REVIEW PAPER

Recovery of actinides and fission products from spent nuclear fuel via electrolytic reduction: Thematic overview

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Summary

Spent nuclear fuel (SNF) from modern light water or thermal reactors containing uranium oxide with small concentrations of plutonium and other actinide oxides is converted into metal by the electrolytic reduction. The obtained metal must be subjected to further processing (electrorefining). This review reflects the achievements in development SNF electrolytic processing, concepts of the technological operations, and a model describing the electrochemical process. The technological scheme for the electrochemical reduction of SNF and MOX fuel is considered. The complexity of a carbon anode application in the process of UO_2 electrolytic reduction is reflected. The reduction processes of alkali, alkaline earth (AE), and rare earth metal oxides as well as oxide compounds of zirconium are demonstrated. The reduction of lanthanum oxide and oxy-chloride to the metallic form by adding metallic nickel to the molten salt is discussed. The solubility of Li_2O in molten salts is interpreted depending on the amount of dissolved alkali and AE metal chlorides. The considered pyroprocessing technology enables a much greater release of the energy accumulated in uranium ore, and recycling all actinides allows reducing significantly the amount of nuclear waste and the time it must be isolated.

KEYWORDS

actinide, fission products, plutonium, salt melt, spent nuclear fuel, uranium

1 | INTRODUCTION

Nuclear energy is a source of long-term energy supply for the needs of a developed society. Stricter ecological requirements toward the nuclear power plant (NPP) operation minimize NPP impact on the environment and ensure reliability, safety, and economic efficiency. However, the production of radioactive waste occurs at all stages of the fuel and energy cycles. When handling radioactive waste, the safety for humans and nature, taking into account the interests of distant descendants, is defined as the main indicator. A prerequisite for large-scale sustainable production of nuclear energy is not only an uninterrupted supply of nuclear fuel over a long period of time, but also the reprocessing and safe disposal of highly radioactive waste. Thus, there is an urgent need to recycle spent nuclear fuel (SNF). The extraction of fissile materials from SNF and refabrication of nuclear fuel for reactors create a kind of closed cycle.

The creation of closed fuel cycles will allow more efficient use of uranium and will simplify the waste disposal. The essence of a closed fuel cycle is to extract uranium and various plutonium isotopes from SNF so that they can be reused as a fresh fuel. Plutonium-uranium recovered from SNF can be mixed and repeatedly used in the form of so-called MOX fuel. MOX fuel is used primarily in fast reactors (FRs). A common usage of FRs will reduce the consumption of uranium fuel by 50 to

100 times compared to the current fuel consumption.[1] Reprocessing and recycling of SNF reduces significantly (approximately four times) the volume of stored waste and reduces its storage time by 100 times or more.[2]

The methods for reprocessing SNF are conventionally divided into two groups: water processes and pyroprocesses. Water-based processes include PUREX, which is currently the only commercially available SNF reprocessing technology. PUREX is a process for reprocessing spent uranium fuel using tributyl phosphate (TBP), as an extractant. This process consists of the following stages: dissolution of fuel assemblies in nitric acid, preparation of extraction solutions (ie, organic flocculants, filtration is also carried out at this stage), extraction isolation, and separation of U, Pu, Np with a 30% solution of TBP in synthetic saturated hydrocarbons with subsequent reductive stripping of Pu into the aqueous phase.

Pyroprocessing refers to the anhydrous method of SNF reprocessing. This electrolytic method was developed at the Argonne National Laboratory.[3] Pyroprocessing or the pyrochemical separation process is based on high-temperature oxidation and reduction reactions involving molten inorganic salts, gases, and liquid metals at the stages of electrolysis or electrolytic refining. Industrial pyroprocessing is an integrated system that includes: (a) fuel-element chopping and decladding, (b) high temperature voloxidation, (c) electrolytic reduction, (d) electrorefining, (e) electrowinning, (f) salt purification, and (g) fuel fabrication.

In this article, we consider works related to the electrolytic reduction (c) as a part of industrial pyroprocessing, which is considered as the most promising developing option for SNF reprocessing. It should be noted that SNF pyroprocessing does not provide a complete fuel recycling, so that along with the processed products, waste, which requires disposal, is generated. Uranium metal (U) and transuranium metal (TRU) ingots are the processed products. Used filters, metal, and ceramic scrap form waste. The starting SNF oxide material is taken in the form of porous granules, which are further pressed into pellets. This is necessary not only to facilitate the lithium penetration through the surface inside the pellet, but also mainly to transport released oxygen into the salt melt. In addition, the basket material must have high corrosion resistance and high permeability; that is the melt content may easily penetrate into the material for its further reduction and oxygen released from the pellets may evolve without any obstacles. If these conditions are violated, the recovery process may not be completed.

Fuels, mainly composed of uranium oxides (such as UO_2 or U_3O_8), are pyrochemically processed to form uranium metal. Initially, the oxide fuel is loaded into a permeable cathode basket, which is immersed into a bath filled with the molten LiCl-(1 wt%)Li_2O salt at the temperature of 650°C. By passing a controlled electric current, oxygen ions leave the cathode basket, they dissolve in the molten salt and oxidize at the anode, and then they are evolved in the gas form from the pyroelectrochemical cell.[4,5]

LiCl or $CaCl_2$ electrolytes are the usually used for UO_2 and UO_2-PuO_2 recovery. When electrolysis is carried out in the $CaCl_2$ bath at 850°C, a dense layer of reduced metallic uranium particles is formed at the cathode in the near-surface region of SNF. This layer prevents oxygen evolution and disrupts the subsequent recovery of SNF. When SNF is reduced in the LiCl bath at 650°C, such strong adhesion of the reduced particles is not observed, which is most likely due to the lower process temperature. Therefore, here the obstacle to the oxygen ion diffusion is not as significant as in the $CaCl_2$ salt bath. For the successful implementation of the electrolytic reduction of SNF, in addition to the U and Pu movement pattern, it is necessary to know the behavior of minor actinides and main fission products (FPs).

The reduced metallic granules, as a rule, contain a significant variety of transition elements, all kinds of actinides, as well as rare earth elements. After distilling off the residual salt, the reduced metal is subjected to electrorefining. In this review, we will not consider works related to the electrorefining of uranium-containing products, since a recently published work[6] is devoted to this topic. FPs such as cesium (Cs), strontium (Sr), and barium (Ba) are detected in the LiCl salt after the pyroprocessing. The salt may be recycled and these elements may be removed.[7] However, FPs such as zirconium (Zr) can also be present in the recovered granule (ingot). As a result of the fission of U and Pu, several isotopes of zirconium are formed.[8] By its electrochemical properties, in particular, by the value of the standard apparent electrode potential, zirconium is the closest to uranium among all elements of FPs.[9] It was shown that a Ga-Zn cathode gives a high efficiency of separation of uranium from zirconium at using chloride melts.[9] Attempts are currently being made to separate alkali metals (AMs) and alkaline earth (AE) metals by the electrolytic reduction.

Ultimately, the reduction of UO_2 compounds involves the removal of oxygen from this compound. A detailed structural analysis and theoretical study of the stability of the hypostoichiometric phases of UO_2, which constitutes the overwhelming part of the processed SNF, were performed in Reference 10. The strategy of recent years is aimed at recycling long-lived actinides together with plutonium in FRs. After this processing, only short-lived FPs should remain. This may solve the problem of SNF

storage. Also it is planned to burn the obtained metal actinides in a liquid salt reactor. However, in order to do this, it is necessary to solve the problem of a low effective neutron multiplication factor in liquid nuclear fuel.[11]

In the last 10 years, several reviews[12-16] appeared on the topic of electrolytic reduction of SNF. Each of them specializes in the problems related to this process. For example, the review[16] focuses on the effect of metallic lithium on the SNF reduction process. The process of electrochemical recovery of SNF is an important stage in pyroprocessing. In this review, we consider the studies focused on the creation of an advanced technology for reprocessing of SNF using molten salts in a broader aspect, namely, promoting the developing approaches and technologies for industrial implementation.

