Basis for a Minimalistic Salt Treatment Approach for Pyroprocessing Commercial Nuclear Fuel

Michael F. Simpson* and Prashant Bagri

University of Utah, Department of Metallurgical Engineering, 3450 S Highland Dr, Salt Lake City, Utah, USA

A simplified flowsheet for pyroprocessing commercial spent fuel is proposed in which the only salt treatment step is actinide drawdown from electrorefiner salt. Actinide drawdown can be performed using a simple galvanic reduction process utilizing the reducing potential of gadolinium metal. Recent results of equilibrium reduction potentials for Gd, Ce, Nd, and La are summarized. A description of a recent experiment to demonstrate galvanic reduction with gadolinium is reviewed. Based on these experimental results and material balances of the flowsheet, this new variant of the pyroprocessing scheme is expected to meet the objectives of minimizing cost, maximizing processing rate, minimizing proliferation risk, and optimizing the utilization of geologic repository space.

Keywords: Salt waste, Pyroprocessing, Drawdown

*Corresponding Author.
Michael F. Simpson, University of Utah, E-mail: michael.simpson@utah.edu, Tel: +1-801-581-4013

ORCID
Michael F. Simpson   http://orcid.org/0000-0002-0099-0097   Prashant Bagri   http://orcid.org/0000-0003-3361-0000

1. Introduction

Pyroprocessing is currently being developed by several nations, most notably the Republic of Korea (ROK) and the United States of America (USA), for potential implementation to process commercial spent fuel and reduce the needed capacity of permanent nuclear waste repositories [1-2]. The key unit operation in pyroprocessing is metallic fuel electrorefining, where either purified U or an actinide alloy (U/TRU) is recovered on a cathode. This serves the key requirement of separating actinides which can be recycled to make new fuel from radioactive fission products which should be permanently and safely disposed. The partitioning and management of these fission products can be problematic and lead to costly processing equipment, decrease in processing rates, and the generation of large volumes of radioactive waste. What is very well understood at this time is how these fission products partition in both the electrorefiner (ER) and the preceding step, which will be referred to in this paper as direct electrolytic reduction (DER). DER is needed in order to reduce oxide fuel to metallic form prior to loading into the ER. In the United States, much of the pyroprocessing technology/science was developed for the purpose of treating metallic spent fuel from Experimental Breeder Reactor-II (EBR-II). This work was carried out under the Integral Fast Reactor program in collaboration with Japan [3]. By the late 1990s, pyroprocessing had been demonstrated for treating EBR-II fuel at Argonne National Laboratory (ANL), and Korea Atomic Energy Research Institute (KAERI) started studying its potential for application to spent oxide fuel from ROK commercial reactors [4]. Such application of pyroprocessing to oxide fuel was made possible by development of processes to reduce oxide fuel [5].

2. Fission Product Partitioning in Molten Salts

In the DER process, it has been shown that Cs, Sr, and Ba partition into the molten $LiCl-Li_2O$ electrolyte [6]. It is well known that alkaline, alkali earth, lanthanide, and actinide elements that are found in the metallic spent fuel feed partition into the molten LiCl-KCl in the ER [7]. A useful tool to determine whether a given element will form a soluble chloride and partition into the ER salt is to compare its free energy of formation per mole of Cl to that of UCl_3. Under normal operating conditions, there is always UCl_3 included in the ER salt. It is also commonly the case that there is U metal in equilibrium with the salt. Therefore, the redox potential of the ER salt can be calculated using the Nernst equation for U^{3+}/U reduction/oxidation.

$$E_{eq} = E^o_{U^{3+}/U} + \frac{RT}{3F} \, ln \left(\frac{a_{UCl_3}}{a_U} \right) \qquad (1)$$

The standard reduction potential ($E^o_{U^{3+}/U}$) relative to the standard Cl^-/Cl_2 reference potential can be calculated from the free energy of formation of UCl_3.

$$E^o_{U^{3+}/U} = \frac{\Delta G^o_{f,UCl_3}}{3F} \qquad (2)$$

For the standard state to be meaningful, it should correspond to pure UCl_3 at the temperature of interest (773 K). The problem is that pure UCl_3 is a solid at 773 K. The workaround that has been proposed and used in previous published works is to calculate the free energy of formation for pure super-cooled liquid UCl_3 at 773 K [8].

