Sorption of NdF_3 and ThF_4 from the LiF-NaF-KF Melt

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Abstract—The sorption of neodymium and thorium fluorides by AG-3 activated carbon from molten alkali metal fluorides LiF-NaF-KF has been studied. The sorption isotherm of neodymium fluoride at 650°C has a pronounced convex and is adequately described by the Langmuir equation. The sorption of thorium fluoride under the same conditions is much weaker than that of neodymium fluoride, which is determined by the size of the neodymium and thorium fluoride complexes. The kinetic dependence of the sorption of neodymium fluoride at a temperature of 650°C is adequately described by a first-order equation for a reversible reaction. The temperature dependence of sorption capacity in the range 550–750°C passes a maximum within 600–650°C.

Keywords: fluorides, melts, alkali metals, neodymium, thorium, sorption, activated carbon

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INTRODUCTION

Expanding the fuel base and reducing the volume of long-lived radionuclides from SNF reprocessing, a subject to geological disposal, are the promising directions for the stable development of nuclear energy. In this regard, non-water technologies based on processes in molten salts (eutectics) have prospects.

The expansion of the fuel base in the future is associated with a new approach to the thorium fuel cycle with the production of uranium-233. In this cycle, formation of long-lived transplutonium elements, the presence of which in waste requires geological disposal, is insignificant, and this is one of the advantages of the method.

New concepts for the production of uranium-233 are associated with the use of a fusion-fission hybrid thermonuclear reactor [1, 2]. The approach is based on fast irradiation of a thorium blanket with high-flux neutrons with an energy of 17 MeV, after which the extraction of protactinium-233 and subsequent accumulation of uranium-233 are required. Owing to the short irradiation time, the fraction of side reactions producing uranium-232 is sharply reduced, which, in principle, allows production of uranium-233 with a minimum content of uranium-232. This approach

requires rapid recovery of protactinium-233. For such a purpose, the best blanket is molten fluorides of some metals, and the LiF-ThF_4 eutectic in particular.

In recent years, interest has increased all over the world in the use of molten salts as applied to the thorium fuel cycle. An example is the extensive collection of works [3] devoted to this topic.

Another area of using molten salts is associated with the development of molten salt reactors for burning long-lived americium, curium, and neptunium. The most elaborated approaches for this purpose are based on the use of LiF-NaF-KF [4, 5] and LiF-BeF_2 [6–8] eutectics with melting temperatures of about 450°C.

The reprocessing of the fuel salt of a molten salt reactor is a complex process consisting of many procedures, including treatment with fluorine with distillation of hexavalent actinides, reductive extraction of TPE into liquid metal, anodic oxidation of metal actinides and cathodic reduction of liquid metal (in particular, thorium or bismuth), anodic oxidation of lanthanides, precipitation of oxides, and other processes, which are described in detail in [7]. Sorption processes in relation to molten metal fluorides have practically not been systematically studied; only few studies on zeolites are available. For the purification of molten salts, following extraction of fissile nuclides, the ion-exchange process

Fig. 1. X-ray phase analysis of synthesized NdF_3 samples. Dash lines refer to reference data.

Fig. 2. X-ray phase analysis of synthesized ThF_4 samples. Dash lines refer to reference data.

through a column filled with NaA zeolite under dynamic conditions has been considered for chloride systems in [8, 9] and for the fluoride eutectic LiF-CaF_2 in [10].

The above studies show the possibility of using scarcely studied sorption methods for purifying salt melts. In practice, a variety of sorbents is applied, including activated carbons, which, among other properties, have selectivity with respect to heavy metal cations in sorption from liquid media [11]. Therefore, it is appropriate to study the possibility of using activated carbons for sorption of fluoride eutectics.

The eutectic LiF-NaF-KF mixture is considered as one of the possible components of the fuel salt for molten salt reactors [4, 5]; it can also be a convenient model for the LiF-ThF_4 eutectic as a molten salt blanket of a fusion-fission thermonuclear reactor [1, 2]. In the latter case, the LiF-NaF-KF eutectic is a convenient object to study the sorption of thorium fluoride and its effect on other elements.

The aim of this work is to study the sorption of NdF_3 and ThF_4 from the molten LiF-NaF-KF eutectic onto activated carbon under static conditions. Such studies are being carried out for the first time and are of both scientific and practical importance in relation to the problems of molten salt purification.

