**DE GRUYTER OPEN**

# Uranium and neodymium partitioning in alkali chloride melts using low-melting gallium-based alloys

**Stanislav Yu. Melchakov,
Dmitry S. Maltsev,
Vladimir A. Volkovich,
Leonid F. Yamshchikov,
Dmitry G. Lisienko,
Aleksandr G. Osipenko,
Mikhail A. Rusakov**

**Abstract.** Partitioning of uranium and neodymium was studied in a 'molten chloride salt – liquid Ga-X (X = In or Sn) alloy' system. Chloride melts were based on the low-melting ternary LiCl-KCl-CsCl eutectic. Nd/U separation factors were calculated from the thermodynamic data as well as determined experimentally. Separation of uranium and neodymium was studied using reductive extraction with neodymium acting as a reducing agent. Efficient partitioning of lanthanides (Nd) and actinides (U), simulating fission products and fissile materials in irradiated nuclear fuels, was achieved in a single stage process. The experimentally observed Nd/U separation factor valued up to $10^6$, depending on the conditions.

**Key words:** neodymium • uranium • gallium • separation factor • reductive extraction • pyrochemical reprocessing

S. Yu. Melchakov✉, D. S. Maltsev, V. A. Volkovich,
L. F. Yamshchikov, M. A. Rusakov
Department of Rare Metals and Nanomaterials,
Institute of Physics and Technology,
Ural Federal University,
19 Mira Str., Ekaterinburg, 620002, Russia,
Tel.: +7 343 375 4741, +7 912 689 3893,
Fax: +7 343 375 4154,
E-mail: s.yu.melchakov@gmail.com

D. G. Lisienko
Department of Physical and Chemical Methods
of Analysis,
Institute of Physics and Technology,
Ural Federal University,
19 Mira Str., Ekaterinburg, 620002, Russia

A. G. Osipenko
JSC "Research Institute of Atomic Reactors",
10 Dimitrova Str., Dimitrovgrad, Ul'yanovsk Region,
435510, Russia

## Introduction

One of the factors determining the future of nuclear power industry is the choice of the fuel cycle, including the type of fuel, reactor and the method of spent nuclear fuel (SNF) disposal. Fast reactors can replace thermal reactors for power generation or can be used to burn long-lived fission products and actinides separated from the thermal reactor SNF. Gradual commissioning of fast reactors would eventually allow closing the nuclear fuel cycle (NFC) and reducing the stockpiles of dangerous long-lived isotopes. Efficient work of fast (Generation IV) reactors requires shortening the time between discharging the spent fuel from the reactor and reprocessing in addition to developing on-site fuel fabrication and reprocessing facilities. Implementation of a short closed NFC depends on the ability to work with high burn-up SNF after relatively short cooling time, employing the working media stable towards ionizing radiation. From this point, a pyrochemical technology using molten salts and liquid metals is a prospective way of SNF reprocessing.

Cadmium is traditionally considered as the low-melting metal in the pyrochemical separation processes. Cadmium is compatible with low-carbon steels and its high vapor pressure at elevated temperatures allows the separation of uranium and plutonium from the liquid metal matrix. However, the separation factors of lanthanides from actinides in

the processes involving liquid cadmium are quite low [1, 2]. Thermodynamic calculations of separation factors of 4f- and 5f-elements show [3, 4] that the majority of the low-melting metals can be arranged in the following sequence, in which the effectiveness of the inter-group separation of f-elements decreases from Al to Cd:

(1)         Al > Ga > Sn > Bi > In > Zn > Cd
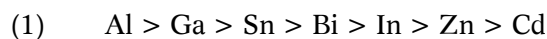
The above sequence shows that the low-melting metals of the groups 13 (Al, Ga, In) and 14 (Sn) of the Periodic Table can be used for separating 4f- and 5f-elements. Relatively high melting point of Al (660.37°C) limits its application in pyrochemical technologies in chloride media [5]. Gallium was considered as a prospective liquid metal medium [6, 7] but the high price of this trace element will likely limit its wide industrial scale application. Binary alloys of gallium with other elements, e.g. In or Sn, can be employed as an alternative to pure Ga. Ga-In and Ga-Sn eutectics contain 21.4 wt% In or 13.5 wt% Sn and melt at 15.3 and 20.5°C, respectively [5]. Diluting gallium by another metal can decrease the cost of the liquid alloy. Low melting temperatures of the eutectics allow working with the liquid alloys in a wide temperature range, starting from the room temperature.