Thus, the partitioning of fission products into the salt can be assessed either based on free energy of formation in the super-cooled state or on equilibrium potentials. If the free energy of formation is more negative than that of UCl_3, it will be stable in the salt. If the equilibrium potential is more negative than that based on UCl_3/U, again it will be stable in the salt. As an example, consider Fe and Pu. Assume that the only stable chemical forms for U, Fe, and Pu are UCl_3, $FeCl_2$, and $PuCl_3$. Iron may also be present in the salt as $FeCl_3$, but this is disregarded for the sake of simplicity in this discussion. The super-cooled free energy of formation at 773 K for each have been calculated as follows

based on thermodynamic data available in Barin's thermo-chemical property database [9].

$$\Delta G^o_{f,FeCl_2} \quad = \quad -236.2 \text{ kJ/mole}$$
$$\Delta G^o_{f,UCl_3} \quad = \quad -679.9 \text{ kJ/mole}$$
$$\Delta G^o_{f,PuCl_3} \quad = \quad -771.8 \text{ kJ/mole}$$

When normalized by the number of Cl atoms per mole-cule, the free energies of formation can be written as follows.

$$\Delta G^o_{f,FeCl_2} \quad = \quad -118.1 \text{ kJ/mole Cl}$$
$$\Delta G^o_{f,UCl_3} \quad = \quad -226.6 \text{ kJ/mole Cl}$$
$$\Delta G^o_{f,PuCl_3} \quad = \quad -257.3 \text{ kJ/mole Cl}$$

Using the above progression, it can be determined that $FeCl_2$ is unstable in the ER salt, while $PuCl_3$ is stable in the ER salt. This is also the thermodynamic basis for why any Pu metal that is cathodically reduced will spontaneously re-oxidize to $PuCl_3$ if left in contact with the ER salt after cathodic reduction is halted. This is essentially the thermo-dynamic basis of the ubiquitous claim that pyroprocessing is proliferation resistant [10, 11].

Obviously, there are limits to fission product concentra-tion in both the DER and ER molten salt baths. But, inter-estingly, these limits have not been well established. Solu-bility limits of the fission product chlorides at the operating temperatures (923 K for DER, 773 K for ER) would be a reasonable basis for the upper limits. But there is scarcely any such data currently available in the open literature. INL and ANL-West have operated the Mark-IV and Mark-V electrorefiners since 1996 and 1998, respectively, for pro-cessing fuel from EBR-II. Fission product concentrations are significant in the molten salt baths contained in these electrorefiners, but the concentration limits have not been attained yet. This can be considered to be due to the in-termittent operation of these systems, as neither has been used for sustained, production operations. Since these are the only known electrorefiners that have been used for pro-cessing irradiated fuel, there is no other data to support the establishment of fission product concentration limits. In a previously-published analysis, salt waste projections were calculated using 15 and 20wt% fission product limits for DER and ER salt [12]. Starting with commercial spent ox-ide fuel, it was calculated that running the DER and ER salt to 20wt% fission product chlorides would result in 14.4 MT of salt waste per 100 MT of spent fuel processed. This as-sumed that all of the actinide chlorides were removed from the ER salt using an actinide drawdown process. This cor-responds to 11.5 MT of LiCl-KCl or LiCl-Li$_2$O per 100 MT of spent fuel. At an estimated industrial price of $1000 per metric ton, this equates to only $115 per MT of spent fuel. It is acknowledged that a greater cost is likely to be incurred from the disposal of the waste rather than the cost of chemi-cals. But whether or not the fission products are separated from re-usable salt compounds, the mass of fission prod-uct chlorides per mass of spent fuel is unchanged. From a waste disposal perspective, LiCl, KCl, and Li$_2$O are only extra matrix components that take up extra space. Remov-ing them from the waste only serves to reduce the volume occupied by the waste. If a repository is limited by heat generation or total radioactive dose, then there is no benefit to excluding LiCl, KCl, and Li$_2$O. Ultimately, a leach-resis-tant waste form should be produced from the waste salt—likely based on a glass or ceramic composite. Such a waste form would likely be just as compatible with a salt contain-ing only fission product chlorides than one also containing LiCl, KCl, and/or Li$_2$O.

