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# Applied aspects of using the identified regularities of the joint behavior of structural components in water-salt systems of cesium, strontium and neodymium nitrates

[1] The carried out complex study gives a reliable idea of the trends in the joint behavior of structural components in water-salt systems of nitrate precursors of neodymium, cesium, strontium in the preparatory stages of technological regulations for both concentration and immobilization of liquid radioactive waste of the nuclear energy industrial complex $^{137}$Cs, $^{90}$Sr and thermal activation. The stages of such transformations have been revealed; the patterns of complex and phase formation in systems and the factors influencing them have been clarified. It has been studied a number of physicochemical properties of the resulting intermediate phases (coordination neodymium nitrates: their composition, types of compounds, atomic crystal structure, shapes of Ln coordination polyhedra, types of ligand coordination, features and patterns of behavior in heat treatment processes. It has been established that, under the conditions of the existence of solutions, the system $CsNO_3 – Nd(NO_3)_3 – H_2O$ is characterized by the formation of 2 anionic complex compounds $Ln^{3+}$, the system $Sr(NO3)_2 – Nd(NO_3)_3 – H_2O$ – is of the eutonic type. The ongoing competing reactions are a powerful technological factor that has a significant impact on changes in the activity of structural forms of $Ln^{3+}$. Systematized information enables to elucidate the mechanisms and kinetics of transformations of structural components in similar objects. Also, it enables to transfer the resulting system of knowledge to the promising technological solutions for the solidification of liquid radioactive wastes.

**Keywords:** neodymium; cesium; strontium; nitrates; water-salt systems; complex formation; properties.

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## Introduction

Develop knowledge about the interaction of structural components in water-salt systems of nitrates of rare earth elements and IA, IIA elements of the periodic table in full concentration ratios and a wide range of temperatures, phases formed in them, conditions of their existence and properties; thermal transformations; available information about the state and possible ways of improving the technologies of formation of complex oxide materials of transition elements, methods of activation of processes, existing requirements for their reproducibility and stability initiated this study and open up new areas of their practical use in the creation of framework materials for immobilization of liquid radioactive waste of the nuclear power industry complex (porous and layered types), as well as in the processes of modeling and experimental substantiation of the possibility of using certain engineering forms of sorbents and mineral-like technogenic phases-fixers of radionuclides $^{137}$Cs, $^{90}$Sr.

## Problem statement and solution methods

Due to the diversity of sources of origin, radioactive waste has a wide variety of compositions and physicochemical properties. The greatest danger to the biosphere is represented by liquid high-level waste containing radionuclides $^{137}$Cs and $^{90}$Sr with high heat release, often in combination with long-lived ($T_{1/2} \geq 10^5$ years) α-emitting actinides. High-level waste of complex composition includes a number of categories of liquid radioactive waste with a wide radioisotope and chemical composition, such as emergency waste from nuclear power plants, the lanthanide-actinide fraction of high-level waste from processing in nuclear fuel cycles, unfractionated high-level waste from temporary storage tanks that contain rare earth and transuranium metals, radionuclides of cesium and strontium, transition metals, and often against the background of high concentrations of salts and increased acidity.

The multicomponent composition of liquid high-level waste and the joint presence in their composition of transuranium elements and fission products with a high content of $^{137}$Cs and $^{90}$Sr complicate their further processing, therefore, with the development of extraction separation methods, further fractionation of high-level waste is carried out with the separation of different groups of radionuclides in accordance with their chemical properties and half-life [1-7].

In his study, scientist Milyutin, V.V. et al., investigated the content of actinides and lanthanides in the actinide-lanthanide fraction of high-level waste that became waste after a 5-year soaking of spent nuclear fuel, which shows that the bulk of this fraction is represented by lanthanides, and the content of uranium and transuranic elements is about 4% by weight of lanthanides. The absolute majority among the lanthanides is represented by elements of the cerium subgroup (Ce-Sm), with the highest neodymium content (36.5%). It should also be noted that, despite the progress achieved in the fractionation of high-level waste by extraction processing, the concentrate of rare earth and transplutonium elements may contain several percent of cesium and strontium radionuclides. This available information has determined both object and directions of the research.

The international strategy for the safe management of all types of radioactive waste is waste minimization and aims to reduce the amount of waste by concentrating and retaining radionuclides within stable solid materials. In this case, the most dangerous components of high-level waste are supposed to be included in mineral-like matrices with their subsequent safe multi-barrier burial in stable geological formations of the Earth's crust.

The international strategy for the safe management of all types of radioactive waste is waste minimization and aims to reduce the amount of waste by concentrating and retaining radionuclides within stable solid materials. In this case, the most dangerous components of high-level waste are supposed to be included in mineral-like matrices with their subsequent safe multi-barrier burial in stable geological formations of the Earth's crust.

One of the promising technological solutions for solidifying liquid radioactive waste is the use of inorganic sorbents, which, after being saturated with radionuclides in the form of nitrate soluble structural components, are actually precursors of the final form of radioactive waste. Further structural rearrangement of the precursor with the inclusion of radionuclides in the target phases is carried out in the process of solid-phase crystallization upon heating.