This overview has the following structure. First, we touch on issues related to the fundamentals of the electrolytic reduction process, including electrode reactions (cathodic and anodic). Then the factors influencing the degree of reduction of actinide oxides are discussed, the problem of optimization of the reduction process is investigated, and the ways to increase the rate of this process are considered. In addition, considerable attention is paid to the recovery of decomposition products, in particular, the extraction of alkali, AE, and rare and noble metals. Finally, we consider the effect of the FPs dissolved in the electrolyte on the reduction rate of actinide oxides.

2 | PROCESS OF ELECTROLYTIC RECOVERY OF SNF

2.1 | Electrochemical processing of SNFs

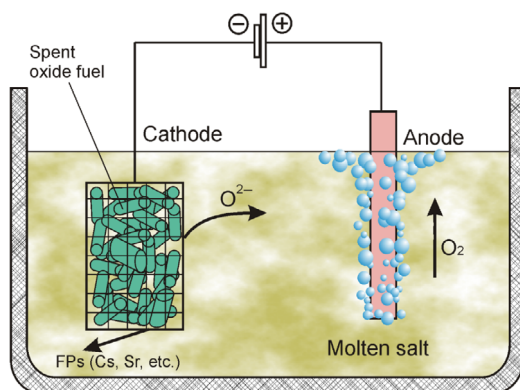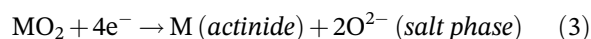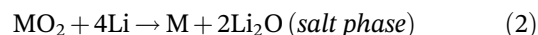A schematic diagram of the electrolytic reduction of spent oxide fuel is shown in Figure 1. The figure shows

FIGURE 1 Schematic diagram of the electrochemical reduction process

how metal oxides in SNF are converted to metal. The crushed spent oxide fuel is contained in a permeable stainless steel basket (cathode) that is surrounded by molten salt electrolyte. An electric current is passed through the fuel basket, producing the reduction of metal oxides. Oxygen gas forms on the surface of the often used platinum anode. The search for a cheaper alternative to the anode material is still ongoing.

The UO_2 reduction occurs at lower absolute values of the cathodic potential, that is, when Li_2O has not been reduced yet. Herrmann et al[17] believe that direct reduction of UO_2 (without the participation of lithium) can occur subject to quasi-stationary mode. An increase in the cathodic potential value above the allowable one leads to the formation of metallic lithium, which partially dissolves in the salt, and also interacts chemically with UO_2 forming metallic uranium.

Dividing the electrolytic cell into three zones, we can attribute the reactions occurring in them to each of the zones. Generalized cathodic reactions are represented as:

$$Li^+ + e^- \rightarrow Li \tag{1}$$

$$MO_2 + 4Li \rightarrow M + 2Li_2O \, (salt \, phase) \tag{2}$$

$$MO_2 + 4e^- \rightarrow M \, (actinide) + 2O^{2-} \, (salt \, phase) \tag{3}$$

In the zone where the molten LiCl salt is located, the reaction has the following form:

$$Li_2O \rightarrow Li^+ + O^{2-} \, (salt \, phase) \tag{4}$$

Finally, oxygen is reduced at the anode according to the reaction

$$O^{2-} \, (salt \, phase) \rightarrow O_2 \, (gas) + 4e^- \tag{5}$$
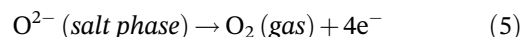
Consequently, according to the chain of Equations (1) to (5), by applying an electric potential, the actinide metal oxide should be reduced to the metal remaining on the cathode. Oxygen ions formed at the cathode are transported through the molten salt to the anode, where they are discharged to form oxygen gas.

Monitoring the recovery process requires continuous measurement of electrode potentials. This electrochemical operation is carried out using a working electrode and a reference electrode (Figure 2). This reference electrode (Ag/Ag^+) is often used in laboratory experiments to recover UO_2.[18] A more stable reference potential can be expected when using a Ni/NiO reference electrode for electrochemical studies in the $LiCl-Li_2O$ system.
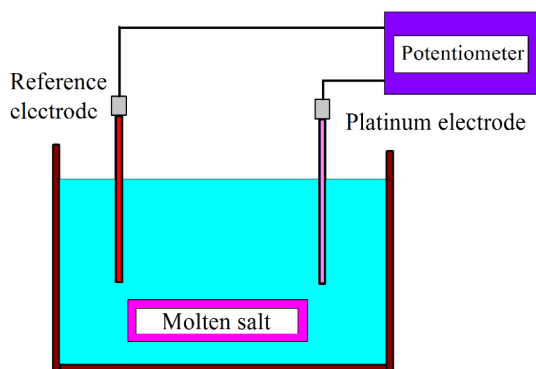
FIGURE 2 Elementary diagram of measuring the electrode potential in the electrolytic process of SNF reduction. SNF, spent nuclear fuel

The electrochemical method for SNF recovery has a number of advantages over other methods used for this purpose. In particular, metallic lithium is easily handled. It is also important that the oxide ion, formed at the cathode during the reduction process, is consumed at the anode. As a result, the concentration of oxide ions in the electrolytic bath is maintained at the desired low level, which contributes to the complete recovery of SNF. In addition, there is no theoretical limitation on the amount of electrolyte used in the electrolytic process. The latter circumstance can significantly reduce the required volume of equipment. In addition, pyroprocessing can be applied to SNF with high burnup, and the cooling time is not very long. The inorganic chemicals used have very high performance characteristics, which makes it possible to process SNF having intense radiation levels. Already at the stage of the voloxidation head process, more than 90% of long-lived radioisotopes (such as iodine, technetium, and tritium) can be removed from oxide SNF. The chloride salts used have a high neutron absorption cross section. Due to this, a large amount of SNF can be loaded for pyroprocessing. As a result, the installation for pyroprocessing is highly productive, and the equipment used is quite compact.

The loaded oxide fuel can have various physical forms, for example, rods, crushed particles, powder, and porous granules.[19-23] In addition, various states of oxidized uranium are used, that is, both UO_2 and U_3O_8.[24,25] On the basis of X-ray structural analysis, it was shown that intermediate compounds such as $LiUO_3$, U_4O_9, and UO_2 can be formed in the initial stage of processing.[6] It was concluded that the reduction is initiated by a direct ionization mechanism that reduces the oxidation state of uranium and lithium uranate perovskite.[13,24] Subsequently, the reduction of UO_2 proceeds in two different ways: direct reduction described by Equations (1) and (3) and electrolithiothermal reduction using metallic lithium, that is,

$$UO_2 + 2yLi \rightarrow xU + yLi_2O \left(or\ 2yLi + yO^{2-} \right) \quad (6)$$
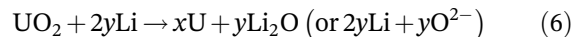
These cathodic mechanisms are based on the assumption that the decomposition of actinide oxides and Li_2O occurs at close voltage values.[14,26] Thermodynamic calculations show that most likely alkali and AE metals, such as Cs, Ba, and Sr, diffuse from the fuel and accumulate in the salt phase.[27] The oxides of noble metals and actinides can be relatively easily reduced. However, rare earth elements and zirconium are practically not reduced to their metallic states.