3. Alternative Pyroprocessing Flowsheet

Consider a new, simplified flowsheet for pyroprocess-ing of oxide fuel shown in Fig. 1. This flowsheet contains the major unit operations that are always included in py-roprocessing systems—direct electrolytic reduction (DER), electrorefining (ER), cathode processing (CP), metal waste processing, actinide drawdown, and salt waste processing. But it does not include any chemical separations of salts
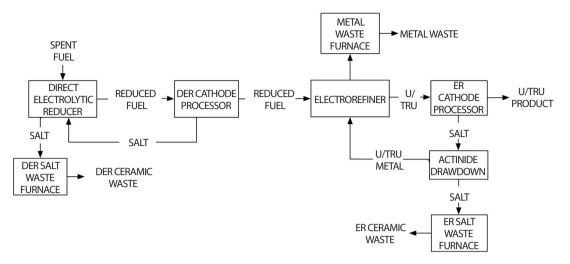
Fig. 1. Proposed flowsheet for pyroprocessing with only actinide separation from waste salt.

intended to recycle the base salt back to either DER or ER. The only chemical separation applied to the waste salt is actinide drawdown of the salt coming out of the ER via the ER cathode processor. This is a system design that would yield only 144 kg of salt waste per MT of oxide spent fuel.

The U.S. has had a policy against nuclear fuel reprocessing since the Carter Administration in the 1970s. There is currently no shortage of terrestrial uranium resources. Any separation of actinides from fission products increases risk of proliferation of fissile materials. This raises the question of whether the actinide drawdown should even be included in this flowsheet. The total mass of salt waste would increase from 144 to about 250 kg per MT of spent fuel without implementation of actinide drawdown. Perhaps more important is the impact on waste loading in a repository. Wigeland et. al. calculated that removal of plutonium and americium from the spent fuel waste could increase the capacity of a repository by a factor of 4.3 to 5.4 [13]. When Cs and Sr removal are also included, the capacity improvement factor reaches upward to about a factor of 40. In the scheme shown in Fig. 1, the DER ceramic waste will contain virtually all of the Cs and Sr, which has about a 30-year half-life. This waste could be placed in short-term, near surface disposal.

While the ER ceramic waste could be put directly into permanent, deep geologic disposal. The final space requirements for permanent, deep geologic disposal would be 40 times less than if the fuel were to be directly disposed without treatment.

To evaluate the level of drawdown efficiency needed for this process, consider the impact on classification of the salt waste. It is highly likely that there will be no permanent, deep geologic disposal site in either the U.S. or Republic of Korea for many years to come. If actinide drawdown can be applied efficiently enough to the ER waste salt, it could perhaps be disposed of as non-high level waste. This is a complicated situation to consider without specific regulatory guidance that would apply to waste streams from reprocessing spent nuclear fuel. Under ROK law, there are two radioactive waste classifications—low and intermediate-level radioactive waste (LILW) and high-level radioactive waste (HLW). A LILW disposal site is currently operational at the Wolsong LILW Disposal Center in Gyeongju. An important question, thus, arises as to how efficient would actinide drawdown need to be to qualify ER waste salt to be disposed of under the classification of LLILW. Two important criteria of the waste are that it have less than 3700 Bq of alpha emitting radionuclide per gram and that it gen-

