

Physicochemical Studies of Uranium and REE Chromites and Niobates for Use as Radioactive Waste Immobilization Matrices

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The work presented herein is applied to immobilization of the most environmentally hazardous actinide fraction of radioactive waste (RW). Immobilization techniques and technology advances may be also applied to the rare earths, cesium and strontium fractions. Our work on improving environmental safety of radioactive waste storage is directed primarily to the use of mineral-like matrices possessing high chemical resistance to water and rather simple technology of production. Among others, those materials are represented by basalt-like matrices and chromite - niobate based ceramic composites.

Materials used for RW immobilization should meet rather stringent requirements, namely, high radiation and thermal stability, high mechanical strength, and low water solubility rate.

In our studies we bypassed the technical difficulties inherent in the development of synrocks, boron and phosphate glass systems, etc. by using other systems suitable for immobilization of α -bearing radwaste but produced by means of less complicated technology as compared to synrocks and glass. Such systems should possess the operating characteristics and complex of physicochemical and operating properties such as high thermal and radiation stability, thermocycling stability sufficient to meet high requirements imposed on the matrices for incorporating and long term retention of radioactive waste.

From the reference data the chromite compounds of uranium, lanthanum, plutonium and others as well as uranium and REE niobates are known to exist. Properties of those compounds such as low solubility in water, high thermal stability, high content of U and TPE in chemical compounds make those systems promising for use as the matrix material for disposal of α -bearing waste. However, the solid phase technique (SPT) of synthesis reported for those systems has quite a number of flaws, namely,

- handling highly radioactive dusty powders of the synthesized insoluble products, which makes decontamination of equipment an issue and worsens the environmental situation at the radiochemical plant site;
- the technique employs complex technological equipment for fabrication of compact products which is difficult to maintain in hot cells and canyons;
- solid phase synthesis assumes high temperatures, long process duration, and requires intermittent stirring thus reducing the production output of the facility.

We rejected the solid phase powder techniques and tried more promising liquid phase techniques (LPT) of synthesis which assumes co-precipitating hydroxides of the elements followed by drying and calcination or direct drying and calcination of mixed solutions of the components.

Studies conducted at IPC RAS showed the chromite - niobate based ceramic materials to be not worse than the conventional synrocks (titanates and zirconates). The

Chromite - niobate matrix under development may be either the uranium chromite of the formula UCrO_{4+x} or chromites of rare earth elements of the formula RCrO_3 and represents an excellent material for actinide immobilization. The materials in question possess high chemical stability, mechanical strength, heat resistance, etc. Because the uranium and REE chromites melting points are above 1800°C , it complicates the compacting of the materials. Niobates with many desired characteristics have lower melting points and when used as an additive to the chromite matrix reduce the melting point of the latter thus allowing creation of a more simple compacting technique. It is also possible to select other melting point reducing additives for the chromite matrix. Chromite - niobate based ceramic material allows considerable actinide loading up to 50% by weight.

Those materials will be advantageous to synrocks because of the less complex technique of synthesis and compacting. It's also worth mentioning that the chromite - niobate technology could be also used to immobilize the excess of defense plutonium for long term safe storage.

Physicochemical studies have been performed for the techniques for synthesis of uranium and REE chromite and niobate based matrix composites intended for retention of radionuclides. Basically, the liquid phase techniques for synthesis of uranium chromite of the formula UCrO_{4+x} and uranium niobate of the formula UNbO_{5+x} as well as corresponding REE compounds have been elaborated.

Development of the liquid phase technique for synthesis of uranium and REE chromite has been completed. The technique assumes mixing of uranium and chromium nitrate solutions in the appropriate proportions followed by co-precipitation of U and Cr hydroxides by means of adding ammonia solution and following drying and calcining at different temperatures and process durations. Completeness of the compound synthesis, i.e. the content of uranium chromite of UCrO_{4+x} in the resulting mix was determined by means of X-ray phase and chemical phase analytical methods. Results of the experiments are given in Table 1 and Figure 1, Curve 1.

Table 1. Completeness of synthesis for uranium chromite depending upon the temperature and the calcination process time

	Completeness of synthesis, % (the residue insoluble in concentrated HNO_3)								
τ , hr/ T , $^\circ\text{C}$	500	600	700	800	850	900	1000	1100	1200
0.5	15.1	16.2	25.9	59.8	74.2	78.7	89.8	94.1	95.9
1.0	18.0	19.3	29.0	66.3	80.1	84.0	93.2	95.8	98.2
2.0	20.3	215	32.5	70.4	85.3	89.1	95.2	97.4	99.0