The present work, therefore, is aimed at studying separation of uranium and neodymium (as imitators of fissile materials and fission products) on gallium-indium and gallium-tin eutectic alloys, in addition to comparing experimentally determined separation factors with the results of thermodynamic calculations.

## Thermodynamic calculations

The mathematical model allowing calculating separation factors of two metals in a 'molten salt – liquid metal' system was developed by Lebedev [3]. If both separating metals are present in the salt melt in the same oxidation state ($n$) the separation factor ($\Theta$) can be calculated from the following equation:

$$(2) \qquad \log \Theta_{\frac{Me_1}{Me_2}} = \frac{nF}{2.303RT}\left(E^*_{Me_2} - E^*_{Me_1}\right)$$
$$+ \log \gamma_{Me_1(liq)} - \log \gamma_{Me_2(liq)}$$

where $E^*$ is the formal standard potential of the metal in the salt phase; $\gamma$ is the activity coefficient of the metal in the liquid metal phase; F and R are the Faraday and the universal gas constants, respectively. Activity coefficients $\gamma$ can be derived from the known activity ($a$) and solubility (X) of the given metal in the liquid metal phase:

$$(3) \qquad \log a = \log \gamma + \log X$$

Thermodynamic properties ($a$ and X) can be determined in various ways but the most reliable data is obtained employing direct methods, i.e., electromotive force measurements for activity and direct physical measurements (precipitation, filtration) for solubility.

To calculate the separation factor $\Theta$, the elements must be brought to the same standard state. In the present work, the supercooled liquid state of the separating metals was taken as the standard, and the thermodynamic correction $\log a^0_{ph.trans}$ was used to account for the phase transformations in calculating activity coefficients of liquid metals.

$$(4) \qquad \log \gamma_{(liq)} = \log \gamma_{(sol)} - \log a^0_{ph.trans}$$

$$(5) \qquad \log a^0_{ph.trans} = a_{ph.trans} + \frac{b_{ph.trans}}{T}$$

$$(6) \quad a_{ph.trans} = \frac{-\Delta H_{ph.trans_1}}{2.303R \cdot T_{ph.trans_1}} + ... + \frac{-\Delta H_{melt}}{2.303R \cdot T_{melt}}$$

$$(7) \qquad b_{ph.trans} = \frac{\Delta H_{ph.trans_1}}{2.303R} + ... + \frac{\Delta H_{melt}}{2.303R}$$

where $\Delta H_{ph.trans}$ and $T_{ph.trans}$ are the enthalpy change and temperature of the phase transitions in the solid state, and $\Delta H_{melt}$ and $T_{melt}$ is the same for melting of a given metal.

The formal standard potential of uranium and neodymium (with supercooled liquid state of the corresponding f-element chlorides taken as the standard) were reported previously [8, 9]. Thermodynamic functions of these elements in the alloys with gallium, and Ga-In and Ga-Sn eutectics are summarized in Table 1. Activity coefficients ($\gamma$) were calculated using Eq. (3). Table 1 also contains the parameters of $\gamma_{liq} = f(T)$ dependencies obtained employing Eqs. (4)–(7). The required thermodynamic parameters of phase transitions $\Delta H_{ph.trans}$, $T_{ph.trans}$, $\Delta H_{melt}$ and $T_{melt}$ were taken from [19].