2.2 | Carbon anodes in the oxide reduction process

Often, a platinum electrode serves as an anode under laboratory conditions for the recovery of spent nuclear fuel. However, the platinum electrode cannot be used in an industrial electrolyzer. This is due not only to the high cost of this material, but also to its corrosion in this aggressive environment (oxidation of platinum and the formation of lithium platinate, Li_2PtO_3, at the electrode surface is observed).

Carbon could serve as an alternative anode material. However, as was shown already in the first experiments,[28] the carbon anode is a consumable electrode. The oxygen released during the reduction of UO_2 diffuses through the molten salt to the carbon anode. The reaction between oxygen and carbon results in the formation of CO_2 gas (carbon dioxide), which is released at the anode. As a result of the interaction between Li_2O and CO_2, lithium carbonate (Li_2CO_3) is formed at the anode boundary, the decomposition reaction of which is difficult. The presence of Li_2CO_3 complicates the process of UO_2 reduction.[29] As a result, this process is not completed even with 95% recovery. To some extent, the problem of UO_2 reduction using a carbon anode can be solved by applying a high anode potential. In this case, gaseous chlorine is formed at the anode, which oxidizes Li_2CO_3. This makes it possible to slightly increase the efficiency of UO_2 recovery. Further studies have shown that lowering the UO_2 content in the final product can be achieved not only by a large applied anode potential, but also by the increasing current density at the cathode.[30] The use of high currents and a large anode surface area is necessary to optimize technological operations with a carbon anode.

2.3 | Pyroprocessing as the most promising option for SNF reprocessing

There are three main technologies for SNF reprocessing: gas-fluoride, hydrometallurgical, and pyrochemical. The last two are applicable for reprocessing SNF from thermal and FRs. Gas-fluoride technology is primarily intended for the reprocessing of thermal reactor fuel, in which uranium is the main component. The end product here is uranium hexafluoride, which can be immediately sent to the separation cascade. This shortens the route to obtain enriched uranium.

The other two technologies (hydrometallurgical and pyroelectrochemical) have their own advantages and disadvantages. Hydrometallurgy is based on continuous processes with continuous mass transfer. The use of an aqueous solution introduces significant temperature limitations. This method does not allow operation with low aging fuels, because this hot fuel poses risks. Hydrometallurgical technology implies using the counterflow principle, the essence of which is that two phases go toward each other. As a result, a deep recovery and high purity of the processed product can be achieved in addition to the separation performed. This is not possible in the pyroelectrochemical process, which is carried out periodically. Despite the fact that, in the hydrometallurgical process, it is impossible to work with hot fuel, it is possible to obtain pure products. The main difficulty in the implementation of the hydrometallurgical method is tritium contamination of water from the fuel. As a result of isotope exchange, the entire volume of water becomes tritium-containing radioactive waste. Tritium is a hazardous element, despite high concentration thresholds. Separation of protium, deuterium, and tritium is extremely costly.

Pyrochemistry is a high temperature process. Therefore, the use of this technology makes it easy to get rid of the harmful effects of tritium. Pyrochemistry is not very sensitive to SNF aging. A 1-year aging is sufficient, or even 6 months in the future. At the same time, it takes 2 to 3 years to process fuel using the hydrometallurgical method. This difference in the required fuel aging gives pyrochemistry a significant advantage over hydrometallurgy. However, at present it is impossible to obtain pure products using pyrochemistry, whereas hydrometallurgical technology allows obtaining pure processed products. The reprocessed fuel is intended for use in FRs and has a high plutonium content. In this respect, pyrochemistry also has a pre-empted position that is nuclear safety. There is no water in pyrochemical technology, that is, there is no neutron moderator. This circumstance makes it possible to work in a single electrolyzer with much larger volume of nuclear material than is allowed when using the hydrometallurgical process.

Therefore, at present, creating a closed nuclear fuel cycle, it is advisable to use a combined technology. In other words, head operations must be implemented pyrochemically, that is, a rough primary cleaning and separation of valuable components. Then these components—uranium, plutonium, and neptunium (ideally also americium and curium)—are further purified and separated by hydrometallurgical methods. In the development of new technologies for SNF reprocessing, safety and minimization of environmental impact are the priority.

3 | FACTORS AFFECTING THE DEGREE OF REDUCTION OF ACTINOID OXIDES

3.1 | Experimental study of the UO_2 reduction mechanism

The reduction of UO_2 in the LiCl molten salt, including the addition of alkali and AE metals chlorides, was studied in Reference 31. It was previously found that some salt-soluble FPs accumulate in the LiCl salt bath during the reduction of UO_2.[32] Among the inclusions in the LiCl molten salt LiCl, KCl, CsCl, $SrCl_2$, and $BaCl_2$ were considered. Although the addition of additives such as KCl reduced the electrolysis operating temperature, the UO_2 reduction was performed at a constant salt bath temperature of 650°C to investigate the effects of the additives.

To reduce corrosion, it is advisable to conduct electrolysis at lower temperatures. This can be achieved by using a multicomponent salt system as an electrolyte instead of a one-component one. Table 1 shows the melting points of some one-component electrolytes and the LiCl-KCl salt mixture.

The eutectics formed in some molten salt mixtures can have a melting point much lower than the constituent components of the mixture. As can be seen from the phase diagram shown in Figure 3, the LiCl-KCl melt is characterized by eutectic at 59-41 M composition. The

TABLE 1 Melting temperatures of salt mixture and pure salt constituents

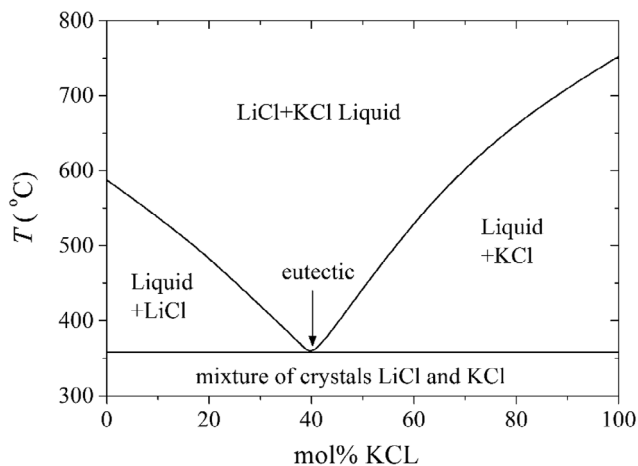| Constituents	Amounts (mol%)	Melting point
LiCl-KCl	59–41 (eutectic)	352°C
LiCl		610°C
KCl		770°C
$CaCl_2$		772°C

FIGURE 3 State diagram of the LiCl + KCl system with eutectic point

decrease in the melting point of this eutectic relative to the melting point of LiCl (which is lower than T_m of KCl) is 258°. Usually, a eutectic mixture is formed when a multicomponent system in a solid state forms a superlattice, which simultaneously releases all its components into a liquid mixture during a low-temperature transition to a liquid state.[33]

The solubility of oxygen in the LiCl melt is about 11.6 mol%, but it decreases significantly with the addition of KCl or CsCl. It is shown that when AE metal chlorides are introduced into the melt, the behavior of the O_2 solubility turns out to be ambiguous: $BaCl_2$ somewhat reduces the solubility, while $SrCl_2$ increases it. The higher O_2 solubility in the molten salt results in the higher rate of UO_2 reduction during the electrolysis. The reduction of UO_2 to metal starts from the pellets surface. However, the formed metal crust on the UO_2 surface is not continuous, there are gaps through which the molten salt penetrates into the UO_2 bulk, and oxygen evolves into the melt. Note that the oxygen diffusion coefficient in molten salt is higher than in solid UO_2 or metallic U. The concentration of O_2 is determined by its solubility at the metallic U/UO_2 interface and sets the driving force for oxygen diffusion. The solubility of oxygen, and, hence, its diffusion decrease due to the shrinkage of the outer metal layer at the surface of the UO_2 pellet. As a result of shrinkage, the outer U layer turns out to be dense, while the inner uranium metal turns out to be porous. As the O_2 concentration increases, the melt viscosity increases, which decreases the oxygen diffusion coefficient. However, at the initial stage of electrolysis, this does not happen, because the reaction surface is still large.