erate less than 2 kW decay heat per m^3. The issue is further complicated by automatic designation of byproducts from the nuclear fuel cycle as high level waste, though it is speculated that this stipulation could be removed based on ROK legislative action. Currently, there is no material generated from the nuclear fuel cycle in the ROK, so this restriction currently serves no purpose and could be reassessed. The heat decay requirements should be met due to the separation of Cs and Sr from the spent fuel into the DER salt. The activities of various U isotopes (^{234}U, ^{235}U, and ^{238}U) are so low that virtually no removal of uranium would be required to meet this requirement. ^{239}Pu is a much more significant contributor to the activity of the salt, however. It is estimated that the Pu concentration in the salt would need to be reduced to a mass fraction of 1.6×10^{-6} to meet this requirement. This requires an extraordinary degree of actinide drawdown efficiency. But as the results of recent experiments indicate, it may be realizable. This is discussed in the following section. Another issue to consider with regard to disposal at the Wolsong LILW Disposal Center is that the accepted waste is contained in 55-gallon drums. Ceramic waste forms containing ER waste salt, thus, must be sized to fit into these drums. The waste drums are also not well sealed against the ingress of air and water, thus processes that dechlorinate the waste salt or otherwise make it impervious to water may be needed.

4. Recent Developments in Actinide Drawdown

Several different processes have been investigated for achieving actinide drawdown from molten LiCl-KCl [14-21]. This includes extraction into a molten Cd or Bi phase loaded with Li [14-18], direct addition of pure Li metal [20], electrowinning to a liquid Cd or Bi cathode [21], or electrowinning to a solid metal cathode [19]. These methods can be broadly categorized into electrochemical and chemical reductions. The electrochemical reductions are non-passive, meaning that they are actively controlled with an electric
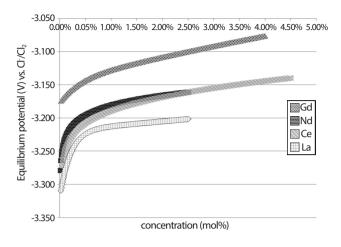

Fig. 2. Measured equilibrium reduction potentials for rare earths in molten LiCl-KCl at 500℃ versus Cl$^-$/Cl$_2$ standard reference electrode.

power supply. They can be run in controlled potential or controlled current mode. Controlled potential requires accurate reference electrodes, while controlled current requires real time measurement of concentrations in the salt. Liquid cathodes induce co-reduction of lanthanides, because of the non-ideal solutions that are formed for the actinides and lanthanides in molten Cd or Bi. Solid cathodes are not affected by this problem but are subject to spontaneous re-oxidation of TRU elements. Both solid and liquid cathode based electrowinning involve generation of highly corrosive Cl$_2$ gas at the anode. Meanwhile, using lithium as the reductant is a difficult process to control. While controlled addition of lithium to the molten salt can be performed to reduce only the actinides, its reduction potential is so negative(-3.574 V versus Cl$^-$/Cl$_2$) that it can reduce any of the lanthanide fission products in addition to any of the actinides. This potential can be increased by dissolving the Li into Cd or Bi, but that leads to complicated processing with large volumes of liquid metals. A new approach has recently been reported by Bagri and Simpson in which a solid metal (Gd) is used to galvanically reduce actinides out of the molten LiCl-KCl [22]. The idea is based on the using the optimal potential to reduce only actinides out of the ER salt. GdCl$_3$ has been calculated to have a standard reduc-
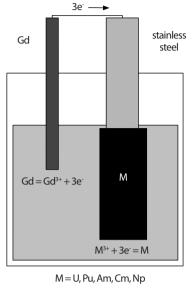
Fig. 3. Conceptual drawing of galvanic reduction cell for actinide drawdown.

tion potential for super-cooled liquid at 773 K of -2.804 V. This is more positive than the corresponding potentials for $NdCl_3$ (-2.909 V), $CeCl_3$ (-2.941 V), $PrCl_3$ (-2.95 V), and $LaCl_3$ (-2.997 V). Thus, there is no thermodynamic driving force for Gd metal to reduce any of these other lanthanides out of the molten salt. But it is about 0.137 V more negative than $PuCl_3$ and 0.455 V more negative than UCl_3. In recent experimental investigations, the equilibrium reduction potentials have been measured for various lanthanide chlorides at 773 K [8, 23-24]. This data has been compiled and plotted in Fig. 2. The measured potentials deviate from the standard potentials because of very low activity coefficients for the chloride salts. But the Gd^{3+}/Gd equilibrium reduction potential is still more positive than the others over a range of concentrations from 0 to 4 mol%.