1. The mechanism of synthesis was studied by means of X-ray phase and chemical phase analytical techniques and thermal weight pattern analysis. When heating the mix of chromium dioxide and ammonium diuranate, at $T = 250^\circ\text{C}$ the ammonium nitrate is decomposed with high exothermal effect; at $T = 320^\circ\text{C}$ the chromium hydroxide is dewatered with endothermal effect. On the X-ray pattern of the reaction mix one can conclude the following: at 400°C no bands of the crystalline phase are present, and at 600°C only weak bands of the crystalline uranium chromite phase are observed. X-ray patterns of the

powders calcined at 800, 1000, and 1200 °C in the crystalline phase indicate that band intensity increases and starting at about 1000 °C no bands except the uranium chromite ones are visible. As seen from the data presented in Table 1 and in Figure 2, at 600 °C the synthesis is incomplete, to the extent of 20%. At 600 °C, a partial decomposition of UO_3 into U_3O_8 occurs. At more elevated temperatures, formation of uranium chromite out of U_3O_8 and Cr_2O_3 accompanied by capturing O_2 from the air continues and finishes at $T = 1000 - 1100$ °C. From the data given, one can see that the 60-70% completeness of uranium chromite synthesis may be attained even at $T = 800$ °C and $t = 0.5 - 1.0$ hr, which greatly simplifies the technology of obtaining uranium chromite by the liquid phase synthesis as compared to the solid phase synthesis by means of oxide blending and calcining. Moreover, incompletely synthesized uranium chromite powders show higher chemical activity on account of being calcined at lower temperatures, thus greatly facilitating the fabrication (sintering) of compact high density products.

Further studies were devoted to the synthesis by direct drying and calcining mixed solutions of U and Cr nitrates.

Uranyl nitrate and chromium nitrate solutions were blended (to get the stoichiometric ratio of $\text{U}:\text{Cr} = 1:1$), dried, and the residue was calcined in the electric furnace. Afterwards, the completeness of synthesis was determined by X-ray and chemical phase analytical techniques, and the mechanism of processes accompanying the synthesis was studied by means of the thermal weight pattern analysis (derivatography). Results are shown in Table 2 and in Figure 1, Curve 2.

Table 2. Completeness of synthesis for uranium chromite depending upon the temperature and the calcination process time

	Completeness of synthesis, % (the residue insoluble in concentrated HNO_3)							
t, hr/ T, °C	500	600	700	800	900	1000	1100	1200
1.0	7.2	25.1	63.3	85.0	89.1	94.0	96.1	98.6
2.0	8.5	27.3	64.6	86.3	90.4	95.1	97.0	99.0

Basic processes accompanying synthesis, dewatering, and denitration are the same as for synthesis through hydroxides, except violent decomposition of the ammonium nitrate does not occur. Slow heating of the mix within the temperature range up to 300 °C is very desirable to avoid escape of the substance during denitration. Application of a highly concentrated solution of chromium anhydride is preferable as compared to chromium nitrate because it saves process energy and time otherwise consumed for dewatering and denitration. At high temperatures, the mechanisms of synthesis through hydroxides and through nitrates are alike. It is shown that keeping the reaction mix at 500 - 600 °C is desirable to allow the major portion of UO_3 to react with Cr_2O_3 prior to the conversion into U_3O_8 . Incomplete synthesis at $T = 600$ °C may be explained by partial

decomposition of UO_3 into U_3O_8 leading to further formation of uranium chromite out of U_3O_8 and Cr_2O_3 which occurs at higher temperature with the capture of oxygen from the air and ends at $T = 1000 - 1300^\circ\text{C}$. If so, the synthesis through the nitrate solutions goes more completely at lower temperatures (to the extent of 63 - 85% at $T = 700 - 800^\circ\text{C}$) as compared to the synthesis through hydroxides. However, to complete the process of synthesis, the more elevated temperature of about 1300°C is required. When using the nitrate technique of synthesis, calcining powders at lower temperatures of $800 - 900^\circ\text{C}$ is also preferred to obtain the incompletely synthesized chemically active uranium chromite powder which is readily compacted by pressing and sintered to the high density (the synthesis of uranium chromite being accomplished at the product sintering stage).

Drying and calcining may be combined in one apparatus operating in either continuous or batch mode, for example, in a spray - radiation dryer or in a plasmochemical reactor. Feed may be arranged either as the hydroxide sludge or as a solution of nitrates depending on the technological and economic reasons. Other things being equal, the solution of nitrates is more convenient.

Synthesis and properties of uranium niobates were also investigated. Products of U_3O_8 and Nb_2O_5 interaction were detected by the X-ray study after calcining the oxide mix at 850°C , the phase of the ratio $\text{U/Nb}=1/3$ was identified. Calcining of ground and compacted mixtures at 1000°C for 40 hours leads to the formation of two more phases of the ratio $\text{U/Nb}=1/1$ and $\text{U/Nb}=1/3$, the former reaction $\text{U/Nb}=1/1$ being slower and requiring a long time at 1200°C to complete. Earlier, the reaction in the mixture of oxides was found to finish completely at the higher temperature of $\approx 1300^\circ\text{C}$. Compounds with atomic ratios of $\text{U/Nb}=1/1$ and $\text{U/Nb}=1/3$ were assigned the formulae of UNbO_5 and $\text{UNb}_3\text{O}_{10}$ respectively. Later it was found that the content of oxygen in the above compounds varied with the conditions of fabrication thereof (duration and temperature of the calcination process, partial pressure of oxygen, etc.) resulting in a negligible change in lattice parameters, and more accurate formulae assigned to the compounds in question, which seem to be UNbO_{5+x} and $\text{UNb}_3\text{O}_{10+x}$, respectively. It was found that in the compound of $\text{U/Nb}=1/3$, the x value may vary within the range of 0.17 - 0.39. The phase of $\text{U/Nb}=1/3$ formed by sintering in the air does not match the section $\text{UO}_2 - \text{Nb}_2\text{O}_5$ and contains much more oxygen than necessary for the compound of $\text{UNb}_3\text{O}_{10.17}$. Hence, the niobium pentaoxide stabilizes the hexavalent state of uranium. We studied the synthesis and some properties of UNbO_{5+x} compound, however, in the future we are going to proceed with the ratio of $\text{U:Nb} = 1:3$.