Today, the optimal strategy for the immobilization of such waste within the framework of the sorption-mineralogical approach may be the use of a sorbent, the composition of which is focused on the extraction of a wide range of elements and the formation of polyphase ceramics based on compositions of phase concentrators of alkali and alkaline earth elements ($^{137}$Cs, $^{90}$Sr), on the one hand , and the lanthanide-actinide fraction in combination with other metals, on the other hand.

When choosing a matrix material for the immobilization of actinides, one of the determining properties is the radiation resistance of their crystal structure to the effects of β-radiation.

The group of such radiation-stable phases – potential matrix materials – includes REE framework zirconomolybdates of the composition $Ln_2Zr_3(MoO_4)_9$, Ln – La ÷ Tb, (for example, neodymium, see Fig. 1) [8].

To implement the above projects for the development and improvement of the above-described composite sorption-active systems and technologies for the purification and immobilization of high-salt radioactive waste of complex composition based on them, it is concerned data on the processes of chemical interaction of structural components, phase formation in water-salt systems of neodymium and cesium nitrates and strontium in the range 25 - 100 °C, along with properties of the phases they form.

## Setting objectives

For a systematic study of cooperative processes in the technological objects under consideration and to determine the possibility to control them, it is necessary to use a complex of physical and chemical methods:

a) to study the chemical interaction nature and mechanisms, phase equilibria in model water-salt systems $CsNO_3 - Nd(NO_3)_3 - H_2O$, $Sr(NO_3)_2 - Nd(NO_3)_3 - H_2O$ at a temperature 25 – 100°C;

b) to construct polythermal solubility diagrams of systems; to determine both the concentration and temperature limits of crystallization of the starting substances and detected new phases;

c) to find out the optimal growth conditions and to carry out the synthesis of neodymium coordination nitrates (as a representative of the natural series of rare

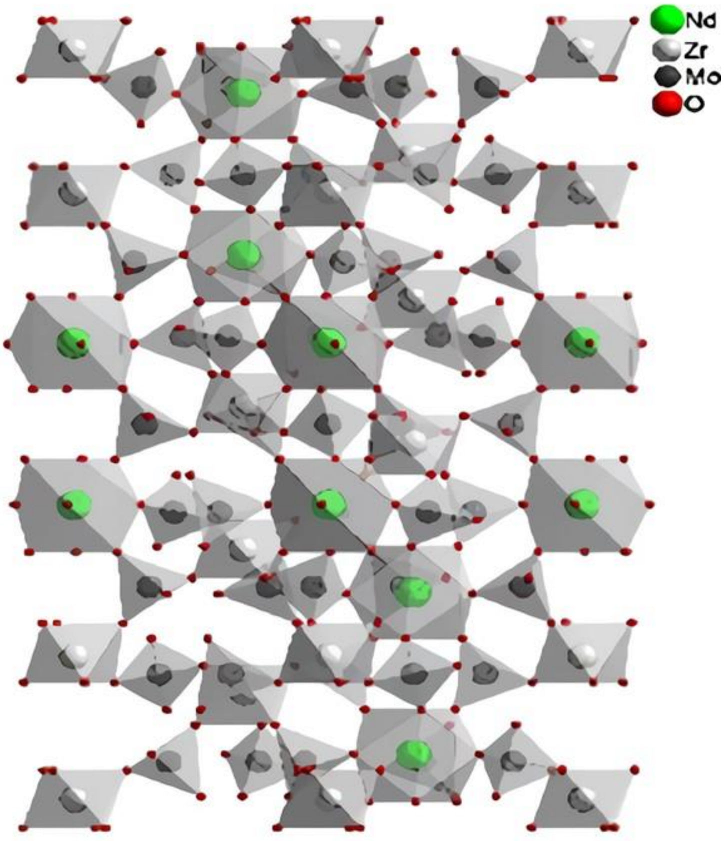


**Figure 1 - Frame structure $Nd_2Zr_3(MoO_4)_9$ (trigonal space group R3c, Z=6), [13]**

earth elements, where changes both in the composition and structure of compounds occur with the highest probability); to study their properties and confirm their individuality;

d) to establish patterns of dependence of the number, composition, properties of coordination nitrates formed in the systems, on the nature of the $Ln^{3+}$ complex-forming ion, and conditions of formation.

### The experimental methods

The solubility method and the technique described in [9, 10] were used to clarify the nature of the chemical behavior of structural components and phase equilibria in the studied water-salt systems isothermally, in the temperature range of existence of solutions in full concentration ratios. Phase equilibrium was achieved within 1–2 days. Hydrated and anhydrous nitrates of the indicated grade elements were used as the starting reagents «pro analys».

Chemical analysis of liquid and solid phases and “residues” was carried out for the content of $Nd^{3+}$, $Sr^{2+}$ ions. The $Ln^{3+}$ content was determined trilonometrically; $Sr^{2+}$ was determined by complexometric titration of the substituent in the filtrate, where $Ln^{3+}$ was expelled with ammonia buffer. The experimental data obtained from the studied systems for individual ions were listed for salt content, summarized in Tables 1, 2 and, according to the principle of correspondence, plotted on polythermal solubility diagrams of the systems (Fig. 2, 3). Graphic display of the composition of hard phases formed in systems was carried out according to the Schreinemaker` method [9, 10]. Chemical analysis of double nitrates isolated in single crystal form confirms element mass ratio in the above formulas. Their individuality was also confirmed by crystal optical, X-ray diffraction, X-ray structural, thermographic, IR spectrometric and other methods of analysis.