Thus, Gd metal has a large driving force for actinide reduction but not for lanthanide reduction. Its reducing action must be fundamentally different than lithium, because of its solid state at the operating temperature. Also, there is no known solubility for Gd metal in LiCl-KCl. If a pure Gd metal rod were to be placed into the molten salt, it would

remain solid as the actinides quickly plate onto it and cover its surface. That would be an inefficient way to run the drawdown process, as the Gd would be passivated by actinide plating. But if the Gd rod where to be electrically coupled to a relatively large, inert metal surface, then the potential of that metal would be equal to the equilibrium potential formed by the $Gd/GdCl_3$ redox couple. A galvanic cell would effectively be formed in which Gd oxidizes at the surface of the rod, and actinides deposit onto the larger metal surface. By this route, it would be possible to reduce all of the actinides out of the salt by oxidizing Gd to $GdCl_3$. The extra $GdCl_3$ added to the salt would go along with the salt waste to permanent geologic disposal. There would be no reason to recover the Gd from the salt, because it is simply not valuable enough to do so. At 773 K, it has been determined that $GdCl_3$ has about a 70 mol% solubility in LiCl-KCl, thus it would be impossible to add too much $GdCl_3$ to the salt [24]. A drawing of what this cell could look like is shown in Fig. 3.

The first set of experiments to verify this process was reported in Journal of Nuclear Materials in 2017. A Gd metal rod was loaded into a stainless steel mesh-covered basket and immersed in a molten salt mixture of LiCl-KCl containing 1.39 mol% UCl_3 and 0.83 mol% $MgCl_2$ (surrogate for $PuCl_3$) [22]. The basket was rotated at 100 rpm for only 3 hours. Based on ICP-MS analysis of molten salt samples, up to 91% of the UCl_3 and up to 89% of the $MgCl_2$ were removed. At the end of the run, the stainless steel mesh basket was plated with metal, and its top opening was partially occluded with reduced metal. It is likely that access to the Gd rod became blocked before the end of the run. In the next set of experiments, the Gd rod was separated from the steel cathode in order to drive U deposition away from the Gd rod [25]. The theory was that U deposition near or on the Gd rod could interfere or effectively block the Gd from completely reducing the UCl_3. A stainless steel basket was again used as the cathode and was rotated at 100 rpm to promote mass transfer. The resulting final U concentrations in the salt were much lower than the first test with less than

Table 1. Summary of Second Phase of Gd Galvanic Drawdown Experimental Results using eutectic LiCl-KCl as Base Salt (T=500℃, reaction time = 2 hr, separated electrodes, cathode rotating at 100 rpm) [25]

Test	Metal Chlorides in Mixture	Initial UCl_3 Concentration (mol %)	Final UCl_3 Concentration (mol %)
G5	UCl_3	0.168	4.0×10^{-5}
G7	UCl_3-$MgCl_2$	0.161	6.1×10^{-5}
G8	UCl_3-$MgCl_2$-$NdCl_3$-$CeCl_3$-$LaCl_3$	0.235	4.2×10^{-4}

0.4 ppm residual U in the salt after only 2 hr of reaction [25]. Additional experiments were run with $MgCl_2$ and a variety of rare earth chlorides added to the salt. $MgCl_2$ was used as a surrogate for $PuCl_3$, based on similar reduction potentials. Excellent selectivity was demonstrated for U or U/Mg co-removal [25]. Concentrations of $NdCl_3$, $CeCl_3$, and $LaCl_3$ were unaffected by the galvanic reduction process using Gd, which is consistent with the equilibrium potentials plotted in Fig. 2 [25]. Results of the second phase of Gd galvanic reduction experiments of UCl_3 are summarized in Table 1. Details of the experimental procedures and time-dependent concentrations can be found elsewhere [25]. These results suggest that the goal of achieving high enough drawdown efficiency to quality the salt as LILW may be achievable.