The UNbO_{5+x} compound has the diamond-shaped subcell with the parameters slightly deviating with the content of oxygen. At average. they are equal to **$a' = 6.46$; $b' = 3.78$; $c' = 4.03 \text{ \AA}$** .

True cell is also diamond-shaped with the parameters of

$a = 5a' = 32.32 \pm 0.04$; $b = 8b' = 30.26 \pm 0.04$; $c' = 32.16 \pm 0.04 \text{ \AA}$.

For samples of UNbO_{5+x} and $\text{UNb}_3\text{O}_{10+x}$ the melting temperature of $T_m = 1500^\circ\text{C}$ and 1520°C , respectively, has been determined by heating with electric current in the air, and high resistance of the samples to evaporation has been also found.

A number of techniques for synthesizing uranium niobate were developed, synthesis through the powdered niobium pentaoxide Nb_2O_5 (the so called semi-solid phase technique) being one of them.

To get the stoichiometric ratio in the compound of $\text{U/Nb} = 1/1$, aliquot weight of the powdered niobium pentaoxide Nb_2O_5 was impregnated with the titrated uranyl nitrate solution. The resulting mix was dried with continuous stirring, and calcined at a different temperature and for a different period of time, with completeness of UNbO_{5+x} synthesis being monitored by XRPA and CPA techniques. The mechanism of the synthesis was studied by means of thermal weight pattern analysis and XRPA technique. Results obtained are shown in Table 3 and in Figure 2, Curve 1.

Table 3. Completeness of uranium niobate synthesis through niobium pentaoxide depending upon the calcination conditions

	Completeness of synthesis, % (the residue insoluble in concentrated HNO_3)								
T, °C	400	600	800	1000	1100	1200	1300	1350	1390
τ , hr	30 min	30 min	3 hr	3 hr	3 hr	3 hr	3 hr	3 hr	3 hr
	11.6	18.3	36.3	42.2	65.6	84.3	86.6	97.4	99.0

At about 250 °C, the denitration of uranyl nitrate to $\gamma\text{-UO}_3$ occurs with release of the gas NO_2 . At 500 °C the uranium trioxide starts to react with niobium pentaoxide. As niobium pentaoxide has rather low activity, a considerable portion of uranium trioxide is converted into U_3O_8 . Therefore, under the circumstances, formation of the uranium niobate is controlled by the solid phase reactions with oxygen capture from the air, which creates kinetic difficulties and requires high temperature to complete the process of synthesis. Niobate is synthesized within the temperature range of 800 - 1300 °C, and the completeness of its synthesis and properties of the resulting product depends of the process conditions. From the data given in Table 3, one can see that the synthesis of uranium niobate is completed when sintering at $T = 1300 - 1390$ °C the semi-product compacted from the powder incompletely synthesized and insufficiently calcined at 800 °C and above. Diffraction patterns of the sintered samples shows nothing except the uranium niobate. Raising the sintering temperature up to 1500 °C led to melting of niobate samples which, after cooling, have the density of 6.7 g/cm³ (95% of theoretical value).

Uranium niobate synthesis through soluble complex compounds of niobium with organic acids was studied. In the first stage of the studies, the development of a reliable technique for synthesis of different uranium - niobium compounds became necessary on account of the methods reported in the literature appeared to be useless. To improve the synthesis, we conducted the process from the mixture of uranium and niobium solutions that allowed mixing at the molecular level. Considerable difficulties were faced when selecting the soluble niobium species. The majority of niobium salts are subject to hydrolysis even in strong solutions of mineral acids. Therefore, we selected a method of dissolving niobium in organic solvents which, in addition, makes rather strong complexes

with niobium. After a number of search runs, it was found that niobium dissolves as a complex with trioxylglutaric acid (TGA) at the pH value of 10 and remains in solution until the pH value drops to about 1. Thus, the technique for synthesis was recommended as follows:

the stoichiometric mix (U:Cr = 1:1) of appropriate amounts of uranyl nitrate solution and the complex niobium compound solution with one of the organic acids, namely, malic or trioxylglutaric, was dried in the crucible under the IR-lamp and the remainder was calcined at a different temperature and for different period of time. Completeness of UNbO_{5+x} synthesis was determined by XRPA and CPA techniques.

To select the optimum synthesis conditions we have compared the thermal weight and X-ray patterns for different components in the reaction mix. It was found that dewatering takes place at 100°C (endothermal effect), and at 160°C and at 210°C very strong exothermal effects are observed which correspond to the burn up of organic matter under the impact of the nitrate ion. At 500°C already formed UO_3 and Nb_2O_5 react partially with one another, with the formation of niobate and heat evolving. Completeness of synthesis depending upon the process conditions is shown in Table 4 and in Figure 2, Curve 2.