Thus, among the alkali and AE metals, Cs poses the greatest problems for a reduction of actinide oxides. Therefore, before starting the electrolytic reduction

process, it is desirable to minimize the Cs content in the SNF. This can be achieved, for example, by Cs evaporation at high temperatures.[34,35]

3.2 | Electrochemical reduction of (U-Pu-Np[Am])O$_2$ in the molten LiCl electrolyte

Electrochemical reduction of (U-40Pu-5Np)O$_2$ was performed in molten LiCl at 923 K.[36] The reduction of Np and Am transuranic element oxides, which are formed during b-decay from [241]Pu, is investigated. The cyclic voltammograms are measured in lithium chloride melts using the platinum anode. In this work, two series of electrochemical reduction tests were performed to compare the behavior of transuranic elements in the system. These tests differed in the amount of MOX fuel loaded into the cathode basket. In the second test, the amount of MOX was 2.72 times higher than the corresponding value used in the first test. The current in the bath was gradually reduced to avoid lithium reduction. The initial current value (50 mA) in the first test was 1.5 times lower than in the second test. The ratio of the electric charge passed through the melt to the theoretical value of the charge required to restore completely the loaded MOX was 1.91 times higher in the first test than in the second. The LiO$_2$ concentration in both cases was the same (0.51 wt%). As the electrochemical reduction proceeded, the cathodic potential decreased gradually. At a potential value of about 0.75 V, lithium begins to recover to its metallic form. From this point on, the current was lowered in a stepwise mode to avoid deposition of a significant amount of lithium.

To compare quantitatively the degree of recovery of elements in the final product, the "enrichment" E_M factor was introduced:

$$E_M = [C_M/C_U]/[C_M^0/C_U^0], \qquad (7)$$

where C_M and C_U are the concentrations of reduced actinide metal (M) and uranium (U) obtained for the cathode product, respectively, C_M^0 and C_U^0 are corresponding concentrations of these elements in the initial MOX.

If the actinide under consideration is concentrated in the reduction product, then the corresponding enrichment factor turns out to be greater than unity. The EM ratios of the elements studied here varied within 5% of unity (Figure 4). Moreover, there is no correlation in the ratios between the actinide values obtained for two carried tests. Most likely, the tendency in the ratios between
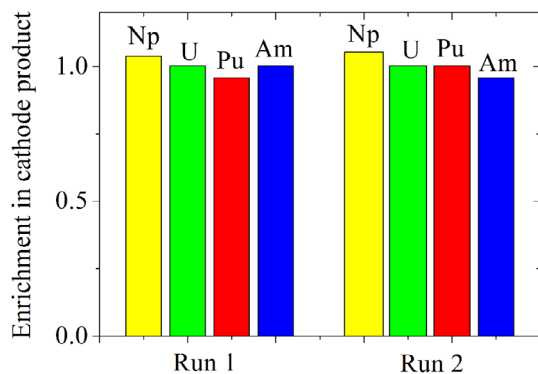
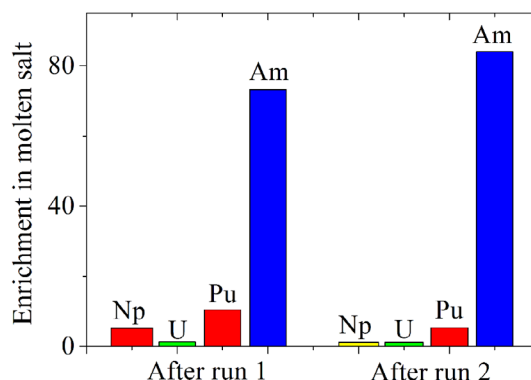**FIGURE 4** "Enrichment factor" of actinides in the reduction products[36]

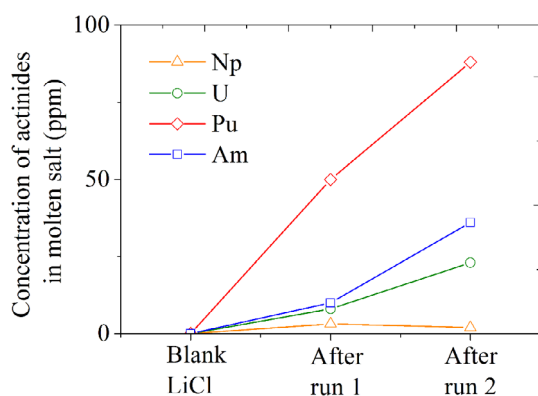**FIGURE 6** "Enrichment factor" of actinides in the molten salt.[36]

FIGURE 5 Change in the actinide concentrations in the molten salt[36]

them is at the level of error, usually found by the chemical analysis.

The changes in actinide concentrations that occurred in the molten salt at the end of two tests are shown in Figure 5. As can be seen, Pu demonstrates significant solubility in molten LiCl, while the Np solubility is negligible and after the second test it is even lower than after the first test. The solubility of Am and U also increases and occupies an intermediate value. The difference in the behavior of the considered elements is more clearly traced with the introduction of the "enrichment" factor E_{Mm} of each actinide against uranium. The E_{Mm} value is similar to the actinide enrichment factor in the cathode product and is defined as

$$E_{Mm} = [C_{Mm}/C_{Um}]/[C_M^0/C_U^0], \quad (8)$$

where C_{Mm} and C_{Um} are the concentrations of reduced actinide M and uranium in molten LiCl, respectively.

The "enrichment" factors of the elements in molten LiCl are shown in Figure 6. The concentrations of Am

and Pu are greater than those of U and NP. There is an indication that lanthanide oxides could not be reduced. They dissolve easily into the LiCl melt. The oxychlorides of these elements must form at the higher Li_2O concentration.[36] Given that the chemical characteristics of lanthanides are largely similar to those of actinides, it can be assumed that plutonium and americium dissolve into the LiCl melt in the same manner.

The technological scheme for the electrochemical reduction of SNF and MOX fuel assumes knowledge of the behavioral characteristics both of the main (U, Pu) components and of the minor elements. An indication of the recovery process completion has been determined, which is detected by a rapid decrease in the cathode potential and in the content of lithium ions in the electrolyte. When MOX fuel is recovered, its composition maintains uniform, that is, a selective recovery of actinides is not observed.