Crystal optical determinations of compounds were performed by the immersion method using a МИН-8 microscope. Phase analysis was performed on a DRON–3M diffractometer (Cu $K_{\alpha}$ radiation, Ni filter) using the “powder” method. The diffraction patterns were interpreted using the JCPDS PDF file. Determination of symmetry, parameters of unit cells and measurement of the intensity of diffraction reflections from single crystals was carried out on an automatic X-ray single-crystal diffractometer CAD - 4F "Enraf - Nonius" (Mo $K_{\alpha}$- radiation, graphite monochromator; $\omega$ / $2\theta$ - method). To determine and refine atomic structures, all calculations were carried out using the crystallographic software packages SHELX, XTL–SM, AREN. IR absorption spectra of the synthesized compounds in the range 400 – 4000 cm-1 were recorded on a spectrophotometer UR-20, using the standard method of suspension in petroleum jelly. Thermograviometric analysis was carried out on a Q1500 D derivatograph at temperatures from 293 K to 1273 K in the air with a heating rate of 10 degrees. / min and the developed device for DTA.

## Results and discussion

The experimental data of the features and patterns of interaction of structural components, heterogeneous equilibria (25–100 °C) in water-salt systems of neodymium, cesium, and strontium nitrates have been obtained. They are summarized in Tables 1, 2 and generalized in the form of spatial polythermal solubility diagrams (see Fig. .2, 3). On their basis, it has been established the presence of chemical interaction between the constituent elements in the research objects; quantity, composition, nature of solubility, temperature and concentration limits for the formation of initial substances and new phases, and composition of eutonic and transition points. The optimal conditions for the formation have been determined and the synthesis of cesium double neodymium nitrates has been carried out. The growth forms of their crystals and a number of their inherent properties have been studied.

The choice of the proposed tabular and diagrammatic forms for presenting the results obtained is the most visual, informative and useful in the development of effective technological regulations for the solidification of liquid radioactive waste. It enables to predict the behavior of structural components, correctly select modes, stages, methods of forming and obtaining target products with given reproducible characteristics in similar multicomponent production processes using liquid nitrate precursors.

The studied cesium system under solution conditions is characterized by the formation of 2 new coordination nitrate compounds $Nd^{3+}$ $Cs_2[Nd(NO_3)_5(H_2O)_2]$ and $Cs[Nd(NO_3)_4(H_2O)_3]$. The concentration boundaries of saturated solutions from which complex nitrates are released correspond to the compositions of invariant points of the corresponding solubility isotherms. The strontium system is of the eutonic type; no new solid phases have been found in it.

The obtained data obtained enable to identify phases and make quantitative calculations in the processes of evaporation and crystallization for similar objects. All detected phases were synthesized in single crystalline form (Fig. 4). Most of them have an isometric shape, size 4 – 30 mm. Chemical analysis of the isolated compounds confirms the mass ratio of the elements in the proposed formulas. Clarification of the composition of the synthesized compounds and their recording in coordination form was carried out according to the data of a comprehensive study using the above methods (see Tables 3, 4) and by conducting a low-temperature X-ray experiment in the process of studying their atomic-crystalline structure.

Using X-ray diffraction analysis methods, the authors studied the atomic structure of single crystals $Nd^{3+}$ $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ (see [16, 17]), types of coordination of ligands, shapes of coordination polyhedra Ln, the possible variants of the coordination environment of Nd atoms, the spatial arrangement of polyhedra (Fig. 5) in the construction of compounds with aqua-containing complex anions, and the general crystallochemical regularities of the structure of this type of compound were clarified. (More detailed information and analysis of the construction features of this class of compounds are given in the above-mentioned original publications of the authors).