Neodymium and uranium separation factors were calculated using Eq. (2). Separation was modeled for the salt melts based on the LiCl-KCl-CsCl eutectic mixture and liquid alloys based on Ga, Ga-In and Ga-Sn eutectics. The results of the thermodynamic calculations are presented in Table 2. The results show that separation factors increase with decreasing temperature and that Nd/U separation factors achievable on the binary gallium-based alloys are higher than on pure gallium. These calculations, however, show only the thermodynamically possible separation factors and do not take into account kinetics of the exchange reactions between the molten salt and liquid metal phases.

## Experimental

Neodymium and uranium containing salt melts and liquid metal alloys were prepared using the techniques described previously [20]. Separation of uranium from neodymium was studied using the reductive extraction, with neodymium acting as the reducing agent:

$$(8) \quad UCl_6^{3-} + Nd^0(Ga-X) \leftrightharpoons NdCl_6^{3-} + U^0(Ga-X)$$
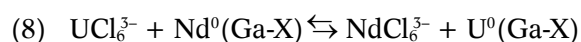
where Ga-X is the eutectic alloy and X = In or Sn.

**Table 1.** Thermodynamic functions of U and Nd in alloys with Ga, Ga-In and Ga-Sn eutectic mixtures

| $f$-Me | Liquid alloy | Function ($\gamma$) | $\log \gamma = a - b/T \pm \Delta$ | | | | Source |
|---|---|---|---|---|---|---|---|
| | | | $a$ | $b$ | $\Delta$ | $\Delta T$ [K] | |
| Nd | Ga | $a_{sol}$ | 5.612 | 15 314 | ±0.011 | 673–975 | [10, 11] |
| | | X | 0.80 | 2 290 | ±0.19 | 400–1079 | [12, 13] |
| | | $\gamma_{sol}$ | 4.81 | 13 030 | ±0.19 | 673–975 | calculated |
| | | $\gamma_{liq}$ | 5.24 | 13 560 | ±0.19 | 673–975 | calculated |
| | Ga-In | $a_{sol}$ | 4.37 | 14 110 | ±0.07 | 723–823 | [14] |
| | | X | 1.18 | 2 900 | ±0.13 | 448–1072 | [13] |
| | | $\gamma_{sol}$ | 3.19 | 11 220 | ±0.15 | 723–823 | calculated |
| | | $\gamma_{liq}$ | 3.62 | 11 750 | ±0.15 | 723–823 | calculated |
| | Ga-Sn | $a_{sol}$ | 4.827 | 14 283 | ±0.013 | 573–1073 | [15] |
| | | X | 2.11 | 3460 | ±0.07 | 440–1062 | [15] |
| | | $\gamma_{sol}$ | 2.72 | 10 820 | ±0.07 | 573–1062 | [15] |
| | | $\gamma_{liq}$ | 3.15 | 11 350 | ±0.07 | 573–1062 | calculated |
| U | Ga | $a_{sol}$ | 3.15 | 8 830 | ±0.08 | 573–1073 | [16] |
| | | X | –2.51 | 1 220 | ±0.34 | 297–600 | [17] |
| | | | 0.41 | 2 950 | ±0.18 | 600–1073 | [17] |
| | | $\gamma_{sol}$ | 2.77 | 5 910 | ±0.20 | 573–1073 | [17] |
| | | $\gamma_{liq}$ | 3.11 | 6 380 | ±0.20 | 573–1073 | [17] |
| | Ga-In | $a_{sol}$ | 3.76 | 9 230 | ±0.26 | 569–1080 | [16] |
| | | X | –0.17 | 2 840 | ±0.47 | 530–1076 | [17] |
| | | $\gamma_{sol}$ | 3.94 | 6 390 | ±0.54 | 573–1073 | [17] |
| | | $\gamma_{liq}$ | 4.26 | 6 850 | ±0.54 | 573–1073 | [17] |
| | Ga-Sn | $a_{sol}$ | 3.17 | 8 910 | ±0.18 | 571–1016 | [18] |
| | | X | –0.02 | 2 770 | ±0.37 | 476–1076 | [18] |
| | | $\gamma_{sol}$ | 3.19 | 6 140 | ±0.41 | 571–1016 | calculated |
| | | $\gamma_{liq}$ | 3.91 | 6 900 | ±0.41 | 571–1016 | calculated |

The subscripts 'sol' (solid) and 'liq' (liquid) denote standard state of the $f$-metal in the alloy.