Table 4. Completeness of uranium niobate synthesis with the application of malic acid depending upon the calcination conditions

	Solubility (% by weight) at the synthesis conditions given							
T, °C	400	800	900	1000	1100	1200	1200	1250
t, hr	30 min	1 hr	1 hr	1 hr	1 hr	1 hr	3 hr	1 hr
Powder after calcination	62.7	16.5	15.3	12.0	9.8	6.9	1.6	1.45
X-ray patterns	very weak niobate bands	weak niobate bands	--	niobate bands noticeable	--	--	--	niobate bands only

Comparison of both techniques shows that the synthesis of uranium niobate through the complex organic compounds requires lower temperatures than through niobium pentaoxide. The process of synthesis is, for practical purposes, complete at 1200°C .

The $\text{Nd}_2\text{Cr}_3 - \text{Cr}_2\text{O}_3$ system was also studied. We also studied different REE compounds for application as a matrix for immobilizing various α -isotopes.

All compounds are rather close in basic parameters, namely, melting point of $1900 - 2300^\circ\text{C}$, specific gravity of $6 - 7 \text{ g/cm}^3$, neodymium percentage (except of orthoniobate) of $60 - 70\%$, low solubility in water, and, hence, potentially suitable for the matrix material. Therefore, the ultimate selection of the matrix material will be affected by the convenience of technology for fabrication of the final waste forms. As the object for study we have selected neodymium chromites and niobates. From the reference data only one compound of NdCrO_3 formula is known to exist in the system. According to its

physicochemical characteristics, the above compound meets the requirements for the matrix material.

Different techniques for synthesizing REE chromites and niobates were studied similar to those used for synthesizing uranium chromites and niobates. XRPA, CPA, and thermal weight pattern analytical techniques in combination were used to study mechanisms of synthesis for chromites and niobates of La and Nd (as the REE representatives). The data obtained for synthesis of neodymium chromite through the co-precipitated hydroxides and through the drying and calcining mixed nitrate solutions are presented as an example. The NdCrO_3 compound has been synthesized. The technique of the synthesis assumes mixing of the appropriate quantities of neodymium and chromium nitrate solutions to obtain the compound with the stoichiometric ratio of $\text{Nd/Cr} = 1:1$, followed by drying mixed solutions at $T = 200 - 250^\circ\text{C}$ and calcining the resulting powder at the temperature of $T = 300 - 1200^\circ\text{C}$ for the certain period of time. Completeness of synthesis was determined using XRPA and CPA methods. As the result of the studies, the effect of temperature and calcination process time on the completeness of synthesis for neodymium chromite has been investigated. It is shown that with the completeness of 98-99% the synthesis of neodymium chromite finishes at $800 - 900^\circ\text{C}$ in 2 hours.

To develop the technology, it is very important to know the mechanism and optimum conditions for synthesizing neodymium chromite. A suggested technological scheme may be outlined as follows.

The mechanism of synthesis has been investigated. From the study of thermal weight pattern obtained by calcining neodymium and chromium hydroxides rinsed of ammonium nitrate, one can see that all the processes which are accompanied with either evolving or absorption of heat are completed at $760 - 780^\circ\text{C}$. We can suppose that at this temperature, the structure of neodymium chromite is completely formed. Results of the studies on the solubility of the powder obtained at $600 - 800^\circ\text{C}$ prove the supposition.

It is shown that the interaction does not occur, at least up to the temperature of 600°C . On the thermal pattern of co-precipitated hydroxides there is no evidence of peaks inherent to the separate hydroxides, hence, during the co-precipitation of hydroxides followed by drying and calcination, the separate hydroxides no longer exist and hydrated neodymium chromite is formed. The process of synthesis (according to the way where drying and calcination of the nitrate mix is supposed), is different. During the drying and decomposition of the nitrate mix, chromium assumes the hexavalent state. Change in the valency of chromium occurs at the temperature of about 260°C . Later, at $600 - 700^\circ\text{C}$ the reverse transition of chromium into a trivalent state and formation of neodymium chromite occurs. Ultimately, the process of neodymium chromite formation ends at the temperature of about $850 - 880^\circ\text{C}$. This temperature is a little higher as compared to the synthesis from hydroxides..

Neodymium chromite (as well as chromites of some other REE) are potentially suitable for use as a RW immobilization matrix. For the synthesis technique, one can recommend both calcining of the co-precipitated hydroxides and drying and calcining the

mixed solution of neodymium and chromium nitrates (chromic acid). Temperature for the calcination may be recommended at 900 °C. This value, however, may be adjusted after the process of compacting is studied.

From the reference data, two compounds are known to exist in the Nd_2O_3 - Nb_2O_5 system, namely, neodymium orthoniobate of the formula of NdNbO_4 and the compound with the formula of $3\text{Nd}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$. To obtain the diffraction patterns, as well as to make additional tests on the possibility of obtaining those substances by means of the solid phase reactions between neodymium and niobium oxides, we have synthesized the substances with the molar ratio $M = (\text{Nd}_2\text{O}_3)/(\text{Nb}_2\text{O}_5)$ of 0.5, 1.0, 2.0, 3.0, and 4.0.