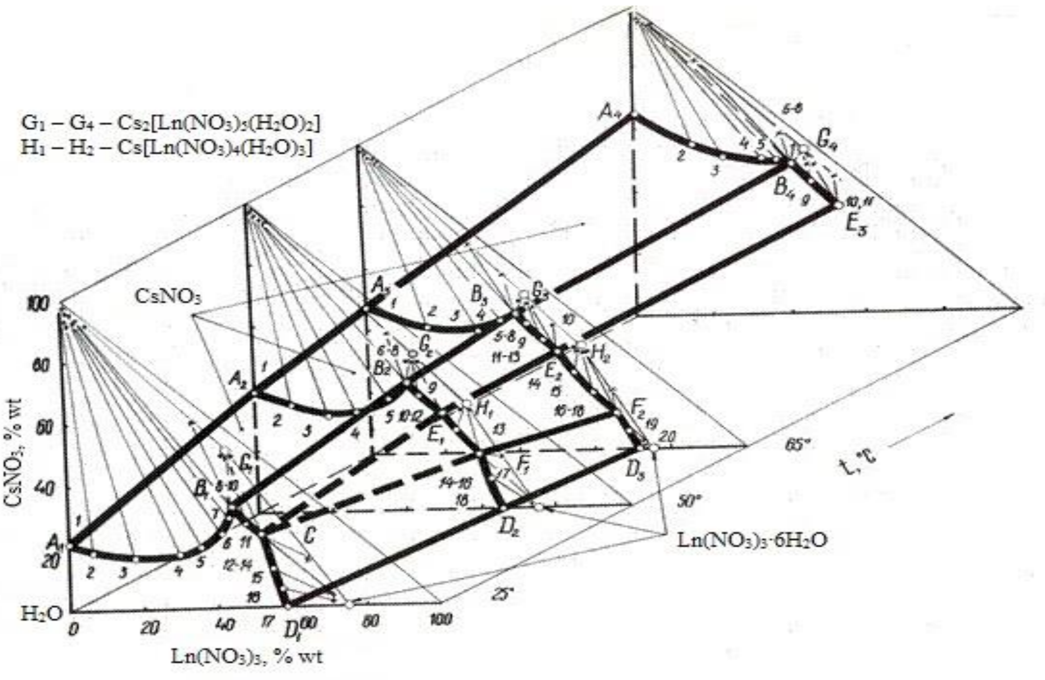


**Figure 2 - Solubility polytherm of system $CsNO_3 – Ln(NO_3)_3 – H_2O$ ( Ln – Nd)**

**Table 1 - Data on the study of phase equilibria in the system $CsNO_3 – Nd(NO_3)_3 – H_2O$ at 25-100°C**

| | | Saturated solution | | «Residue» composition, wt.% | | | | | Saturated solution | | «Residue» composition, wt.% | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Composition, wt. % | | | | | | | Composition, wt. % | | | | |
| t, °C | Composition points | $CsNO_3$ | $Nd(NO_3)_3$ | $CsNO_3$ | $Nd(NO_3)_3$ | Solid phases* | t, °C | Composition points | $CsNO_3$ | $Nd(NO_3)_3$ | $CsNO_3$ | $Nd(NO_3)_3$ | Solid phases* |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 25 | 1 $A_1$ | 20,96 | 0,00 | 99,64 | 0,00 | K | 65 | 1 $A_3$ | 47,16 | 0,00 | 99,69 | 0,00 | K |
| | 2 | 18,59 | 5,91 | 99,58 | 0,00 | Same | | 2 | 40,50 | 16,72 | 98,77 | 0,71 | Same |
| | 3 | 16,58 | 18,51 | 99,14 | 0,67 | -‖- | | 3 | 39,32 | 29,61 | 97,58 | 1,69 | -‖- |
| | 4 | 17,95 | 30,07 | 97,84 | 1,43 | -‖- | | 4 | 43,24 | 35,86 | 95,48 | 3,12 | -‖- |
| | 5 | 20,67 | 35,68 | 97,76 | 1,60 | -‖- | | 5 | 44,92 | 40,11 | 94,61 | 4,08 | -‖- |
| | 6 | 23,92 | 41,17 | 96,90 | 2,34 | -‖- | | 6 | | | 67,95 | 27,47 | K+M |
| | 7 | 31,82 | 43,88 | 95,45 | 3,10 | -‖- | | 7 $B_3$ | | | 57,37 | 36,91 | Same |
| | 8 $B_1$ | | | 60,03 | 34,62 | K+M | | 8 | | | 51,89 | 42,34 | M |
| | 9 | | | 51,08 | 42,15 | M | | 9 | 42,61 | 41,13 | 50,96 | 43,23 | Same |
| | 10 | 27,02 | 48,08 | 50,00 | 43,09 | Same | | 10 | 37,02 | 47,33 | 49,67 | 42,89 | -‖- |
| | 11 | 23,07 | 52,04 | 4992 | 43,16 | -‖- | | 11 | 32,11 | 50,75 | 48,63 | 43,81 | -‖- |
| | 12 C | | | 15,28 | 65,36 | M+L | | 12 $E_2$ | | | 42,12 | 49,50 | M+O |
| | 13 | | | 2,67 | 72,66 | L | | 13 | | | 34,64 | 56,10 | O |
| | 14 | 12,47 | 55,04 | 1,98 | 72,79 | Same | | 14 | 24,51 | 54,79 | 33,76 | 56,77 | Same |
| | 15 | 6,00 | 57,67 | 1,60 | 72,88 | -‖- | | 15 | 18,25 | 59,84 | 33,32 | 56,69 | -‖- |
| | 16$D_1$ | 0,00 | 58,49 | 0,00 | 75,25 | -‖- | | 16 | 11,99 | 66,26 | 30,92 | 57,81 | -‖- |
| 50 | 1 $A_2$ | 39,17 | 0,00 | 99,72 | 0,00 | K | | 17 $F_2$ | | | 15,77 | 66,42 | O+L |
| | 2 | 34,72 | 9,93 | 98,63 | 0,57 | Same | | 18 | | | 4,44 | 72,70 | L |
| | 3 | 31,10 | 20,53 | 98,37 | 1,08 | -‖- | | 19 | 6,25 | 68,91 | 1,86 | 73,23 | Same |
| | 4 | 32,71 | 27,63 | 97,82 | 1,52 | -‖- | | 20$D_3$ | 0,00 | 71,58 | 0,00 | 75,26 | -‖- |
| | 5 | 36,99 | 36,68 | 96,54 | 2,47 | -‖- | 100 | 1 $A_4$ | 64,36 | 0,00 | 99,87 | 0,00 | K |
| | 6 | 40,98 | 40,84 | 94,47 | 3,86 | -‖- | | 2 | 54,44 | 14,95 | 98,76 | 0,83 | Same |
| | 7 $B_2$ | | | 59,34 | 35,74 | K+L | | 3 | 50,32 | 22,89 | 97,71 | 0,95 | -‖- |
| | 8 | | | 50,90 | 43,03 | L | | 4 | 49,51 | 33,23 | 96,69 | 2,16 | -‖- |
| | 9 | 36,54 | 44,23 | 49,48 | 43,12 | Same | | 5 | 49,05 | 36,69 | 94,72 | 3,86 | -‖- |
| | 10 | 30,94 | 50,38 | 49,64 | 43,26 | -‖- | | 6 | 47,56 | 41,28 | 81,74 | 16,14 | K+N |
| | 11 $E_1$ | | | 39,06 | 52,20 | M+O | | 7 $B_4$ | | | 57,48 | 37,98 | Same |
| | 12 | | | 33,64 | 56,35 | O | | 8 | | | 52,89 | 41,93 | -‖- |
| | 13 | 25,84 | 53,72 | 32,87 | 56,43 | Same | | 9 | 41,62 | 46,07 | 50,34 | 43,30 | N |
| | 14 | 17,52 | 59,98 | 32,86 | 56,97 | -‖- | | 10 $E_3$ | 33,80 | 52,92 | 51,71 | 44,41 | Same |
| | 15 $F_1$ | | | 17,54 | 64,69 | O+L | | *K – $CsNO_3$, L – $Nd(NO_3)_3·6H_2O$, M - $2CsNO_3·Nd(NO_3)_3·$ $·3H_2O$, N – $2CsNO_3·Nd(NO_3)_3·2H_2O$, O – $CsNO_3·Nd(NO_3)_3·$ $·3H_2O$ | | | | | |
| | 16 | | | 4,61 | 71,90 | L | | | | | | | |
| | 17 | 9,77 | 62,91 | 2,81 | 72,12 | Same | | | | | | | |
| | 18$D_2$ | 0,00 | 66,16 | 0,00 | 75,28 | -‖- | | | | | | | |