**Table 2.** Calculated Nd/U separation factors on liquid alloys in 'LiCl-KCl-CsCl melt – liquid metal (alloy)' system

| Liquid metal or alloy | $\Theta_{Nd/U}$ | | |
|---|---|---|---|
| | 723 K | 773 K | 823 K |
| Ga | $3.3 \times 10^5$ | $1.1 \times 10^5$ | $0.4 \times 10^5$ |
| Ga-In eutectic | $8.0 \times 10^5$ | $1.7 \times 10^5$ | $0.4 \times 10^5$ |
| Ga-Sn eutectic | $25.0 \times 10^5$ | $4.8 \times 10^5$ | $1.1 \times 10^5$ |

The experimental cell is schematically presented in Fig. 1. Its construction is similar to that used previously [20] but includes a stirring device. The stirrer vibrated with the frequency of 50 Hz, and the amplitude of vibrations of the lower part of the stirrer was around 15 mm. Two types of stirrers were tested. One consisted of a spiral made of molybdenum wire, and another of a molybdenum plate blade. The ratio between the salt and the metal phases was determined by the geometry of the beryllium oxide container and was kept constant in all experiments. The crucible contained ca. 30 g of a chosen eutectic alloy and 40 g of the salts.

Molybdenum is sufficiently compatible with gallium, solubility of Mo in Ga is $4.8 \times 10^{-4}$ and $1.7 \times 10^{-3}$ at.% at 673 and 773 K, respectively [13]. The experiments were performed at 723–823 K under argon (99.998%). A slow flow of the gas was maintained through the cell for the duration of the entire experiment to protect the salt melt from the effect of oxygen and moisture. Separation factors of neodymium from uranium were calculated from the following expression:
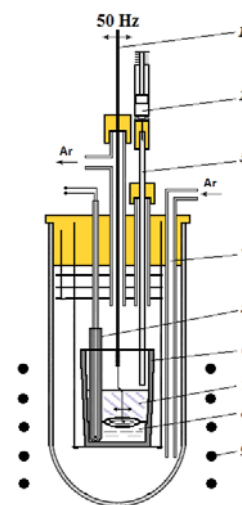


**Fig. 1.** Experimental cell for studying separation uranium from neodymium in a 'fused salt – liquid metal' system. 1 – molybdenum rod with a stirrer; 2 – syringe for sampling salt melt; 3 – silica capillary sampling tube; 4 – Ar inlet; 5 – beryllia thermocouple sheath; 6 – beryllia crucible; 7 – salt melt; 8 – liquid metal alloy; 9 – heating elements.
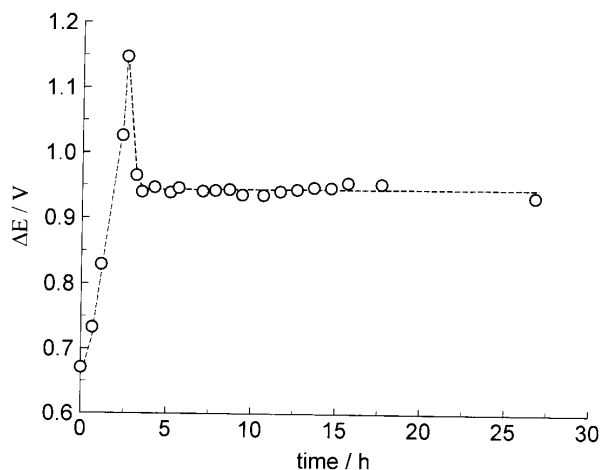
**Fig. 2.** Change of potential difference between the molten metal and salt phases upon contacting Ga-In-Nd (0.97 wt% Nd) alloy and LiCl-KCl-CsCl-UCl₃ (0.85 wt% U) melt at 735 K under static conditions.