Classic techniques for synthesizing ceramic material and oxides are of little use in the radiochemical industry. Therefore, we made an attempt to look for a more convenient way of combining neodymium and niobium in the solution. Similar to the synthesis of uranium niobate, complex compounds of niobium with trioxylglutaric acid appeared to be suitable for the purpose. To avoid precipitating neodymium hydroxide when adding neodymium nitrate into the solution of niobium complex, the solution was acidified to obtain a pH of 2 - 3. This adjustment did not cause the destruction of the niobium complex. Acidified solution of the niobium complex combined well with the neodymium nitrate solution and was stable for long period of time. Synthesis was performed according to two versions, namely, direct drying of the mixed nitrate solution followed by calcining or by co-precipitating the minimally soluble neodymium and niobium compounds, followed by drying and calcining as well.

The solution was dried and calcined at the temperature of 1200 °C. X-ray diffraction patterns of the samples give a good match with those for substances obtained by means of the solid phase reaction technique. Earlier, a similar method was used to study the synthesis of neodymium orthoniobate through the malic niobium complex and the mechanism of reactions occurred during the process of synthesis.

Thus, liquid phase synthesis techniques provide contact of the components at the molecular level and allow substantial attenuation of the conditions of synthesis as compared to the classic solid phase technique, and the so-called semi-solid phase method of synthesizing uranium niobate through the Nb_2O_5 powder as well.

Therefore, the possibility to obtain mixed chromite - niobate composites has been shown by means of either mixing solid components (powders) or directly from the mixed chromium, uranium (REE), and niobium solutions (see Figure 2, Curve 3). Substantial advantage of the developed liquid phase techniques over the solid phase ones (including mixing uranium and chromium, uranium and La or Nd oxide powders followed by calcining at $T = 1200$ °C and intermediate crushing to obtain a homogeneous product) was shown.

The possibility of performing synthesis of uranium and REE chromites, niobates, and mixtures thereof in the radiation - dispersing dryer or in the plasmochemical reactors has been shown.

Work on the study of the melting diagram for the system of UCrO_{4+x} - UNbO_{5+x} has been started. Knowledge of the phase diagram for the system under study is of

applied and scientific importance as well. Since the precision drawing of a phase diagram is a rather complicated matter, we state the task of identifying the type of phase diagram and the location of liquids line. Since the melting points for those compounds and mixtures thereof are very high, we determined the melting points by means of heating the mix in the iridium eye in the sealed chamber. Melting was monitored by a polarizing microscope, and the temperature was determined with an optical pyrometer. We used high temperature microscopy and isothermal holding of mixtures at predetermined temperatures, and X-ray phase analysis. It has been shown that as the uranium niobate is added, the eutectic mixtures are formed and the melting point decreases.

In the reported work, the study of 15 mixtures ranging from pure uranium chromite to pure uranium niobate, obtained by means of either solid component mixing or joint synthesis from solutions, has been conducted.

In the range of 1400 - 1600 °C the micropyrometer data were verified by means of isothermally holding the mixtures No.1 - 15 in 25°C intervals, with visual evaluation of the substance condition after cooling. To do that, the pellets were placed on a platinum plate in the furnace at a predetermined temperature and held there for 1 hour. The temperature was maintained with an accuracy of ± 5 °C.

Eutectic behavior with the melting point at 1460 - 1475 °C containing 90 - 93% of niobate by weight was discovered in the system. The phase diagram for uranium chromite - uranium niobate system is shown in Figure 3.

Studies of the solubility of uranium chromite and uranium niobate in HNO₃ and other solvents have been performed. Results are presented in Table 5.

Table 5. Stability of uranium chromite and uranium niobate in different solvents

Solvent	Holding time, minutes	Weight loss percentage	
		Uranium chromite	Uranium niobate
HNO ₃ 1:1; 20 °C	5	0.1	
	15	0.22	
	30	0.4	
HNO ₃ , concentrated; 20 °C	30	0.5	
HNO ₃ , concentrated; 75 °C	30	0.87	1.1
HCl, concentrated; 75 °C	30	0.33	4.6
H ₂ SO ₄ , concentrated; 20 °C	30	0.1	
H ₂ SO ₄ , concentrated; 75 °C	30	0.97	5.0
NaOH 100 g/L at 20 °C	5	+0.17	
	15	+0.5	
	30	+0.17	
Na ₂ CO ₃ , 200 g/L at 75 °C	30	0	
HF, concentrated, 26.5N	30	0	35
HClO ₄ at 120 °C	30	100	100

From the presented data, one can see that uranium chromite and uranium niobate are extremely inert compounds and are not dissolved in the most aggressive liquid chemical solvents and, what is most important, in nitric acid. Leach rate in bidistilled water at 20 °C from pelletized samples is about 1×10^{-6} - 1×10^{-7} g/cm²/day. However, the above value is preliminary and is to be further clarified depending upon the composition, conditions of fabrication, and sample (pellet) density. The technique for digesting uranium and REE chromites and niobates in perchloric acid has been elaborated.

Cold compacting and sintering uranium chromite, niobate, and mixtures thereof in the atmosphere of air was also studied.

The ability to press and sinter the system of "uranium chromite - uranium niobate" was studied within the entire composition range. Pure uranium chromite presses poorer than the mixtures and the pure uranium niobate. As the uranium niobate content increases, marked elevation in the relative density is observed, probably on account of better pliability of the uranium niobate as compared to that of the uranium chromite. The phenomenon is implicitly confirmed by comparison of the melting points thereof.