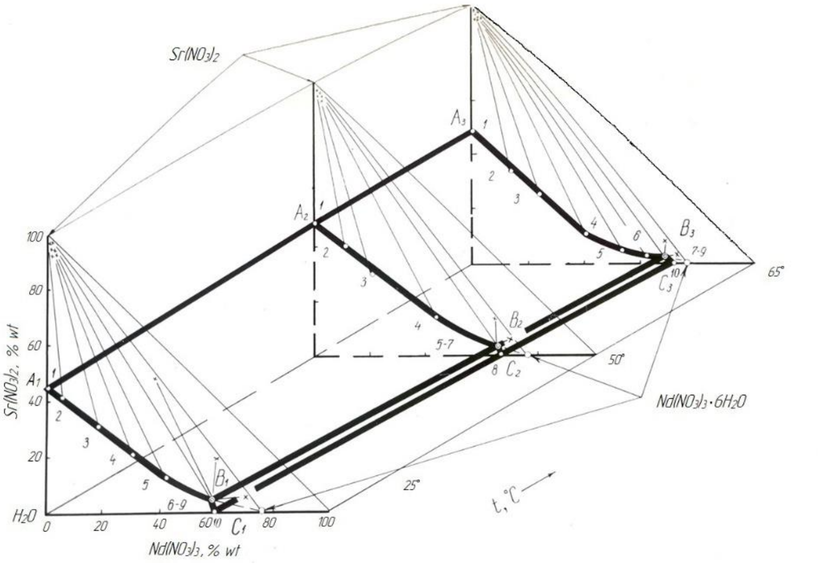
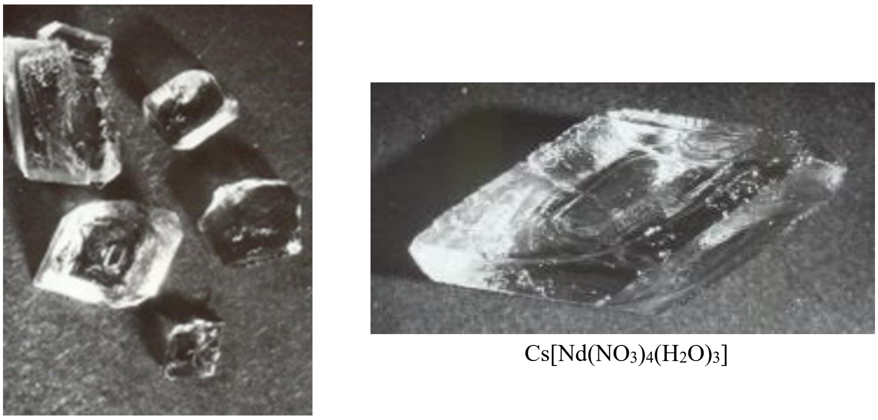