$$(9) \qquad \Theta_{Me1/Me2} = (c_1 \cdot x_2)/(c_2 \cdot x_1)$$

where $c$ and $x$ are the concentrations (in molar fractions) of a given element in the salt and the metal phases, respectively. After completing the experiments, the salt and metallic phases were analyzed to determine U and Nd content employing ICP-MS spectrometry (ELAN-9000, PerkinElmer).

## Results and discussion

To determine time required for completing the reaction, the potential difference between the salt and the metal phases was monitored over time in the course of the exchange reaction. An example of the results obtained for 'LiCl-KCl-CsCl-UCl₃ – Ga-In--Nd' system under static conditions is shown in Fig. 2. The potential difference initially increased, then decreased and after ca. 4 h remained essentially

constant for the following 23 h indicating that the system reached a steady state. In the subsequent studies, the experiments lasted for 12 h or longer to ensure that the reaction went to completion under given conditions.

Experimentally determined Nd/U separation factors in 'Ga-X-Nd – LiCl-KCl-CsCl-UCl₃' systems are summarized in Table 3. Ce/Am separation factor reported for liquid gallium and LiCl-KCl eutectic based melt [6] is also included for comparison. The presented data show that under static conditions, i.e. in the absence of stirring, Ln/An separation factors for all gallium-based alloys were sufficiently lower than expected from the thermodynamic calculations. The difference between the calculated and observed values likely resulted from the kinetic difficulties of the exchange reaction (8) involving redistribution of *f*-elements between the salt and metallic phases. After the system has reached a stationary state (Fig. 2) the concentrations of Ln or An are close to the equilibrium only in the near interface layers of the salt and metallic phases. The completeness of the process is then determined by the rate of diffusion of uranium away from the interface into the bulk of the metallic alloy and neodymium to the interface. Equation (2) allows estimating maximal thermodynamically possible separation factors but does not give an answer concerning the reaction and diffusion rates. Stirring the salt and metallic phases intensifies the process [3], and a number of experiments were conducted using the experimental cell equipped with a stirrer. Stirring the phases resulted in increasing separation factors. Type of the stirrer can influence the rate of heterogeneous reactions [21]. In the present study, bladed stirrer was more efficient than the spiral. Separation factors obtained with the spiral stirrer increased by an order of magnitude and with the plate stirrer by two orders of magnitude compare to the static conditions. Increasing contact between the phases (interface surface area) would enhance the rate of the exchange process. Tables 2 and 3 also show

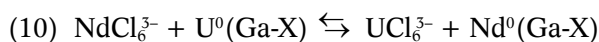**Table 3.** Experimentally determined Ln/An separation factors on liquid metals (alloys)

| Liquid metal or alloy | Ln/An couple | $\Theta_{Ln/An}$ | $T$ [K] | Conditions | Source |
|---|---|---|---|---|---|
| Ga | Ce/Am | ca. $1.0 \times 10^2$ | 773 | static | [6] |
| Ga-In eutectic | Nd/U | $1.9 \times 10^2$ | 722 | 12 h, static | present work |
| | | $1.6 \times 10^2$ | 735 | | |
| | | $4.9 \times 10^2$ | 737 | 13 h, static | |
| | | $2.6 \times 10^2$ | 735 | 27 h, static | |
| Ga-Sn eutectic | Nd/U | $3.0 \times 10^2$ | 723 | 12 h, static | present work |
| | | $2.6 \times 10^2$ | | | |
| | | $1.1 \times 10^2$ | 773 | | |
| | | $4.5 \times 10^2$ | | | |
| | | $2.1 \times 10^3$ | 723 | | |
| | | $2.7 \times 10^3$ | | 12 h, stirring, spiral stirrer | |
| | | $1.6 \times 10^3$ | 773 | | |
| | | $3.0 \times 10^3$ | | | |
| | | $1.3 \times 10^3$ | 823 | | |
| | | $1.6 \times 10^3$ | | | |
| | | $3.7 \times 10^3$ | 823 | 12 h, stirring, bladed stirrer | |
| | | $10.3 \times 10^3$ | | | |