5. Proliferation Resistance

The galvanic reduction drawdown (GRD) process is inherently passive based on the chemical properties of the reducing metal. It could be used with several different lanthanide metals, but gadolinium is recommended. Gadolinium will theoretically reduce all of the actinides. But the only lanthanides that may be reduced are europium, promethium, and yttrium. In the case of europium, this may only entail reduction to the soluble +2 state, so it would not be collected on the cathode. Yttrium is only slightly more electronegative than gadolinium based on standard reduction potential at 773 K and may also serve as a good choice for the reducing metal.

Consider the sequence of standard reduction potentials (as defined based on pure actinide chloride compounds) from high to low for the following actinides.

U > Np > Cm > Pu > Am

Note that apparent potentials for these salts appear to have a different order (U > Np > Pu > Cm > Am) as published in a review article by Zhang [26]. Thus, in order to isolate plutonium, it would be necessary to completely reduce all of the U, Np, and possibly the Cm from the salt, remove the cathode deposit, replace it with a bare cathode, remove it again before onset of Am deposition. Americium, curium, and plutonium have very closely spaced standard reduction potentials. It would be virtually impossible to determine when to pull the first and second cathode deposits. Non-ideal solution effects as quantified with activity coefficients would further erode the boundaries of deposition between Cm, Pu, and Am. Further processing of the Cm-Pu-Am deposit to separate Cm and Am would be next to impossible because of diffusion limitations. The majority of the deposit would be non-porous plutonium metal. Oxidation of Cm would be limited to near the surface. Overall, it would be a slow and non-productive method of trying to recover weapons-grade plutonium.

For monitoring this process, a combination of electrochemical, spectroscopic, and radiation measurements would be powerful. A simple open circuit potential (OCP) measurement between the cathode with the actinide metal deposits and a reference electrode will indicate the lowest potential metal that has been reduced. Using standard potentials versus Cl^-/Cl_2, it can be calculated that the OCP

would be -2.41 V if only U was present on the surface of the cathode. If Pu is present, the OCP drops to -2.72 V. The presence of Am further drops the potential to -2.75 V. These potentials were calculated from free energy of reaction calculations made using the HSC Chemistry v9 software, assuming a temperature of 500℃ and a Cl^-/Cl_2 standard reference potential [27]. These potentials are purely hypothetical and do not take into consideration non-ideal solution effects. Further study is, thus, needed to make such measurements in molten salt mixtures representative of electrorefining salt after extended periods of processing used nuclear fuel. Laser induced breakdown spectroscopy has been recently studied by researchers in both Korea and the U.S. for application to safeguarding pyroprocessing [28-29]. This referenced work has been focused on directly analyzing the composition of the ER salt. But LIBS would perhaps be better applied to verifying the composition of cathode deposits. Ratios of spectroscopic lines for Am, Cm, Pu, and U could be used to characterize the composition of the reduced metal and determine if the process was somehow perturbed to favor recovery of a particular metal such as Pu. Finally, the use of gamma ray spectroscopy and neutron counting would yield tremendous amounts of useful data regarding the relative amounts of the actinides. The possible algorithms are too numerous to present in this paper. But it should be considered a fertile area for further safeguards-related research.

6. Further Development

In order to optimize this proposed flowsheet, several technical issues need further study. They include the determination of fission product concentration limits for both DER and ER, optimizing the DER waste form, optimizing the ER waste form, further optimizing the galvanic reduction drawdown method, and optimizing remote process material handling. A new promising approach to salt waste forms is being studied at the University of Utah that causes

de-chlorination of the salts along with ion exchange of the salt's cations into a zeolite matrix [30]. This process may prove to be economical and effective at stabilizing both DER and ER waste salt. While it results in disposal of LiCl, KCl, and Gd, the associated cost of these materials should be much less than the capital and operating cost associated with full salt recycle. Further economic analysis of the process is still needed to prove this assumption. But recall that it was mentioned earlier that waste disposed in the Wolsong LILW Disposal Center is contained in simple 55-gallon drums, and resistance to air and water needs to be high. This dechlorination process could achieve exactly that requirement by removing nearly all of the chlorine from the salt and rendering the waste insoluble in waster.