Studies of the effect of the synthesis technique used to obtain the starting material, grinding, niobate additive, compacting pressure and sintering conditions on the sample

density showed that samples with maximum density (90 - 92% of the theoretical value) are obtained from non-crushed uranium chromite with the additive of 5 - 10% uranium niobate by weight. Cold pressing was performed at a pressure of 4 ton per square centimeter, and sintering was performed by holding the product at $T = 1450^{\circ}\text{C}$ for 3 hours. Addition of the above quantity of uranium niobate negligibly lowers the melting point of the material.

Preliminary experiments on compacting uranium chromite and uranium niobate composites have been performed. Fabrication of the compacted products includes two basic stages -- molding of blanks, pellets and sintering thereof to obtain the finished product containing radioactive waste.

Blank molding may be performed either by introducing the binder on some stage or without it. As a rule, the blend for product molding (pellets or blocks) was prepared by means of adding the certain plasticizer quantity to the composite powder. Paraffin appeared to be the best of all the studied plasticizers. Paraffin was introduced into the blend by means of impregnating the latter with a hot solution of the paraffin in heptane followed by thorough stirring and heptane distillation at $100 - 150^{\circ}\text{C}$. Product blanks of different size ($\text{OD} = 2 - 20 \text{ mm}$, $\text{H} = 2 - 20 \text{ mm}$) were molded by means of cold double-sided pressing of the blend aliquot weight with the plasticizer using moulds of different diameter ($\text{OD} = 2 - 20 \text{ mm}$) at $P = 0.5 - 5.0 \text{ t/cm}^2$. The mode of pressing was adjusted to obtain strong, not loose blanks, without causing overpressure cracks. Compacted blanks were subjected to distillation to remove paraffin. The optimum compacting pressure of 4 t/cm^2 resulted in the maximum pellet density with no crevices and stratification, which are likely to occur in overpressurized products.

Molded blanks were sintered into the product in the electric resistance furnaces at different temperatures (up to 1600°C), various holding times, and in different atmospheres -- oxidizing (air), inert, and vacuum. Sintering conditions were selected to obtain a high quality product -- strong, transportable, with non-breakable edges.

Good results were obtained rather easily during pressing and further sintering of the uranium niobate. The effect of temperature on the uranium niobate sintering has been studied. The sintering curve reaches saturation at $T = 1400^{\circ}\text{C}$, which is close to the melting point. Since the uranium niobate has a lower melting point, it may be added to the uranium chromite to improve sintering of the latter.

Also, the studies were conducted on pressing and sintering of crushed uranium chromite and uranium niobate mixes. Pressing and further sintering of those powders showed good results with the uranium niobate additive of 5 - 7.5%. Maximum density of the pellets obtained was 7.29 g/cm^3 . The principal technological flowsheet for immobilization liquid RW into chromite - niobate matrices is shown in Figure 4.

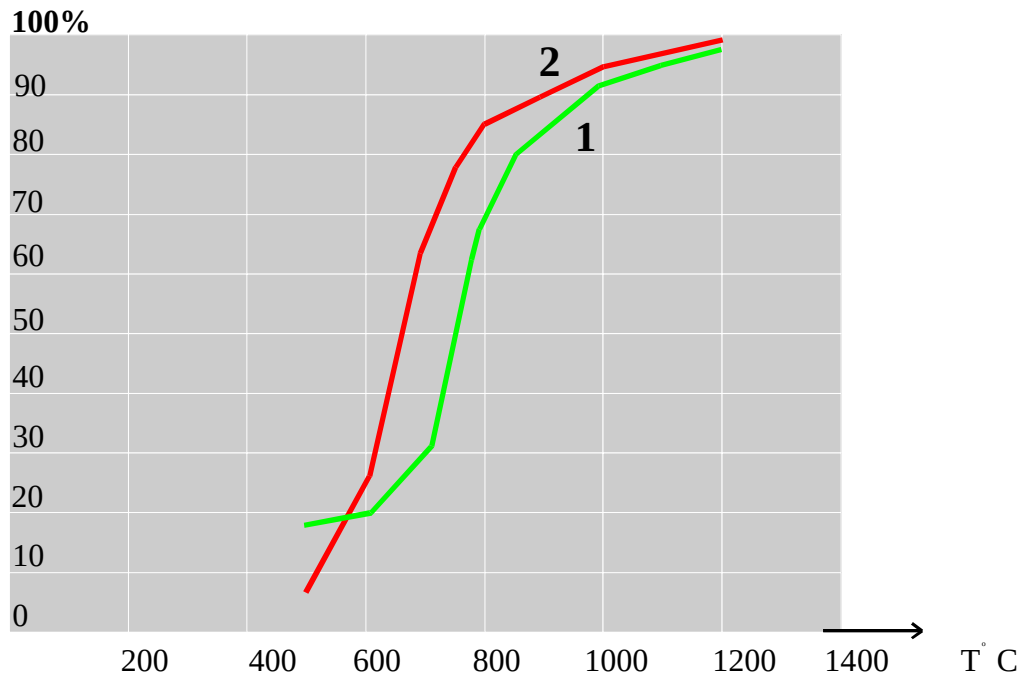


Fig.1. Dependence of the completeness of synthesis uranium chromite upon the process temperature, $\tau=1$ hour; curve 1 - using precipitation of hydroxides Curve 2 - using solution mixture of element nitrates.