**Table 4.** Experimentally determined Nd/U separation factors under conditions imitating reaction (10)

| Alloy | $T$ [K] | $\Theta_{Nd/U}$ |
|---|---|---|
| Ga-In | 738 | $4.7 \times 10^5$ |
| Ga-Sn | 723 | $32.3 \times 10^5$ |
|  |  | $27.0 \times 10^5$ |

that rising temperature generally led to decreasing separation factor values.

In a separate series of experiments, the equilibrium between the salt and metallic phases was imitated using the following reaction and initially adding uranium into metallic alloy and neodymium into salt melt:

$$(10) \quad NdCl_6^{3-} + U^0(Ga\text{-}X) \leftrightarrows UCl_6^{3-} + Nd^0(Ga\text{-}X)$$

The experiments showed that after 12 h there is a very little redistribution of $f$-elements between the phases. Analytically determined separation factors (Table 4) agree very well with the results of thermodynamic calculations (Table 2). The results indicate that separation of uranium from neodymium is possible in a single-stage process.

## Conclusions

Thermodynamic calculations and experimental determination of Nd/U separation factors confirmed the adequacy of the model describing processes of elements distribution in a 'molten salt – liquid metal alloy' system. Stirring the salt and metallic phases intensifies the exchange processes. Binary gallium-containing alloys should be preferred to pure gallium for separating Ln and An. Amongst the alloys studied in the present work, highest separation factors were achieved using Ga-Sn eutectic.