7. Conclusions

Commercialization of pyroprocessing for treating spent commercial fuel will require a trade-off between process performance and economics. Process performance in this sense can be related to separating actinides and fission products, recycling salt streams, and minimizing waste volumes. A basis for adopting a minimalistic approach to salt separations is presented in this paper in which the most important separation process is actinide drawdown. Recently obtained drawdown efficiency results for a galvanic approach indicate that it may be possible to purify the ER salt to the degree that it can be disposed of as low and intermediate level waste in the ROK. The economic and repository benefits of full recycle of direct electrolytic reduction or electrorefining salt are, thus, in question. The improvements in actinide drawdown are expected to lead to development of simple, cost-effective, and proliferation resistant approach to keeping actinides out of the salt waste forms. This approach can be combined with a dechlorination process during waste form synthesis, allowing for recycling of Cl and further reduction in waste mass. It is expected to be economically favored to dispose of the actinide-free salt in

dechlorinated waste forms rather than develop and implement full salt recycle. However, a full economic comparison of these options should be performed.

Acknowledgments

REFERENCES

[1] H.S. Lee, G.I. Park, K.H. Kang, J.M. Hur, J.G. Kim, D.H. Ahn, Y.Z. Cho, and E.H. Kim, "Pyroprocessing technology development at KAERI", Nuclear Engineering and Technology, 43(4). 317-328 (2011).

[2] M.F. Simpson and J.D. Law, "Nuclear Fuel Reprocessing", Encyclopedia of Sustainable Science and Technology, 2nd Edition, Springer, ed. R.A. Meyers, ISBN 978-1-4939-2493-6, in press.

[3] C.E. Till and Y. I. Chang. Plentiful Energy. ISBN: 978-1466384606 (2011).

[4] H.S. Park, "The status of the radioactive waste management in Korea", Technologies for the Management of Radioactive Waste from Nuclear Power Plants and Back End Nuclear Fuel Cycle Activities (2001): 62.

[5] E.J. Karell, K.V. Gourishankar, J.L. Smith, L.S. Chow, and L. Redey, "Separation of actinides from LWR spent fuel using molten-salt-based electrochemical processes", Nuclear Technology, 136(3). 342-353 (2001).

[6] S. Herrmann, S. Li, and M. Simpson, "Electrolytic Reduction of Spent Light Water Reactor Fuel", Journal of Nuclear Science and Technology, 44(3). 361-367 (2007).

[7] J.P. Ackerman, "Chemical Basis for Pyrochemical Reprocessing of Nuclear Fuel", Ind. Eng. Chem. Res., 30, 141-145 (1991).

[8] P. Bagri and M.F. Simpson, "Determination of activity coefficient of lanthanum chloride in molten LiCl-KCl eutectic salt as a function of cesium chloride and lanthanum chloride concentrations using electromotive force measurements", Journal of Nuclear Materials, 482, 248-256 (2016).

[9] I. Barin, Thermochemical Data of Pure Substances, Third Edition. VCH (1995).

[10] T. Inoue and L. Koch, "Development of Pyroprocessing and Its Future Direction", Nuclear Engineering and Technology, 40(3). April (2008).

[11] H.E. Garcia, M. J. Lineberry, S. E. Aumeier, and H. F. McFarlane. "Proliferation resistance of advanced sustainable nuclear fuel cycles", Nuclear Plant Journal, 20(1). 18-27 (2002).

[12] M.F. Simpson, "Projected Salt Waste Production from a Commercial Pyroprocessing Facility", Science and Technology of Nuclear Installations (2013).

[13] R.A. Wigeland, T.H. Bauer, T.H. Fanning, and E.E. Morris, "Spent Nuclear Fuel Separations and Transmutation Criteria for Benefit to a Geologic Repository", Proceedings of the Waste Management 2004 Conference, February 29-March 4, 2004, Tucson, AZ.

[14] L. S. Chow, J. K. Basco, J. P. Ackerman, and T. R. Johnson, "Molten Salt/Metal Extractions for Recovery of Transuranic Elements", ANL-CP-75688, ANL Symposium on Energy, Environment, and Information Management (1992).