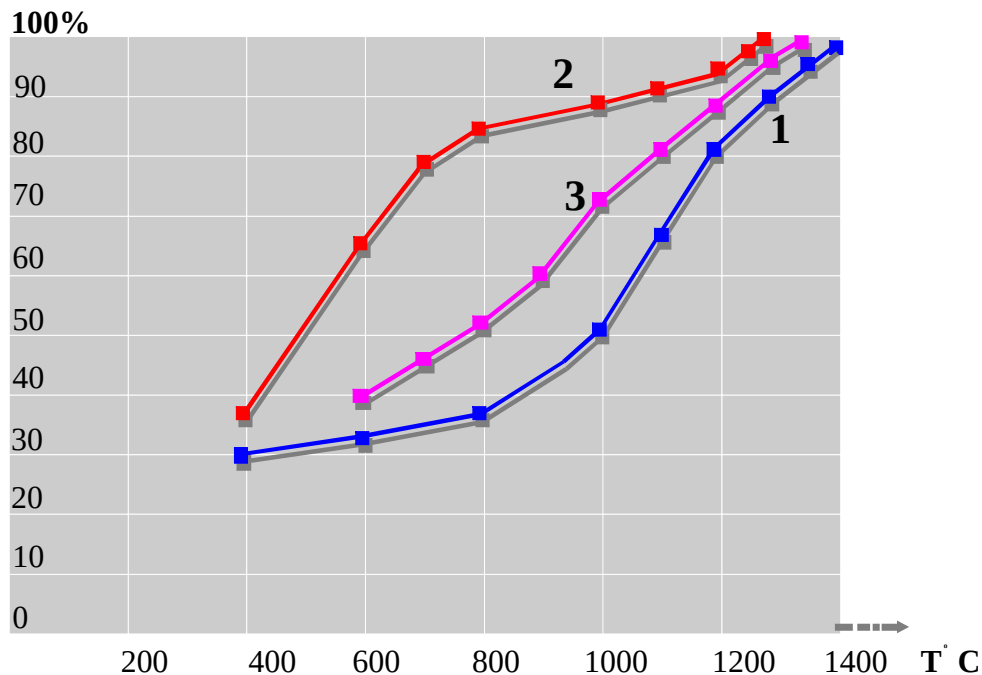


Fig. 2. Dependence of the completeness of synthesis uranium niobate upon the process temperature. Curve 1 - $\tau=1$ hour, using powder Nb_2O_5 . Curve 2 - $\tau=3$ hourss, using organic acid complex of Nb. Curve 3 - $\tau=1$ hour, synthesis of mixture of uranium chromite + 7,5%w. uranium niobate.