EXPERIMENTAL

The components of the mixture should be of high-purity grade, since trace amounts of impurities can significantly distort results of the experiments on processes in molten metal fluorides. For the eutectic of alkali metal fluorides the absence of water is important, since otherwise, the fluorides of rare-earth elements and actinides, which are readily soluble in the LiF-NaF-

KF eutectic, will form poorly soluble corresponding oxyfluorides and HF . The NdF_3 and ThF_4 used in this study should not contain significant amounts of oxyfluorides and hydration water; therefore, special requirements were imposed on the method of producing fluorides used in the study.

Neodymium fluoride was obtained by mixing aqueous solutions of neodymium nitrate and sodium fluoride (in a molar ratio of 1 : 3) with stirring without heating for 2 h. After a lilac precipitate formed, it was washed, separated and dried on a Schott filter and then transferred into a sealed bottle. Immediately before mixing with a melt of alkali metal fluorides, neodymium fluoride was dried in vacuum at 350°C for 3 h.

To obtain thorium fluoride, $\text{Th}(\text{NO}_3)_4$ was heated at 200°C for 1 h, then at 400°C for another 2 h. The resulting ThO_2 was treated with NH_4HF_2 in an eight-fold excess and heated to 500°C for 2 h [12].

X-ray phase analysis (XRD) was performed on a D2 Phaser diffractometer (Bruker, Germany) in CuK_α radiation. The X-ray tube voltage was 30 kV, the current was 1 mA; the recording was carried out in the angular range $2\theta = 7^\circ\text{--}70^\circ$ in the scanning mode with a step of 0.02° at a rate of 0.5 deg/min. The results were processed with the DIFFRAC.EVA.V5.0 program and PDF-2 ICDD card index (NdF_3 PDF 01-078-1859, ThF_4 00-015-0413).

The results of X-ray phase analysis of the prepared fluorides are demonstrated in Figs. 1, 2 for neodymium fluoride and thorium fluoride, respectively, indicative of correspondence of the obtained fluorides to the data of the card files.

The AG-3 carbon used in this study had the following parameters: the micropore volume $V_{\text{mi}} = 0.35 \text{ cm}^3/\text{g}$,

Fig. 3. Diagram of a setup for studying sorption from molten salts.

the mesopore volume $V_{\text{me}} = 0.15 \text{ cm}^3/\text{g}$, the specific surface area $S = 750 \text{ m}^2/\text{g}$, and the specific surface area of mesopores $S_{\text{me}} = 20 \text{ m}^2/\text{g}$. Before the experiment, the AG-3 carbon was dried at a temperature of 200°C for 2 h.

A schematic of the setup for studying the sorption of neodymium and thorium fluorides by activated carbon AG-3 under static conditions from the LiF–NaF–KF eutectic melt at temperatures of $550\text{--}750^\circ\text{C}$ is shown in Fig. 3.

Lithium, potassium, and sodium fluorides (all of analytical grade) were used in the molar ratio LiF (46.5)–NaF (11.5)–KF (42.0) and before the experiments were dried at 400°C for 3 h in vacuum. As measure of the salt quality, we used melting point. The melting point of the prepared salt measured on a derivatograph was 456°C , which practically corresponds to the literature data [3]. To a dry salt, neodymium fluoride or thorium fluoride was added and it was dried again for 2 h in vacuum.

The experiments were carried out at temperatures of $550\text{--}750^\circ\text{C}$ in argon. Eutectic containing neodymium and thorium fluorides was taken in a 200-fold excess in relation to the studied sorbent samples. Sorption was performed directly in a pyrographite crucible (flask), which was inserted in a steel grade 3sp reactor with high heat conductivity. The dry activated carbon was placed in a special basket made of a perforated metallic copper and dipped into the molten salt. After certain intervals of time, the basket with activated carbon was subjected to a vertical-translational motion to mix the salt with the carbon.