**Figure 3 - Polytherm solubility of the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ at 25 – 65 ºC**

**Table 2 - Data on the study of phase equilibria in the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ at 25 – 65 ºC**

| t,oC | Composition points | Saturated solution | | | | Composition „remainder”, wt, % | | Solid phase* |
|---|---|---|---|---|---|---|---|---|
| | | Composition,wt, % | | Properties | | | | |
| | | $Sr(NO_3)_2$ | $Nd(NO_3)_3$ | d x $10^3$,кг/м$^3$ | *n* | $Sr(NO_3)_2$ | $Nd(NO_3)_3$ | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 25 | 1 $A_1$ | 44,60 | 0,00 | 1,539 | 1,4068 | 99,87 | 0,00 | K |
| | 2 | 41,66 | 5,12 | 1,541 | 1,4084 | 99,32 | 0,00 | “-” |
| | 3 | 30,71 | 17,66 | 1,547 | 1,4129 | 97,56 | 0,79 | “-” |
| | 4 | 20,86 | 29,99 | 1,550 | 1,4164 | 95,87 | 1,52 | “-” |
| | 5 | 12,58 | 41,84 | 1,569 | 1,4299 | 95,60 | 1,69 | “-” |
| | 6 $B_1$ | | | | | 95,72 | 2,80 | “-” |
| | 7 | 5,94 | 56,97 | 1,873 | 1,4548 | 52,50 | 34,84 | K+L |
| | 8 | | | | | 19,05 | 59,51 | “-” |
| | 9 | | | | | 2,89 | 70,62 | “-” |
| | 10 $C_1$ | 0,00 | 58,49 | 1,887 | 1,4551 | 0,00 | 75,25 | L |
| 50 | 1 $A_2$ | 48,03 | 0,00 | 1,487 | 1,4055 | 99,91 | 0,00 | K |
| | 2 | 39,75 | 10,75 | 1,544 | 1,4079 | 99,23 | 0,57 | “-” |
| | 3 | 29,35 | 20,28 | 1,589 | 1,4184 | 97,57 | 1,39 | “-” |
| | 4 | 14,38 | 43,08 | 1,623 | 1,4298 | 96,45 | 1,.87 | “-” |
| | 5 $B_2$ | | | | | 94,90 | 3,40 | “-” |
| | 6 | 3,88 | 65,34 | 1,850 | 1,4691 | 13,73 | 64,75 | “-” |
| | 7 | | | | | 7,26 | 9,76 | “-” |
| | 8 $C_2$ | 0,00 | 66,16 | 1,974 | 1,4667 | 0,00 | 75,28 | L |
| 65 | 1 $A_3$ | 48,60 | 0,00 | – | – | 99,92 | 0,00 | K |
| | 2 | 33,85 | 13,40 | – | – | 98,23 | 0,69 | “-” |
| | 3 | 25,84 | 23,91 | – | – | 98,11 | 0,85 | “-” |
| | 4 | 10,93 | 40,17 | – | – | 97,50 | 1,38 | “-” |
| | 5 | 4,.97 | 53,11 | – | – | 95,85 | 1,69 | “-” |
| | 6 $B_3$ | 2,35 | 61,72 | – | – | 95,30 | 2,18 | “-” |
| | 7 | | | | | 94,89 | 2,23 | “-” |
| | 8 | 2,52 | 68,39 | – | – | 10,39 | 67,78 | K+L |
| | 9 | | | | | 3,64 | 72,88 | “-” |
| | 10 $C_3$ | 0,00 | 71,58 | – | – | 0,00 | 72,26 | L |

* K – $Sr(NO_3)_2$;   L – $Nd(NO_3)_3·6H_2O$



$Cs_2[Nd(NO_3)_5(H_2O)_2]$

$Cs[Nd(NO_3)_4(H_2O)_3]$

**Figure 4 - Microphotos of coordination nitrates crystals Nd**

Features of the processes of complex formation and crystal-chemical structure of cesium coordination nitrates of neodymium indicate that:

- the structure of complex compounds is based on rare-earth coordination polyhedra, one way or another connected in space;
- processes of exchange interaction between structural components (their binding) in the studied water-salt systems occur already under normal conditions (at 25 °C, see Table 1, Fig. 2);
- the central atoms of the Nd complexing agent under the studied conditions exhibit a mono- and bidentate nature of the connection with nitrato groups having a coordination number of 10 and the possibility of coordination formations with different compositions ([Nd(NO3)5(H2O)2]2- i [Nd(NO3)4(H2O)3]-) reveal

**Table 3 - Influence of the type of symmetry on the possibility of occurrence of physical properties in crystals of coordination nitrates of rare earth elements**

| Connections | Sononia | Point group | Spatial group | Properties | Temperature range of formation, °C | The nature of solubility | References |
|---|---|---|---|---|---|---|---|
| $Cs_2[Nd(NO_3)_5(H_2O)_2]$ | monocl. | 2/m | C2/c | * ↕ Џ | 25–100 | incongr. | [18] |
| $Cs[Nd(NO_3)_4(H_2O)_3]$ | tricl. | $\bar{1}$ | $P\bar{1}$ | *<br>Џ | 50–65 | incongr. | [19] |