3.3 | Characteristics of the uranium oxide reduction

The activity of Li_2O in the process of uranium oxides reduction is $a_{Li_2O} = 1$ (in the reduction of U_3O_8). Therefore, the concentration of Li_2O, as a rule, is not a limiting factor in the reduction of uranium oxides to metallic uranium. The activity of Li_2O in the reduction of Pu and Am is much lower. It is predicted that for the reduction of americium and plutonium dioxides, the Li_2O concentration in the LiCl salt melt should be at least 5.1 wt%, and the solubility at 650°C should be 8.8 wt%.[37,38] The reduction of rare earth oxides, for example, Nd_2O_3, and Ce_2O_3, in this melt was not observed. The data of a linear sweep voltammetry and a cyclic voltammetry obtained for the LiCl-Li_2O and LiCl-Li_2O-U_3O_8 systems were presented in Reference 39.
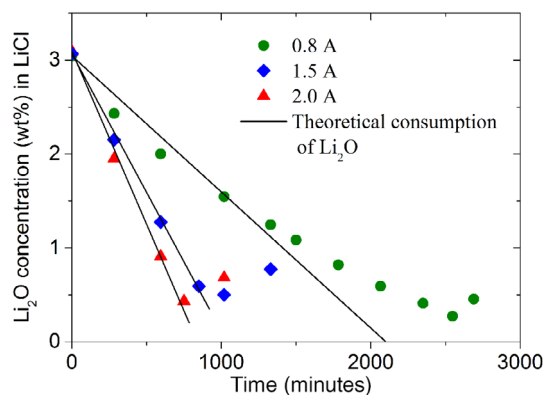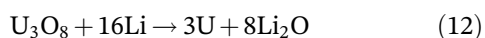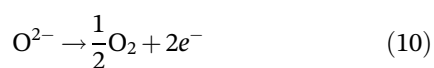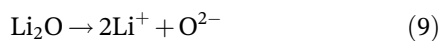
FIGURE 7 Changes in the Li_2O concentration in the molten LiCl salt with time according to the applied current[39]
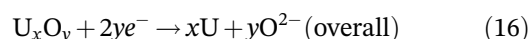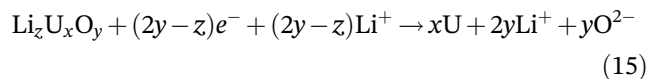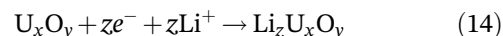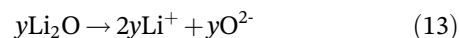
Figure 7 compares the experimental and theoretical Li_2O consumption at applied currents of 0.8, 1.5, and 2.0 A. The theoretical Li_2O consumption is proportional to the applied current according to Faraday's law. At the beginning of the reaction, the experimental consumption of Li_2O prevails over the theoretical consumption. This is due to the formation of a complex corrosion product, for example, Li (Fe, Ni, Cr) O_2, which consumes additional Li_2O. However, at the final stage of the recovery process, the experimental consumption turns out to be less than the theoretical consumption. This is due to the presence of a closed recirculation of Li_2O in such system as $LiCl-Li_2O-U_3O_8$. At the beginning of the reduction cycle, lithium metal is deposited on the cathode surface. The reaction between lithium metal and U_3O_8 results in the chemical reduction of the latter to uranium oxide. At the same time, metallic lithium is oxidized to Li_2O, the concentration of which at the cathode increases. Due to the concentration gradient, Li_2O diffuses into the melt.

When the applied voltage is sufficient to decompose lithium oxide, chemical reduction of U_3O_8 is possible. In this case, the mechanism of electrolytic reduction can be represented as[40]

$$Li_2O \rightarrow 2Li^+ + O^{2-} \qquad (9)$$

$$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- \qquad (10)$$

$$2Li^+ + 2e^- \rightarrow 2Li \qquad (11)$$

$$U_3O_8 + 16Li \rightarrow 3U + 8Li_2O \qquad (12)$$

However, the reduction of uranium oxide can be caused by the formation and electrolysis of lithium uranate.

In this case, the reduction mechanism without the formation of metallic lithium can be represented as[41]

$$yLi_2O \rightarrow 2yLi^+ + yO^{2-} \qquad (13)$$

$$U_xO_y + ze^- + zLi^+ \rightarrow Li_zU_xO_y \qquad (14)$$

$$Li_zU_xO_y + (2y-z)e^- + (2y-z)Li^+ \rightarrow xU + 2yLi^+ + yO^{2-} \qquad (15)$$

$$U_xO_y + 2ye^- \rightarrow xU + yO^{2-} \text{(overall)} \qquad (16)$$

Thus, the deposition potentials determine the reduction of uranium oxide in the molten $LiCl-(3\text{ wt\%})Li_2O$ salt. Lithium metal is formed by the Li_2O reduction when the cathode cell voltage exceeds the decomposition potential of Li_2O. In this case, uranium oxide is chemically reduced to metallic uranium. At the higher anode cell voltage than the decomposition potential of Li_2O, lithium uranate is formed in the reaction between the lithium ion and uranium oxide, which is then reduced to metallic uranium.

4 | RECOVERY OF FPs AND THEIR INFLUENCE ON THE RESTORATION PROCESS RATE

4.1 | Reduction of alkali, AE, and rare earth metals oxides in molten salts

To investigate the reductive behavior of the elements under mixed oxide conditions, electrolytic reduction was performed using simulated oxide spent fuel.[42] Analysis of the resulting molten salt after the reduction of artificially contaminated UO_2 demonstrated that not all metals contained in the accompanying mixture of Te, Eu, Ba, and Sr metal oxides were detected. Ba and Sr were found in the molten salt, but Te and Eu were not detected, although they should have been dissolved during electrolytic reduction. Only a small fraction of Te was found in the sediment. However, Te and Eu were found on the platinum anode.[43] It is assumed that there are two mechanisms for the Te and Eu behavior during electrolysis in the molten salt. On the one hand, they react with platinum and remain on the anode, and on the other hand, they are oxidized by oxygen formed on the anode surface. Both Te and Eu oxides precipitate, but Eu_2O_3 oxide in molten LiCl can spontaneously reduce at 650°C. In the molten LiCl salt, tellurium dioxide TeO_2 appears to be a more stable compound. The metal fractions of Pd, Rh, Ru, and Mo detected at the cathode are supposed to be

present in the granules before the electrolysis and appear during the granules sintering.

In the course of electrolytic reduction, the FPs of Cs, Sr, and Ba present in the SNF (which was prepared artificially) are removed by dissolution in the LiCl + 3 wt% Li_2O salt melt at 650°C.[44] A mixture of metal oxide powders was used as an initial material loaded into the cathode basket to study the effect of FPs on the SNF reduction. The walls of the cathode basket were made of porous magnesia. Such wall material created a certain hindrance to the penetration of the reducing agent into the basket and delayed the release of oxygen from the oxide powder contained in it. This led only to partial reduction of the oxide powder. As a result, pure U_3O_8 was obtained as an output product. Alkali and AE metals are present in the powder diffused from the cathode basket and accumulated in the salt melt. Among three elements considered in Reference 44, the most significant solubility was found for Cs. This is due to the higher diffusion coefficient and the coefficient of mass transfer for this element. After 100 hours, portions of Cs, Sr, and Ba were loaded into the molten salt amounting 76%, 80%, and 99% of the initial value they had in the cathode basket, respectively. Thus, it was shown that the presence of unreduced oxides decreased the degree of uranium dioxide reduction and the current efficiency.

4.2 | Highly enhanced reduction of rare earth and zirconium oxides

Rare-earth metal oxides in the composition of SNF are practically not reduced to the corresponding metal during electrolysis in the molten salt LiCl + 1.0 wt% Li_2O salt. This problem was solved in Reference 45 by using metallic Li in LiCl salt without adding any transition metals. Two oxide reduction runs (OR-1 and OR-2) were carried out with the different lithium metal content in the molten salt at 650°C. In the operation OR-1, lithium in the melt was produced using a high electrical charge, while in the operation OR-2, it was produced due to a low electrical charge.

The charge applied to the simulated spent nuclear fuel (simfuel), in percentage terms, is defined as

$$Q[\%] = \frac{Q_{\text{applied}}}{Q_{\text{theoretical}}} \times 100\% = \frac{Q_{\text{applied}}}{nF\frac{w_{UO_2}}{M_{UO_2}}} \times 100\% \qquad (17)$$

where the number of electrons (4) required for the reduction of UO_2 in reaction (2) is denoted as n, F is the Faraday constant, w_{UO_2} is the mass of UO_2 in the simfuel, and M_{UO_2} is the molecular mass of UO_2. As a rule, the

Q value exceeds 100%, because there are current efficiency losses in the OR cell due to the resistance of the molten salt and the electrodes.