After removing the basket, the content of Nd(III) or Th(IV) in the carbon and in the salt eutectic was determined. The presence of noticeable amounts of eutectic in the carbon pores was not found, since the mass of the initial AG-3 sample before and after analysis practically did not change within the limit of determination accuracy (less than 1%); accordingly, when calculating the amount of the sorbed element, the contribution of the eutectic was not taken into account. The amount of sorption was determined by the ratio of the concentration of an element in the carbon sample to its mass. Due to the significant excess of neodymium or thorium fluorides, their concentration in the eutectic practically did not change.

Samples with carbon and eutectics were treated with sulfuric acid to remove HF and, after evaporation, were diluted with water and analyzed with Arsenazo III in hydrochloric acid on a PE-5300VI spectrophotometer at a wavelength of 650 nm, as described in [13]. The completeness of the extraction of the studied elements was controlled after certain intervals of time by additional treatment of the studied sample. The influence of ash oxides (SiO_2 , Al_2O_3 , CaO , and other oxides) of the initial AG-3 carbon on the measurements (background values) by the method used was not found.

RESULTS

The sorption of activated carbons occurs via both physical interactions in the pores and chemical reactions

Fig. 4. Temperature dependence of the sorption capacity of the AG-3 activated carbon for Nd(III) (A_{Nd} , mg/g) from the molten fluorides LiF-NaF-KF . Neodymium was introduced as NdF_3 . The equilibrium concentration of Nd(III) in the molten fluoride salts 10.5 ± 0.23 mg/g. Sorption time 1.5 h.

(chemisorption) with acidic or basic oxides located on the inner surface. To study the sorption of neodymium and thorium fluorides from the LiF-NaF-KF eutectic melt, we used, as sorbent, the AG-3 activated carbon containing micro- and supermicropores [14], allowing sorption of compounds of various size.

First, the dependence of the sorption value on temperature at a constant Nd(III) concentration was determined to find the optimal sorption mode. Figure 4 shows the temperature dependence of the sorption capacity of the AG-3 carbon in the melt of alkali metal fluorides with respect to Nd(III), which was introduced into the eutectic in the form of NdF_3 . From Fig. 4 it follows that the maximum sorption capacity is in the temperature range 600–650°C.

Then, the kinetics of Nd(III) sorption was studied at its constant concentration in the eutectic, equal to 10.5 ± 0.23 mg/g, by activated carbon at a temperature of 650°C. The results are shown in Fig. 5. From Fig. 5 it follows that more than 90% of the total capacity is reached in 30 min during the sorption of Nd(III) by activated carbon, although it takes about 2 h to reach complete saturation.

Figure 6 shows the sorption isotherms of Nd(III) and Th(IV), introduced in the form of fluorides, at a temperature of 650°C and a sorption time of 120 min. The sorption isotherm of Nd(III) has a pronounced convex character, indicating the extraction efficiency at

Fig 5. Kinetics of sorption of Nd(III), introduced in the form of NdF_3 , by the AG-3 activated carbon from a molten fluorides at a temperature of 650°C. (Points) experiment, (solid line) approximation of by the kinetic Eq. (2). The equilibrium concentration of Nd(III) in molten fluorides is 10.5 ± 0.23 mg/g.

its concentration in the melt less than 5 mg/g. Th(IV) is sorbed by AG-3 carbon significantly less, its sorption capacity is about 0.15–0.20 mg/g at a thorium fluoride concentration in the eutectic of more than 10 mg/g, which is 40–50 times lower than the sorption value of neodymium fluoride.

RESULTS AND DISCUSSION

Activated carbons have a complex surface structure. Owing to double electric layers formed on the surface, activated carbons have, among other properties, ion-exchange properties. Also activated carbons contain a significant amount of oxygen-containing groups: carboxyl, lactone, phenolic, ketone, and other groups [15, 16].

The sorption isotherm for Nd(III) is well approximated by the Langmuir equation (Fig. 6):

$$A_{\text{Nd}} = \frac{A_0 K C}{(1 + K C)}, \quad (1)$$

where C is the current concentration of Nd(III) in the eutectic, A_0 is the limiting content in the sorbent, and K is a constant. Result of the calculation by the equation (1) for $A_0 = 9.5$ mg/g and $K = 0.95$ is presented in Fig. 6 by the line.