## References

1. Kinoshita, K., Kurata, M., & Inoue, T. (2000). Estimation of material balance in pyrometallurgical partitioning process of transuranic elements from high-level liquid waste. *J. Nucl. Sci. Technol.*, *37*(1), 75–83.
2. Moriyama, H., Kinoshita, K., Asaoka, Y., Moritani, K., & Ito, Y. (1990). Equilibrium distributions of actinides and fission products in pyrochemical separation systems (II) LiCl-KCl/Cd system. *J. Nucl. Sci. Technol.*, *27*(10), 937–943. DOI: 10.1080/18811248.1990.9731273.
3. Lebedev, V. A. (1993). *The selectivity of liquid metal electrodes in molten halide salts.* Chelyabinsk: Metallurgya. (in Russian).
4. Toda, T., Maruyama, T., Moritani, K., Moriyama, H., & Hayashi, H. (2009). Thermodynamic properties of lanthanides and actinides for reductive extraction of minor actinides. *J. Nucl. Sci. Technol.*, *46*(1), 18–25. DOI: 10.1080/18811248.2007.9711502.
5. Massalski, T. B. (1996). *ASM binary phase diagrams.* [computer software]. Materials Park: ASM.
6. Toda, T., Maruyama, T., Moritani, K., Moriyama, H., & Hayashi, H. (2009). Separation factor of americium from cerium in molten chloride – liquid gallium reductive extraction system. *Electrochemistry*, *77*(8), 649–651.
7. Lambertin, D., Chedhomme, S., Bourges, G., Sanchez, S., & Picard, G. S. (2005). Activity coefficients of plutonium and cerium in liquid gallium at 1073 K: application to a molten salt/solvent metal separation concept. *J. Nucl. Mater.*, *341*, 131–140. DOI: 10.1016/j.jnucmat.2005.01.009.
8. Novoselova, A. V., & Smolenskii, V. V. (2013). Electrochemical study of the properties of Nd(III) and Nd(II) ions in molten LiCl-KCl-CsCl eutectic and individual CsCl. *Rus. J. Electrochem.*, *49*(10), 931–937. DOI: 10.1134/S1023193513100121.
9. Maltsev, D. S., Volkovich, V. A., Vladykin, E. N., & Vasin, B. D. (2014). An electrochemical study of uranium (III) and (IV) species in fused alkali chlorides. *ECS Trans.*, *64*(4), 357–367. DOI: 10.1149/06404.0357ecst.
10. Kober, V. I., Nichkov, I. F., Raspopin, S. P., & Kuzminikh, V. M. (1979). Thermodynamic properties of saturated by neodymium alloys based on low melting metals. In Proceedings of the IV Soviet Conference on Thermodynamics Metal Systems, 28 May – 1 June 1979 (Vol. 2, pp. 72–76). Alma-Ata: Nauka. (in Russian).
11. Vnuchkova, L. A., Bayanov, A. P., & Serebrennikov, V. V. (1972). Thermodynamics of interaction of gallium with neodymium. *Zh. Fiz. Khim.*, *46*(4), 1052.
12. Yatsenko, S. P. (1974). *Gallium. Interaction with metals.* Moscow: Nauka. (in Russian).
13. Melchakov, S. Yu., Yamshchikov, L. F., Osipenko, A. G., & Rusakov, M. A. (2014). Solubility of neodymium in liquid gallium, indium and metallic compositions on their basis. *Rasplavy*, 6, 41–49.
14. Smolenski, V., Novoselova, A., Osipenko, A., Kormilitsyn, M., & Luk'yanova, Ya. (2014). Thermodynamics of separation of uranium from neodymium between the gallium-indium liquid alloy and the LiCl-KCl molten salt phases. *Electrochim. Acta*, *133*, 354–358. DOI: 10.1016/j.electacta.2014.04.042.
15. Melchakov, S. Yu., Yamshchikov, L. F., Osipenko, A. G., Pozdeev, P. A., & Rusakov, M. A. (2014). The solubility and excessive thermodynamic characteristics of Pr and Nd in the eutectic alloy Ga-Sn. *Rasplavy*, 5, 7–12.
16. Volkovich, V. A., Maltsev, D. S., Yamshchikov, L. F., Melchakov, S. Yu., Shchetinskiy, A. V., Osipenko, A. G., & Kormilitsyn, M. V. (2013). Thermodynamic properties of uranium in Ga-In based alloys. *J. Nucl. Mater.*, *438*, 94–98. DOI: 10.1016/j.jnucmat.2013.03.016.
17. Volkovich, V. A., Maltsev, D. S., Yamshchikov, L. F., & Osipenko, A. G. (2015). Thermodynamic properties of uranium in liquid gallium, indium and their alloys. *J. Nucl. Mater.*, *464*, 263–269. DOI: 10.1016/j.jnucmat.2015.04.054.
18. Maltsev, D. S., Volkovich, V. A., Yamshchikov, L. F., & Chukin, A. V. (2015). Thermodynamics of U in Ga-Sn eutectic alloy. In Physics, Technology, Innovation: II International Conference, 20–24 April 2015 (pp. 195–196). Ekaterinburg, Russia: Ural Federal University. (in Russian).
19. Lebedev, V. A., Kober, V. A., & Yamshchikov, L. F. (1989). *Thermochemistry of alloys of rare earth*

*and actinide elements.* Chelyabinsk: Metallurgya. (in Russian).

20. Melchakov, S. Yu., Maltsev, D. S., Volkovich, V. A., Yamshchikov, L. F., & Osipenko, A. G. (2014). Separation of uranium and lanthanides in a fused salt – liquid gallium based alloy system. *ECS Trans.*, *64*(4), 369–375. DOI: 10.1149/06404.0369ecst.

21. Volkovich, V., Griffiths, T. R., Fray, D. J., Fields, M., & Wilson, P. D. (1996). Oxidation of $UO_2$ in molten alkali-carbonate based mixtures: Formation of uranates and diuranates. *J. Chem. Soc. Faraday Trans.*, *92*(24), 5059–5065.