[15] M. Kurata, Y. Sakamura, T. Hijikata, and K. Kinoshita, "Distribution behavior of uranium, neptunium, rare-earth elements (Y, La, Ce, Nd, Sm, Eu, Gd) and alkaline-earth metals (Sr, Ba) between molten LiCl-KCl eutectic salt and liquid cadmium or bismuth", Journal of Nuclear Materials, 227, 110 (1995).

[16] K. Kinoshita, T. Inoue, S.P. Fusselman, D.L. Grimmett, J.J. Roy, R.L. Gay, C.L. Krueger, C.R. Nabelek, and

T.S. Storvick, "Separation of Uranium and Transuranic Elements from Rare Earth Elements by Means of Multistage Extraction in LiCl-KCl/Be System", Journal of Nuclear Science and Technology, 36, 2 (1999).

[17] T. Kobayashi, "An Assessment of the Multi-Stage Counter Current Extraction of TRUs from Spent Molten Salt into Liquid Metal", Journal of Nuclear Science and Technology, 43, 7 (2006).

[18] J-H. Yoo, H-S. Lee, and E-H. Kim, "Prediction of a Mutual Separation of Actinide and Rare Earth Groups in a Multistage Reduction Extraction System", Nuclear Engineering and Technology, 39, 5 (2007).

[19] M.A. Williamson and J. L. Willit, "Pyroprocessing flowsheets for recycling used nuclear fuel", Nuclear Engineering and Technology, 43(4). 329-334(2011).

[20] M.F. Simpson, T.S. Yoo, D. LaBrier, M. Lineberry, M. Shaltry, and S. Phongikaroon; "Selective Reduction of Active Metal Chlorides from Molten LiCl-KCl using Lithium Drawdown", Nuclear Engineering and Technology, 44(7), 767-772 (2012).

[21] D.Y. Kim, I.S. Hwang, and J.H. Lee. "Controlling the leakage of liquid bismuth cathode elements in ceramic crucibles used for the electrowinning process in pyroprocessing", Journal of Nuclear Materials 478, 91-96 (2016).

[22] P. Bagri and M.F. Simpson, "Galvanic reduction of uranium(III) chloride from LiCl-KCl eutectic salt using gadolinium metal", Journal of Nuclear Materials, 493, 120-123 (2017).

[23] P. Bagri and M.F. Simpson, "Potentiometric Measurement of Activity of Rare Earth Chlorides (La, Gd, Ce, Nd) in LiCl-KCl Eutectic Salt.", Electrochimica Acta, 259, 1120-1128 (2018).

[24] P. Bagri and M.F. Simpson, "Activity Measurements of Gadolinium (III) Chloride in Molten LiCl-KCl Eutectic Salt Using Saturated $Gd/GdCl_3$ Reference Electrode", Journal of The Electrochemical Society, 164(8), H5299-H5307 (2017).

[25] P. Bagri, J. Ong, C. Zhang, and M.F. Simpson, "Optimization of UCl_3 and $MgCl_2$ separation from molten LiCl-KCl eutectic salt via galvanic drawdown with sacrificial Gd anode", Journal of Nuclear Materials (in submission).

[26] J. Zhang, "Electrochemistry of actinides and fission products in molten salts—Data review", Journal of Nuclear Materials, 447, 271-284 (2014).

[27] Outotec, HSC Chemistry, version 9, 2016.

[28] H. Cynthia, S. Phongikaroon, and J. R. Scott. "Temperature effect on laser-induced breakdown spectroscopy spectra of molten and solid salts", Spectrochimica Acta Part B: Atomic Spectroscopy, 97, 79-85 (2014).

[29] S.H. Park et. al., "Status of Development of Pyroprocessing Safeguards at KAERI", Journal of Nuclear Fuel Cycle and Waste Technology, 15(3). 191-197 (2017).

[30] M. Wasnik, K. Carlson, and M.F. Simpson, "Waste Minimization of Electrorefiner Waste Salt via Dechlorination: A New Approach", Proceedings of the Annual Meeting of the American Nuclear Society, June 2017.