Sorption of heavy metal cations onto activated carbon from aqueous solutions has been extensively

Fig. 6. Sorption isotherms of Nd(III) and Th(IV), introduced in the form of NdF_3 and ThF_4 , by AG-3 carbon from a fluoride melt at a temperature of 650°C : Curve: (1) Nd(III), (2) approximation by the kinetic equation (1), and (3) Th(IV).

described in the scientific and technical literature [17, 18]. Also, activated carbons possess a negative surface charge, which allows sorption of many metal cations by the cation exchange with replacement of a positive cation for a proton in particular [15]. A similar behavior is observed in sorption from the LiF-CaF_2 melt onto zeolite, while the efficiency of the process increases with an increase in the cation charge in the order: alkaline, alkaline-earth, and rare-earth elements [10]. In this case, as noted, the mechanism of electrostatic adsorption of complexes existing in condensed phases can be realized as a kind of chemisorption, characterized by not very high values of the adsorption energy. This is also indicated by the nature of the temperature dependence of the sorption capacity of Nd(III) in Fig. 4. In the first section, the Nd(III) sorption increases with increasing temperature to 600°C , and a sorption layer forms on the carbon surface. With temperature increasing further from 650 to 750°C , the adsorption of Nd(III) decreases. A decrease is apparently caused by a weakening of the bond strength of the sorbed component with the surface due to an increase in the kinetic energy of the sorbed component and a significant increase in the solubility of neodymium fluoride in the LiF-NaF-KF eutectic. Thus, the solubility of NdF_3 is 13.3 mol% at 650°C , whereas at 750°C it is already 36.2 mol% [19]. A decrease in the sorption value with an increase in temperature

above 650°C may be due to other processes, such as fluorination of oxyfluorides formed upon interaction with oxygen incorporated into the carbon.

The kinetic dependence of the adsorption of Nd(III) by the AG-3 activated carbon in Fig. 5 can be accounted for as follows. Since the sorption process is equilibrium, the reaction is reversible. For a reversible first-order reaction, the following equation is valid [18]:

$$C = \frac{C_0}{K_+ + K_-} (K_+ + K_- e^{-(K_+ + K_-)t}), \quad (2)$$

where K_+ and K_- are the constants of the direct and reverse reactions, respectively, t is the time, C and C_0 are the current and initial concentrations of the element in the solution, respectively. Since the ratio of the Nd(III)-containing melt and activated carbon is large, and the concentration of Nd(III) in the eutectic during static sorption does not practically change, then Eq. (2) can be used to describe the change in the concentration of neodymium in the sorbent. Then it can be assumed that the number of active centers in the sorbent (apparently, oxygen atoms) decreases with the interaction and the subsequent formation of Nd(III) oxyfluorides or oxides, whereas in this case, the reverse process of neodymium fluoride formation from oxyfluorides (or oxides) takes place due to the presence of a large excess of fluoride ions in the eutectic. When the equilibrium value of Nd(III) in the sorbent is about 9 mg/g and the sorption time is 50 min or longer, the rates of both reactions balance each other. In this case, C_0 will correspond to the limiting content of neodymium in the sorbent or the A_0 value in the Langmuir Eq. (1), and C will correspond to the current concentration of Nd(III) in the sorbent; then the sorption capacity (i.e., concentration in AG-3) of Nd(III) at each moment of time will be $A_{\text{Nd}} = C_0 - C$. The calculation by Eq. (2) taking into account the refined values ($C_0 = 9.5$ mg/g, $K_+ = 0.06$, and $K_- = 0.0050$) are shown in Fig. 5 by the line.

The approximation of the experimental results of Nd(III) sorption according to the Langmuir Eq. (1) cannot indicate the mechanism of the process; however, in the study of sorption, this equation turns out to be useful as a primary estimate. The complexity of the processes occurring directly in molten metal fluorides and the potential effect of active carbons with different functional groups made it difficult to determine the

mechanism or mechanisms of the occurring sorption processes in this pioneering study. Studies to determine the mechanism of sorption from molten salts are an interesting task for the future. However, based on the results obtained, it is already possible to make some assumptions about the possible processes occurring in sorption of Nd(III) and Th(IV) in the eutectic under study.