The cathode potential during the runs was more negative than the Li/Li^+ potential (−0.58 V),[46] in order to reduce UO_2 to metallic U. The high content of metallic Li in the molten salt not only promotes the reduction of RE oxides (REOs), but also contributes to an increase in the content of U in the melt. As a result, recovery time and power consumption are increased. In addition, the presence of a large amount of Li in the molten salt can damage the Pt anode and even cause a short circuit.[27] Considering the above, Park et al[42] revealed the functionality of lithium in LiCl without resorting to electrolysis. The process uses Li dissolved in LiCl as a reducing agent. The reduction was carried out by holding the sample in an electrolyte saturated with lithium, without electrolysis. Moreover, the concentration of metallic lithium in the LiCl salt initially was slowly increased due to the slow dissolution of metallic Li. However, then the Li concentration began to decrease. It was shown that the decrease in the concentration of Li was associated with its evaporation. They also found that Nd_2O_3 did not recover to metallic neodymium under the conditions of successful reduction of rare earth oxide. The reduction of the REOs in the oxide fuel occurs as a process of the coreduction with U.

Thus, the addition of metallic lithium to the molten salt LiCl + 1.0 wt% LiO_2 can be used to reduce oxides of rare earth metals in SNF.

A procedure similar to the reduction of rare-earth metal oxides was carried out for the reduction of the oxide compounds (ZrO_2 and Li_2ZrO_3) with metallic Li in the LiCl salt without Li_2O at 650°C.[47] Metallic Zr was obtained by immersing ZrO_2 into the LiCl salt with a high concentration of metallic Li. In this case, the formation of Li_2ZrO_3 in LiCl without Li_2O did not occur. Metallic Zr was also formed when Li_2ZrO_3 was immersed into LiCl without Li_2O. Choi et al[47] believe that in the case of damaged fuel, which consists of (U, Zr) O_2 in metallic form, reduction with metallic Li is more efficient than electrolytic reduction.

The difference in the reduction potential between UO_2 and Li_2O is small (70 mV).[48] In practice, overvoltage is required to achieve high electrolysis performance. Increasing the voltage often leads to the cell potential exceeding the required electrochemical window.[49] This results in the accumulation of metallic lithium in the molten electrolyte.[49,50] Changes in the chemical composition of the electrolyte can have a negative impact on the passage of the electrolysis process and on the safety of technological operations. The presence of metallic Li in the $LiCl-Li_2O$ electrolyte affects the corrosion of

materials. In particular, the destabilization of the protective oxide film occurs, which leads to significant damage of the stainless steel samples, that is, to their intergranular corrosion.[51]

4.3 | Determination of E-pO^{2-} diagram for lanthanum in the LiCl melt at 923 K

Rare earth elements compile up to 30% of the decay products observed in SNF. The chemical properties of REs are in many ways similar to actinides found during SNF recovery. Lanthanum is a typical rare earth element. The behavior of lanthanum in the LiCl-KCl eutectic at 450°C is well known.[52] However, in the LiCl system at 650°C lanthanum behaves differently. Sakamura[53] studied experimentally the electrolytic reduction of La$_2$O$_3$ to metallic lanthanum. La$_2$O$_3$ pellets were reduced in LiCl without the addition of Li$_2$O. The X-ray analysis showed that LaOCl and not metallic La was obtained as the final product of the reduction. The concentration of LiO$_2$ in the melt can be increased due to the reaction:

$$La_2O_3 + 2LiCl\,(ms) \rightarrow 2LaOCl + Li_2O\,(ms), \qquad (18)$$

where (ms) denotes the molten salt.

The presence of the LaOCl → La transformation leads to the dissolution of O^{2-} ions in LiCl. In this case, the cathode current is fully used for the reduction of Li$^+$ ions to metallic lithium. At the low concentration of Li$_2$O (<0.2 mol%), LaOCl is reduced to metallic lanthanum according to the reaction

$$LaOCl + 3Li \rightarrow La + Li_2O\,(ms) + LiCl\,(ms), \qquad (19)$$
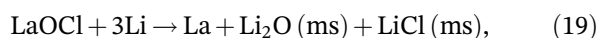
and Li$_2$O dissolves in the molten salt.

This is reflected in the diagram E-pO^{2-} (pO^{2-} = −log [O^{2-}]) (Figure 8).

The dissolution of LaCl$_3$ in the LiCl + Li$_2$O melt gives the LaOCl precipitate. The increase in the Li$_2$O concentration in the salt melt results in the LaOCl transforms into La$_2$O$_3$, and then into LiLaO$_2$. Moreover, the concentration of La in LiCl increases in proportion to the Li$_2$O concentration. It can be seen from the diagram that the stability of LaOCl extends over a wide area. At the same time, LiLaO$_2$ occupies a narrow area with a particularly high concentration of Li$_2$O. The value pO^{2-} = 0.93 corresponds to the solubility of Li$_2$O. The stable compound La$_2$O$_3$ exists in the range of 1.75 < pO^{2-} < 0.98. Note that in the LiCl-KCl melt at 450°C, La$_2$O$_3$ is not formed,[52] possibly because of the lower process temperatures. The reduction with the addition of metallic nickel forms stable alloys with lanthanum. This turns out to be
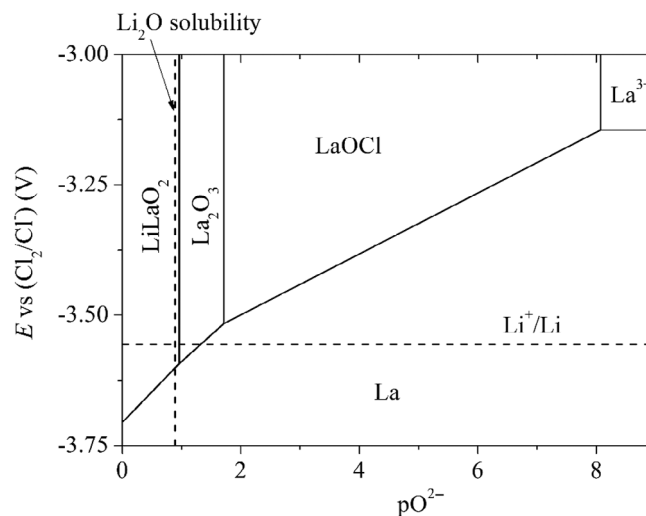

FIGURE 8 E-pO^{2-} diagram of lanthanum in LiCl-Li$_2$O at 650°C with 0.1 mol% of LaCl$_3$[52]

TABLE 2 Solubility of Li$_2$O in the LiCl-KCL melts at 600 and 650°C[54]

Melt	Temperature (°C)	
	600	**650**
LiCl	9.9	11.3
LiCl-KCl (10 mol%)	6.6	7.9
LiCl-KCl (20 mol%)	4.1	5.1

favorable for the reduction of La$_2$O$_3$ and LaOCl to the metallic form.

Thus, during the reduction of SNF, REs, as a rule, remain on the cathode in the oxide or oxychloride forms. However, some of the REs can dissolve in the LiCl salt bath to form complex oxide species. Decay products in the form of precious metals form stable intermetallic compounds with REs. Thus, some part of REs can be reduced in the form of such intermetallics.