**Table 4 - X-ray data of cesium coordination neodymium nitrates**

| $Cs_2[Nd(NO_3)_5(H_2O)_2]$ | | | | $Cs[Nd(NO_3)_4(H_2O)_3]$ | |
|---|---|---|---|---|---|
| d, Å | $I/I_0$, % | d, Å | $I/I_0$, % | d, Å | $I/I_0$, % |
| 6,799 | 11,5 | 2,2191 | 11 | 6,667 | 80,8 |
| 5,9375 | 15,5 | 2,1923 | 28,5 | 5,4070 | 19,6 |
| 5,0980 | 55 | 2,1841 | 26 | 5,2727 | 36,5 |
| 4,8385 | 51,5 | 2,1681 | 16,5 | 4,4489 | 61,9 |
| 4,3708 | 49,5 | 2,0597 | 16 | 4,2467 | 29,2 |
| 4,2148 | 10 | 2,03162 | 23 | 4,1409 | 11,9 |
| 3,6775 | 100 | 1,84121 | 32,5 | 3,9241 | 8,8 |
| 3,4241 | 18,5 | – | – | 3,7231 | 14,2 |
| 3,3334 | 60 | – | – | 3,5700 | 13,1 |
| 3,2995 | 54,5 | – | – | 3,4035 | 8,8 |
| 3,0639 | 27 | – | – | 3,3384 | 49,6 |
| 2,9760 | 8,5 | – | – | 3,2781 | 52,3 |
| 2,9024 | 36,5 | – | – | 3,2314 | 13,5 |
| 2,8013 | 11,5 | – | – | 2,7152 | 8,8 |
| 2,7427 | 23 | – | – | 2,6727 | 100 |
| 2,7041 | 10,5 | – | – | 2,5829 | 11,5 |
| 2,6573 | 41 | – | – | 2,3528 | 16,5 |
| 2,6048 | 26 | – | – | 2,2739 | 5,8 |
| 2,5758 | 17 | – | – | 2,2307 | 9,6 |
| 2,5293 | 18,5 | – | – | 2,1882 | 14,2 |
| 2,4149 | 16 | – | – | 1,91250 | 28,8 |
| 2,4012 | 16 | – | – | 1,62366 | 20,8 |
| 2,3671 | 22,5 | – | – | 1,61946 | 10 |
| 2,3375 | 27,5 | – | – | – | – |
| 2,2939 | 15 | – | – | – | – |
| 2,2728 | 56,5 | – | – | – | – |

Note: d, Å - interplanar distances; $I/I_0$,% - are relative intensities of reflexes

an identically organized coordination sphere, clearly illustrating the dominant role of the $Ln^{3+}$ ion in the structure formation of alkali rare earth nitrates.

- complex formations have the ability to preserve a layered motif of spatial construction (see Fig. 5, [12]) from rows of alternating rows of Nd and Cs atoms along the z axis. These rows are the ends of the layers of the corresponding coordination polyhedra. The planes of the layers are approximately perpendicular to the plane of the drawing. It is possible to distinguish packets consisting of four Nd – Cs – Cs – Nd layers, within which coordination polyhedra are in contact with each other due to common edges and hydrogen bonds. Every fourth layer and the next one do not have common vertices and edges, and the interaction of packages in the structure is carried out through only hydrogen bonds.

In the studied water-salt systems, the mechanism of complex formation can be explained from the standpoint of competing replacements of water molecules in the immediate environment of $Ln^{3+}$ with $NO_3$– groups. The degree of completeness of substitution depends on the nature of $Ln^{3+}$, the influence on these processes of the disordering effect on the structure of solutions of the existing singly and doubly charged cations $Cs^+$, $Sr^{2+}$, the nature of the thermal movement of structural components, the properties of electron-donating oxygen atoms and the spatial structure of solvents. A significant influence of the thermal factor on these processes and their staging have been revealed. The presence of certain temperatures at the beginning of the release of complex compounds into the solid phase indicates the existence of an energy barrier and the need to provide the system with some additional energy to carry out such transformations.

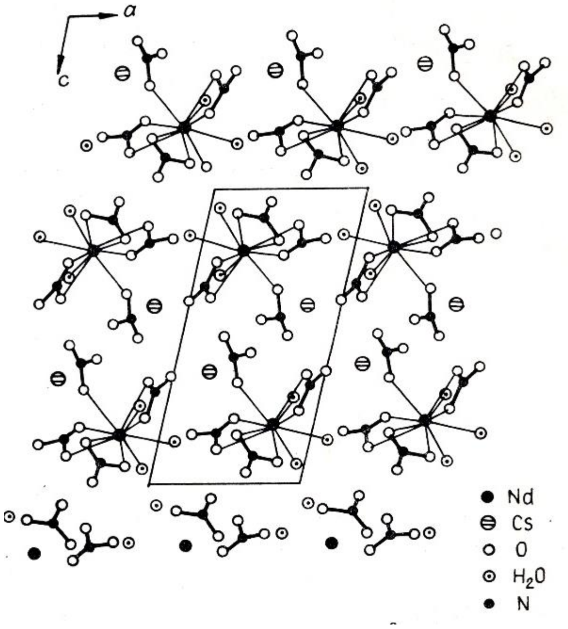


**Figure 5 - Projection of the $Cs[Nd(NO_3)_4(H_2O)_3]$ structure onto the xy plane, [12]**

All this makes the objects under study a promising group of nitrate precursors when developing formulations for liquid technological systems based on them and implementing processing schemes with impregnation, adsorption on radiation-resistant substrates with the possibility of thermal activation and solid-phase reactions. They have a complex of technologically valuable inherent properties: a) high solubility and compatibility with most components; b) a fairly wide temperature range for the existence of complex nitrates; c) detection of high activity by their reacting particles obtained by thermolysis of the solvent, and also nanosized and uniform in size and morphology [13]; d) the availability of a wide range of methods, methods, and technical means for activating such processes. It should also be noted that at present, combined methods of transformation with special requirements and fast-flowing syntheses with combined methods of system activation and mass production are becoming more widespread [14, 15].