Activated carbon (AC) contains a significant amount of oxygen-containing groups [15, 16], which, in principle, can participate in the formation of compounds of the AC-O-NdF_2 type or form NdOF oxyfluorides unbound with carbon. Similar reactions producing various poorly soluble oxyfluorides or oxides with NdF_3 can take place in the LiF-NaF-KF eutectic melt, in which Nd(III) may be separated from the melt by adding sodium oxide [20] or lithium oxide [21, 22]. The nature of the compounds formed in this process (oxides or oxyfluorides) remains controversial, since the formation of oxides under such conditions is questioned by some authors [22].

It is most likely that sorption occurs due to the interaction of Nd(III) with active groups containing oxygen on the surface of activated carbons [17], which leads to the formation of neodymium oxyfluoride (NdOF) poorly soluble in the eutectic and its further absorption by the AG-3 supermicropores as the largest micropores. Depending on the conditions, neodymium oxyfluoride forms the following crystal structures: cubic ($a = 5.64 \text{ \AA}$), tetragonal ($a = 5.67 \text{ \AA}$, $c = 5.68 \text{ \AA}$), or rhombohedral ($a = 6.96 \text{ \AA}$, $\alpha = 33.04^\circ$) [23]. The maximum diagonal dimensions (critical molecular diameter) for cubic and tetragonal lattices are about $10 \text{ \AA}$, which is comparable to the micropore size. According to the M.M. Dubinin classification, accepted in our country, the maximum size of micropores (supermicropores) is $15\text{--}16 \text{ \AA}$, and according to the IUPAC classification, it is $<20 \text{ \AA}$.

The reversibility of the reaction producing neodymium oxyfluorides or oxides can be associated with the formation of neodymium fluoride from oxyfluoride at a large excess of fluoride ion in the eutectic melt.

The weak absorption of Th(IV) by AG-3 carbon may be due to the size of its complexes. Neodymium fluoride in the LiF-NaF-KF melt forms anionic complexes NdF_6^{3-} [24]. The presence of analogous complexes of La and Ce (LaF_6^{3-} and CeF_6^{3-}) in molten alkali metal fluorides is confirmed by a change in chemical shifts

[25] and a decrease in self-diffusion of the fluoride ion in the presence of lanthanides [26]. Thorium fluoride having the larger ionic radius of Th^{4+} compared to Nd^{3+} ($1.05 \text{ \AA}$ vs. $0.97 \text{ \AA}$) [27, 28], forms in molten alkali metal fluorides more complex fluoride complexes, dominated by $[\text{ThF}_8]^{4-}$, than the neodymium fluoride complexes $[\text{NdF}_6]^{3-}$ [24]. In this case, the distance between the Th and F atoms is $2.2 \text{ \AA}$ [29]. Such an anionic complex, which has a large negative charge, must be surrounded by a cloud of positively charged cations of alkali metals in the eutectic. Apparently, due to their large size, the Th(IV) complexes cannot penetrate into micropores, in which, the main sorption process commonly occurs.

Owing to the large size, thorium fluoride complexes cannot penetrate into micropores and are sorbed in mesopores due to interaction with their active groups. The number of active groups in mesopores is significantly less than in micropores due to the smaller mesopore surface containing the active groups (for AG-3 it is smaller by about 40 times). This can explain the significant difference in the values of the sorption capacity for neodymium and thorium fluorides (Fig. 6).

CONCLUSIONS

A setup for sorption of elements from molten salts under static conditions at different temperatures has been developed and manufactured. The sorption of Nd(III) and Th(IV) , introduced in the form of NdF_3 and ThF_4 , by AG-3 activated carbon from molten alkali metal fluorides LiF-NaF-KF has been studied. The kinetic dependence of the sorption capacity of Nd(III) at a temperature of 650°C is well described by a first-order equation for a reversible reaction; equilibrium is reached in about 1.5 h. The highest sorption capacity for Nd(III) is approximately 8.5 m/g of the sorbent in the temperature range $600\text{--}650^\circ\text{C}$. The sorption isotherm of Nd(III) is convex and well described by the Langmuir equation. The extraction of thorium fluoride under the same conditions is much lower, about 0.2 mg/g . It was assumed that the sorption of Nd(III) occurs on the active surface of micropores of the AG-3 activated carbon. The lower sorption of Th(IV) is apparently associated with the large size of the anionic complexes of thorium in comparison with the complexes of neodymium, which does not allow them to penetrate into micropores, and the sorption of thorium occurs on the surface of mesopores.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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