5 | SOLUBILITY OF LI$_2$O IN MOLTEN SALTS

The experimentally determined values of the Li$_2$O solubility in the LiCl, LiCl- (10 mol%) KCl, and LiCl- (20 mol %) KCl melts at two temperatures (600 and 650°C) are given in Table 2.[54] As can be seen from Table 2, the solubility of Li$_2$O decreases significantly when KCl is added to the salt melt. One can also note an increase in the solubility of Li$_2$O from 14.1% to 24.4% with an increase in the temperature of each of the melts by 50°C.
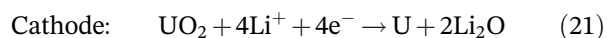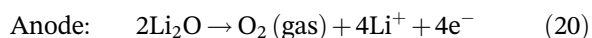
During the electrolytic reduction of UO$_2$ and UO$_2$ + PuO$_2$, the molten LiCl salt at the metal/oxide

interface is saturated with Li_2O. The solubility of oxygen ions (O^{2-}) in the LiCl melt is very high ($\sim$12 mol%).[37] The rate of oxide reduction turns out to be limited by the diffusion of O^{2-} ions through the molten salt.
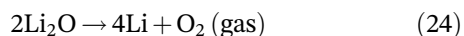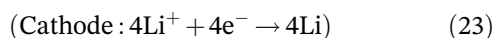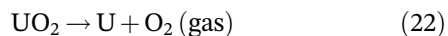
During electrolytic reduction, soluble FPs such as Cs, Sr, and Ba accumulate in the salt melt. Sakamura[32] investigated the solubility of Li_2O in the LiCl melt containing dissolved NaCl, KCl, CsCl, $CaCl_2$, $SrCl_2$, and $BaCl_2$.

This study showed a significant decrease in the solubility of Li_2O when the considered AM chlorides were added to molten LiCl. For example, there was a 2-fold decrease in the solubility of Li_2O in LiCl-20 mol% KCl. The solubility further decreases as the atomic number AMs increases. The solubility of Li_2O behaves somewhat differently when the AE metals enter the salt melt. It decreases slightly with the addition of $BaCl_2$, but increases when $SrCl_2$ is added to the melt. At the same concentration of Cs as that of other alkaline and AE elements, its transition to molten salt is most difficult. Therefore, this element more strongly delays the reduction of actinide oxides. No statistically significant correlation was found between the concentration of Li_2O and the solubility of Li in molten LiCl.[55]
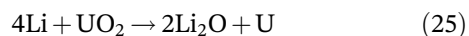
Yoo et al[56] proposed a kinetic model of the uranium oxide reduction to metallic uranium in molten LiCl at 650°C. This model is based on the use of the following equations:

$$\text{Anode:} \quad 2Li_2O \rightarrow O_2\,(\text{gas}) + 4Li^+ + 4e^- \quad (20)$$

$$\text{Cathode:} \quad UO_2 + 4Li^+ + 4e^- \rightarrow U + 2Li_2O \quad (21)$$

Overall electrochemical reactions:

$$UO_2 \rightarrow U + O_2\,(\text{gas}) \quad (22)$$

$$(\text{Cathode}: 4Li^+ + 4e^- \rightarrow 4Li) \quad (23)$$

$$2Li_2O \rightarrow 4Li + O_2\,(\text{gas}) \quad (24)$$

Indirect reduction:
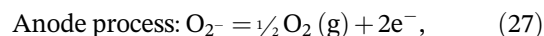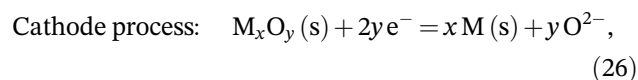
$$4Li + UO_2 \rightarrow 2Li_2O + U \quad (25)$$

When creating the model, the main focus was on the oxygen behavior due to the electrochemical/chemical formation, dissolution and diffusion of Li_2O. Reaction (25) shows that metallic uranium and Li_2O are the resulting products in the vicinity of the cathode. It is believed that Li_2O is electrochemically active and is the main carrier of electric current in the model. Reactions (20) to (25) show

that oxygen is separated from UO_2 and binds to Li^+ in molten LiCl. The formed Li_2O at the oxide/salt interface dissolves in the salt melt and is transferred to the LiCl bulk due diffusion. It was experimentally shown that the concentration of Li_2O in the metallic layers of uranium ranges from 26 to 46 wt%. This is much higher than the limiting solubility of Li_2O in LiCl ($\sim$8.8 wt%) at 650°C.[57] The obtained estimate of the effective diffusion coefficient of Li_2O in the structure of metallic uranium ($2\text{-}6 \times 10^{-5}$ cm^2/s) is consistent with the previously established estimate ($3.5\text{-}4 \times 10^{-5}$ cm^2/s).[21,31]

6 | DISCUSSION

This work is a brief overview limited to the pyroprocessing of real SNF using industrial equipment. In order to start the treatment and recycling of SNF by this method, the SNF must be properly prepared. In particular, SNF is first crushed to the granules (UO_2) of the required size. Then, a vapor oxidation process is carried out. During the volatile oxidation process carried out at the elevated temperatures, most volatiles and semivolatile FPs are removed from the SNF. After the end of this process, granular free-flowing UO_2 is crushed and converted into U_3O_8 powder, which is used for fabrication of pellets of desired size for the electrochemical reduction process.

The aim of research on the electrolytic reprocessing of SNF is to develop a technology for the recovery of SNF. In addition, such studies allow optimizing the design of the electrolysis cell, for example, to testing alternative anodes. These efforts are aimed at increasing the productivity of industrial plants and improving the economics of nuclear fuel production. When designing an appropriate industrial plant, it is necessary to scale up the electrolytic reduction technology. The electrolytic reduction implies the consumption of electrical energy. The electrolysis is performed after loading the cathode basket with solid oxides. To optimize the process, several anodes are usually used. Oxygen ions diffuse from the oxides to the anodes through the molten LiCl-Li_2O salt and release in the vicinity of the anodes in the form of gaseous oxygen. This process can be represented by the following reactions:

$$\text{Cathode process:} \quad M_xO_y\,(s) + 2y\,e^- = x\,M\,(s) + y\,O^{2-}, \quad (26)$$

$$\text{Anode process:} \quad O^{2-} = \tfrac{1}{2}O_2\,(g) + 2e^-, \quad (27)$$

where M is the metal ion to be reduced.

Actinide oxides and most lanthanide oxides, with the exception of extremely stable oxides such as Y_2O_3, are reduced to the base metal. The high purity metal (mostly U) remains in the cathode basket along with some unreduced rare earth oxides. Alkali and AE metals are separated from metal products by converting to chlorides and dissolution in molten salt. After passing through the reduction process, about 15 to 20 wt% of residual salts are still present in metal products. These salts are removed by distillation and the resulting metal is sent to further electrorefining. In addition, metal products are separated from the cathode basket and the salt is extracted in the form of a powder, which is more convenient for the salt transportation.

The cathode deposit can contain various FPs. The composition of these products depends on many factors: their concentration in the molten salt electrolyte, the current used, and also on the anodic and cathodic potentials. The presence of decomposition products and rare earth elements in the cathode deposits is highly undesirable. They can pose problems during the fabrication of recovered fuels due to their solubility in the U-Zr alloys. Thus, the proportion of rare earth elements in the final product intended for the nuclear fuel manufacturing should be minimal (∼1% or less).