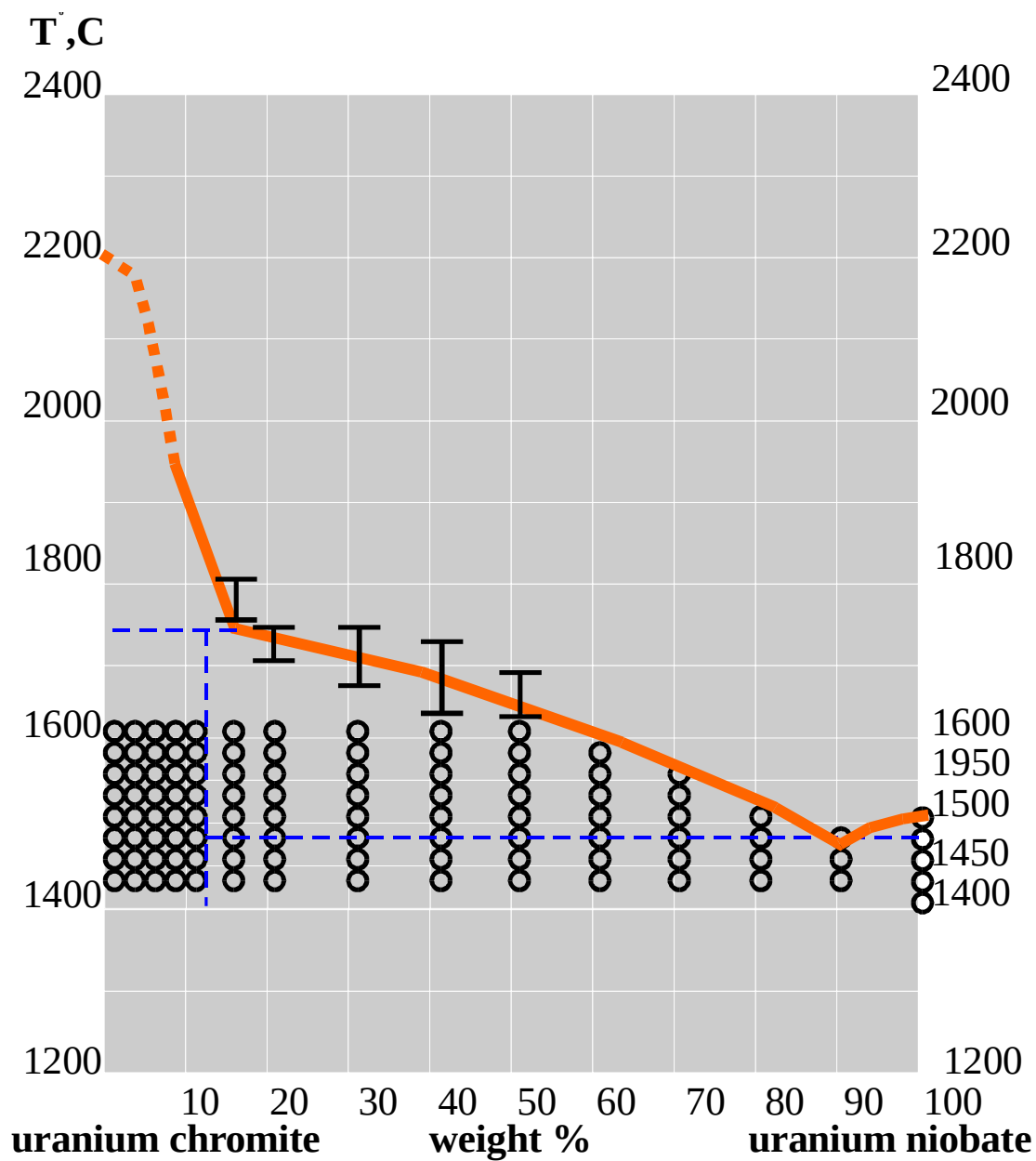


Fig. 3. Melting Diagram of chromite uranium - niobate uranium system.

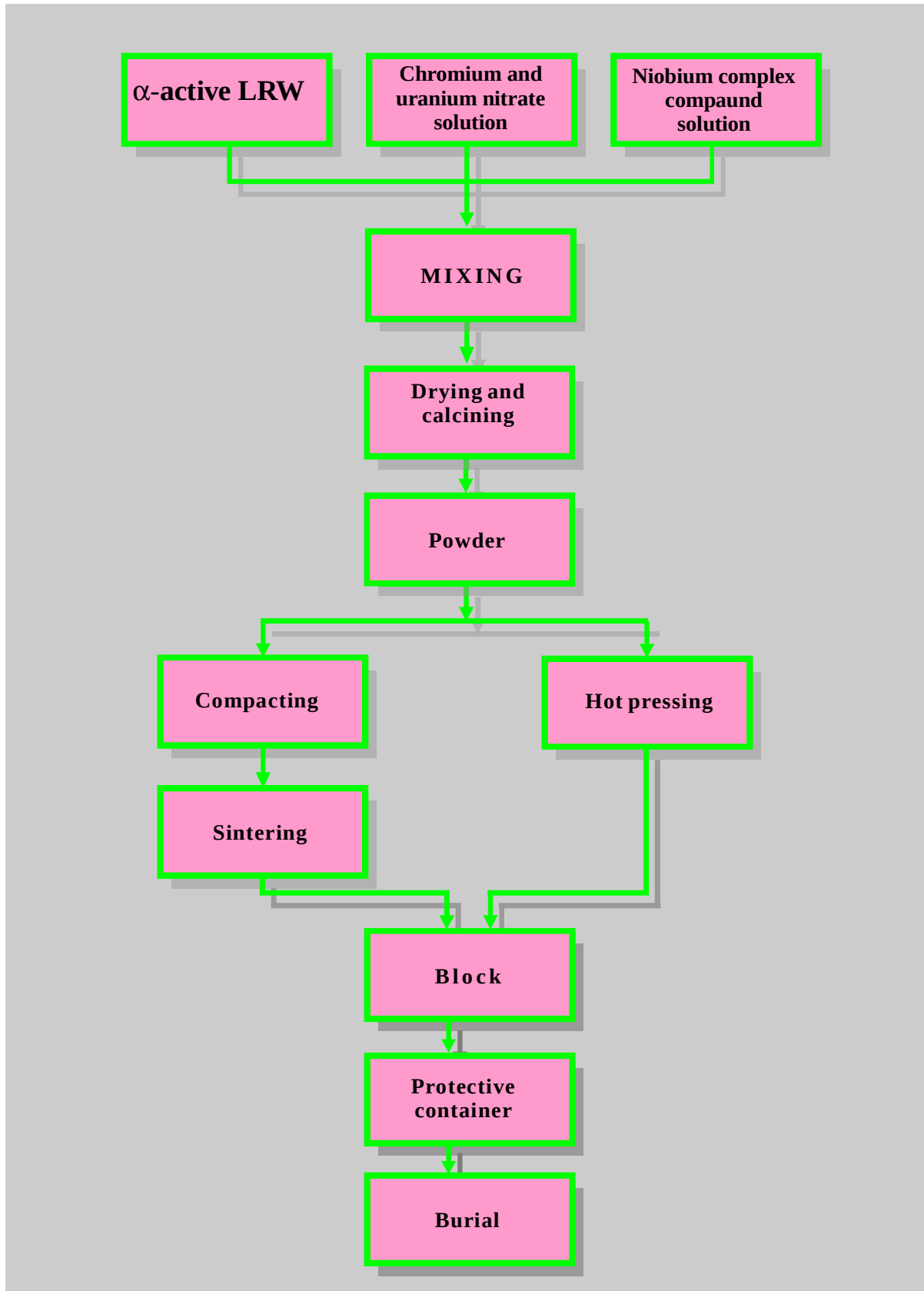


Fig. 4. The principal technological flowsheet for immobilization LRW into chromite - niobate matrices.

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