{Si}_2\text{O}_8$ and 20 % nepheline NaAlSiO_4 , the fraction of residual glass phase was less than 10 % (Fig. 5).

Thus, thermochemical transformation of zeolite structure into the predicted phases pollucite and feldspar proceeds successfully at 900 °C, which is lower by 100 °C than solidification temperature used in [26].

It should be noted that the structural transformation of Cs^+ and Sr^{2+} forms of microspherical zeolite NaP1 proceeding at a temperature of 900 °C leads to almost complete, theoretically possible for a given MZS composition, transformation into the target products pollucite and Sr-feldspar. At the same time, high temperature treatment (up to 1200 °C) of natural high-module zeolites sorbing cesium and strontium selectively (clinoptilolite, heulandite, mordenite) does not lead to obtaining any mineral-like phases [28]. This is one of the advantages of the use of MZS for sorption and subsequent fixation of cesium and strontium radionuclides in the

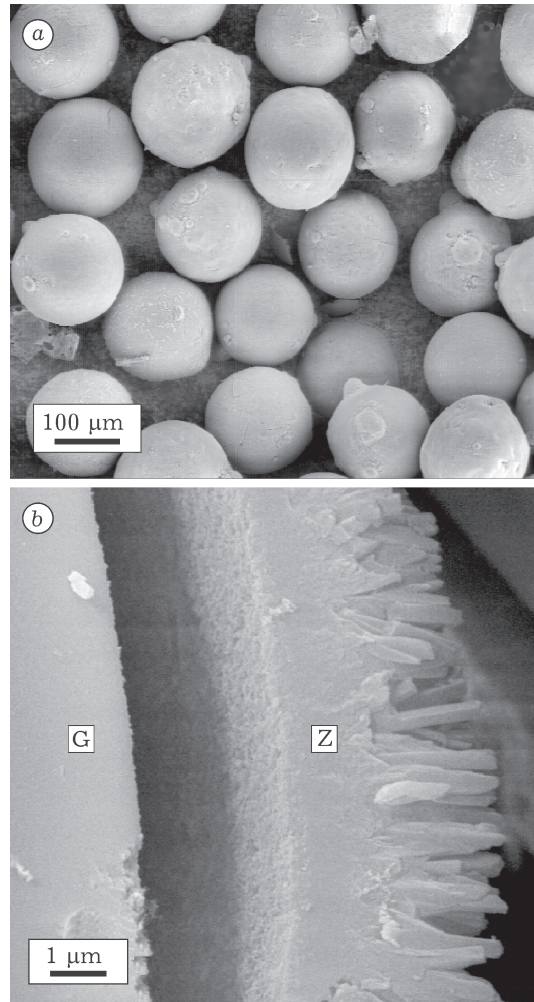


Fig. 4. Microspherical zeolite sorbent NaP1: a – general view, b – wall structure.

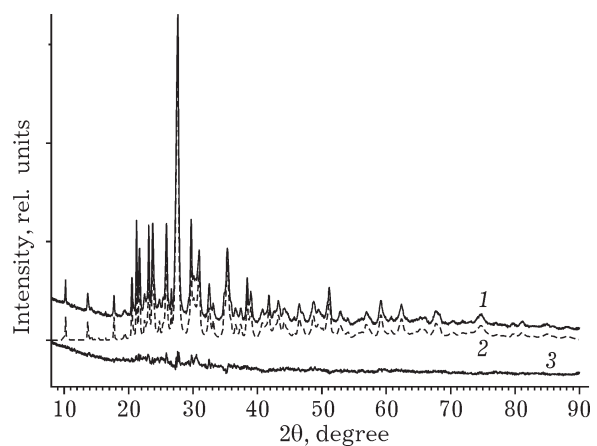


Fig. 5. Diffraction profile of the product of solid-phase transformation of (Sr,Na)P1-MZS (68.59 mg Sr/g, 900 °C, 24 h): 1 – experimental, 2 – calculated, 3 – difference curve; the phase composition of the product, mass %: strontium feldspar 62.4, nepheline 20.5, diopside 5.4, quartz 0.6, mullite 0.9, hematite 0.7, residue 9.6.

structures of tectoaluminosilicates for the purpose of long-term burying in granitoids.

CONCLUSION

The use of the narrow fractions of cenospheres of ash from the combustion of Kuznetsk coal allows one to prepare microspherical aluminosilicate sorbents which are characterized by the ratio of framework-forming oxides ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.8\text{--}3.5$) and thus can act as precursors of crystal aluminosilicates of the structural type of rock-forming minerals of granitoids that fix cesium and strontium radionuclides in their crystal lattice.

Glass crystalline compounds in which the content of target phases incorporating cesium and strontium reaches 66–80 % using porous aluminosilicate matrices and microspherical zeolite sorbents under relatively soft conditions (750–900 °C) were obtained.

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