The recycling of spent fuel from light water reactors can provide 99.7% conversion of uranium oxide to the metal.[58] The industrial use of pyroprocessing of SNF will reduce the amount of accumulated SNF and drastically reduce the disposal load by recycling and destroying toxic waste, including long-lived waste generated by FPs. In the course of pyroprocessing, unprocessed FPs are separated from SNF. This relatively small residue must be disposed. As a result, the use of pyroprocessing leads to a significant reduction of nonrecyclable FPs that are considered waste.[59]

There are certain requirements for the electrolyte (molten salt) used for the electrolytic reduction of SNF. These requirements are: (a) the possible lowest melting point and the highest ionic conductivity, (b) low viscosity, (c) low vapor pressure and large decomposition voltage, (d) the highest possible corrosion-resistance, (e) readily purified and nonpolluting, and (f) low cost.

So, the electrolyte must have a high degree of ionic conductivity and low electronic conductivity to reduce the current leakage. A high degree of electronic conductivity leads to large voltage losses and a decrease in the efficiency of the cell. An important property of an electrolyte is its ability to carry oxygen ions. The liquid electrolyte must have high thermal stability in order to withstand thermal stress. Since a large mass of electrolyte is used in industrial production, it must have a low cost. The platinum anode is not quite satisfactory even under

laboratory conditions due to its degradation under the severe oxidizing conditions encountered during the electrolytic reduction. Inconel (a superalloy based on nickel and chromium) and elemental tungsten were also investigated as anode materials.[60] It has been shown that the tungsten anode is the best in terms of achieving an acceptable corrosive behavior and cost reduction.

For various systems of molten salts, the electrochemical stability of a number of electrode materials, such as glassy carbon, platinum, stainless steel, molybdenum, and tantalum, were investigated.[61] The required characteristics of the anode material are mainly related to two determining factors: large surface area and the creation of conditions for rapid gas transport. The first factor allows a large surface area of the triple phase boundary to be achieved, which helps to maximize anodic reactions. Important properties of anode materials are stability in an aggressive environment, high electronic conductivity and electrocatalytic activity. In addition, among the properties of such material must be thermal efficiency with respect to the other components of the cell. A candidate anode material should also have minimal polarization losses and relatively low cost.

In principle, the cathode can be made of various conductive materials. However, taking into account the need to clean it from precipitated salt and lithium, when selecting a material, its mechanical strength should be taken into account. The shape and material of the cathode influences the course of the UO_2 and other oxides reduction processes. Initial studies were performed using single UO_2 tablets. A nichrome spiral wrapped around such pellets served as a cathode.[62] The increasing mass of the compound to be reduced, that is, the larger number of pellets to be recovered, promoted the usage of magnesium oxide crucibles with holes for the penetration of liquid electrolyte. At the bottom of the crucible, there was a flat spiral made of molybdenum wire, along which the current was supplied.[62] However, subsequently, due to the interaction between lithium and magnesium, the magnesium oxide cathode crucible was replaced by a spiral molybdenum basket. The cathode basket serves as a container for loading the reconstituted tablets and at the same time carries out a current supply. The use of a cathode basket has two disadvantages. First, the lithium release process takes place not only on the surface of the pellets, but also over the entire surface of the basket. As a consequence, nearly twice as much electricity is required for the same degree of UO_2 reduction. Second, there is no rigid fixation of the basket relative to the current lead, the basket can be deformed and the tablets may fall out into the electrolyte. At the Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, a steel mesh cathode basket is used in

experiments for the oxides reduction. A parallelepiped stainless steel mesh basket allows achieving a more complete pellet recovery.

Nuclear reactors operate in Russia with a spectrum of both thermal and fast neutrons. In addition to FRs, MOX fuel is also used (to a limited extent) in thermal reactors. Partial loading of the core of thermal reactors with MOX fuel is carried out in the form of ∼9% Pu mixed with depleted uranium. To date, Russia has accumulated about 24 000 tons of SNF. Annually, up to 700 tons of SNF are unloaded from NPP reactors, and about 15% of this volume is processed.[63]

In the near future, the implementation of fast-neutron power reactors and transition to a two-component nuclear system with a single fuel cycle are planned in Russia. Such system should combine the needs both of the existing thermal reactors and of the FRs. A closed nuclear fuel cycle is a means of obtaining a sustainable and long-term source of energy. In addition, the introduction of a closed nuclear fuel cycle with FR will significantly solve the problem associated with the accumulation of SNF and radioactive waste.

In Russia the irradiated fuel can be either stored or processed, the underground disposal is prohibited. Storage technologies are well developed and successfully used. This raises a problem in the area of the fuel cycle itself: what to do with the products separated from fuel through the processing?

From the point of view of noninterference in the ecological environment, the task is to approach the radiation-ecological equivalent disposal. In other words, it is necessary to create a technical guarantee that the radioactivity of the waste within the specified time intervals does not exceed the level achieved with conventional fuel extraction. To this end, the currently existing norms for losses of uranium, plutonium, americium, and curium should be tightened by about 10 times.

The real hydrometallurgical production already allows solving the problem of repeated usage of uranium, plutonium, and neptunium, but the industrial separation of americium and curium has not been implemented yet. The main difficulty in solving this problem lies in the fact that in the foreseeable future (Am—200 years, Cm—18 years) these elements transform into the most dangerous alpha-emitters, namely neptunium and plutonium, which have a half-life of millions of years. In addition, americium and curium have a high neutron flux and a strong heat release, when they are used as nuclear fuel. At present, the problem of the industrial separation of americium and curium has not yet been resolved, but it is posed in the program for creating a power complex with the BREST-OD-300 reactor being implemented in Russia. The experimental isolation of americium (60 g)

from the fuel has been performed. Minor actinides have similar chemical properties to rare earth elements and must be separated during the SNF reprocessing.

The construction of a new generation BREST-OD-300 power unit with a capacity of 300 MW has begun in Russia. In addition to the reactor, the unit includes a complex for the production of mixed nitride uranium-plutonium nuclear fuel, as well as a complex for the reprocessing of spent fuel. As a result, a closed fuel cycle will be implemented. In other words, in one territory not only electricity will be generated, but new fuel will be prepared from SNF discharged from the reactor.

7 | CONCLUSION

The currently existing fuel cycles, without any recycling, are essentially wasting the natural resources of uranium with an efficiency that is lower than 1%. This practice yields a massive accumulation of SNF, which is transferred as a burden toward future generations. The need to create a partially closed fuel cycle that includes recycling strategies and Generation IV FRs is increasingly felt. The main raw material for the electrolytic reprocessing is SNF from light water reactors, and the final products of this procedure are uranium, transuranics (Np, Pu, Am, Cm), and FPs. Moreover, the first two products are fuel for FRs (with a certain amount of uranium). Treatment and recycling involve extracting the valuable elements, U and Pu, from the ultimate waste as well as FPs and minor actinides. Until now, the main task was to separate the U and Pu. However, recently, the growing attention is paid to the extraction and separation of minor actinides. The extraction of minor actinides from SNF is carried out after their dissolution in the molten salt. Once recycled, they can be incinerated in nuclear reactors. Such processing will dramatically reduce the residual toxicity and the subsequent lifetime of the final waste. Recently, certain successes have been achieved in the development of effective laboratory methods for the selective separation of minor actinides, taking into account their subsequent recycling. However, several technological and scientific issues are still under investigation to obtain efficient and relevant for the development of relevant industrial scale processes, in particular with regard to understanding the actual molecular processes and the origin of selectivity, chemical process simulation, solvent cleanup, and so on.

The following problems accompanying the electrolytic process of SNF recovery still occur: the achievement of highly efficient recovery of actinides, minimization of the generated high-level waste, and effective corrosion protection of materials of the SNF reprocessing facility.

Solving these problems is a top priority for the implementation of a closed fuel cycle of modern nuclear power.

Thus, the ongoing search for recycling of the uranium and transuranic actinide elements from SNF enable the expansion of cheaper and more environmentally friendly nuclear power production.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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