With the use of thermoanalytical, chemical, and X-ray phase methods, an analysis of the nature and stages of dehydration processes, the nature and temperature intervals transformed into $Cs_2[Nd(NO_3)_5(H_2O)_2]$, $Cs[Nd(NO_3)_4(H_2O)_3]$ (20 – 1000 °C).

On the $Cs_2[Nd(NO_3)_5(H_2O)_2]$ derivatogram, the endoeffects of 95, 122, 156 °C correspond to the stepwise process of dehydration. The decrease in mass at 95 °C corresponds to the loss of one water molecule. At 156°C, the incongruent melting of the sample in the water of crystallization occurs, followed by the formation of an anhydrous double salt, the melting point of which is 236°C.

For $Cs[Nd(NO_3)_4(H_2O)_3]$, the dehydration process is also three-stage (endoeffects 62, 90, 162 °C). The loss of one water molecule according to the TG curve corresponds to a temperature of 139 °C. An increase in temperature to 162 °C entails incogruent melting of the double nitrate dihydrate; subsequent heat treatment – formation of $CsNO_3 \cdot Nd(NO_3)_3$ from temperature 355 °C. The thermal decomposition products of both coordination salts at t > 920 °C contain neodymium oxide.

## Conclusions

The conducted comprehensive study provides a reliable idea of the trends in the general behavior of structural components in water-salt systems of nitrate precursors of neodymium, cesium, strontium in the preparatory stages of technological regulations for the concentration and immobilization of liquid radioactive waste of the nuclear power industry complex according to the schemes using porous and layered matrix fixators of radionuclides $^{137}Cs$, $^{90}Sr$ and thermal activation. The stages of such transformations have been revealed; the patterns of complex and phase formation in systems and the factors influencing them were clarified; a number of physicochemical properties of the resulting intermediate phases - coordination neodymium nitrates - have been studied: their composition, types of compounds, atomic crystal structure, shapes of Ln coordination polyhedra, types of coordination of ligands, features and patterns of behavior in heat treatment processes. It has been established that, under the conditions of the existence of solutions, the system $CsNO_3 – Nd(NO_3)_3 – H_2O$ is characterized by the formation of 2 anionic complex compounds $Ln^{3+}$, the system $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ is of the eutonic type. The ongoing competing reactions are a powerful technological factor that has a significant impact on changes in the activity of structural forms of $Ln^{3+}$. Systematized information enables to elucidate the mechanisms and kinetics of transformations of structural components in similar objects and allows us to transfer the resulting system of knowledge to the plane of promising technological solutions for the solidification of liquid radioactive waste.

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# Прикладні аспекти використання виявлених закономірностей сумісної поведінка структурних компонентів у водно-сольових системах нітратів цезію, стронцію і неодиму

Проведене комплексне дослідження дає достовірне уявлення про тенденції у спільній поведінці структурних компонентів у водно-сольових системах нітратних прекурсорів неодиму, цезію, стронцію у підготовчих стадіях технологічних регламентів концентрування й іммобілізації рідких радіоактивних відходів ядерного енергопромислового комплексу за схемами з використанням пористих і шаруватих матричних фіксаторів радіонуклідів $^{137}Cs$, $^{90}Sr$ і тепловою активацією. Виявлено стадійність таких перетворень; з'ясовано закономірності комплексо- і фазоутворення в системах та фактори впливу на них; вивчений ряд фізико-хімічних властивостей утворюваних проміжних фаз – координаційних нітратів неодиму: їхній склад, види сполук, атомно-кристалічну будову, форми координаційних поліедрів Ln, типи координації лігандів, особливості і закономірності поведінки в процесах термооброблення. Встановлено, що в умовах існування розчинів система $CsNO_3 – Nd(NO_3)_3 – H_2O$ характеризується утворенням 2 аніонних комплексних сполук $Ln^{3+}$, система $Sr(NO_3)_2 – Nd(NO_3)_3 – H_2O$ – евтонічного типу. Протікаючі конкуруючі реакції є сильнодіючим технологічним фактором суттєво впливаючим на зміну активності структурних форм $Ln^{3+}$. Систематизовані відомості дозволяють з'ясовувати механізми, кінетику перетворень структурних компонентів в аналогічних об'єктах та дають можливість перенести одержану систему знань у площину перспективних технологічних рішень отвердження рідких радіоактивних відходів.

**Ключові слова:** неодим, цезій, стронцій, нітрати; водно-сольові системи, комплексоутворення, властивості.

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