

# **Study of Electrorefiner Sediment Re-Chlorination Options**

June 2022

S. D. Herrmann Pyrochemistry and Molten Salt Systems Department

C. R. Heathman Aqueous Separations and Radiochemistry Department



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#### S. D. Herrmann Pyrochemistry and Molten Salt Systems Department C. R. Heathman Aqueous Separations and Radiochemistry Department

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Idaho National Laboratory Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the U.S. Department of Energy Office of Nuclear Energy Under DOE Idaho Operations Office Contract DE-AC07-05ID14517 Page intentionally left blank

#### ABSTRACT

During the final operations of a kg-scale uranium electrorefiner with used light water reactor fuel at Idaho National Laboratory's Hot Fuel Examination Facility, researchers identified a bed of sediment at the bottom of the electrorefiner's salt pool. The sediment was removed from the electrorefiner and subjected to reduced pressure and elevated temperature to distill away occluded salt. Samples of the distilled sediment and electrorefiner salt pool were subjected to elemental and isotopic analyses to characterize their compositions. The literature was then reviewed to identify and evaluate options for re-chlorinating the sediment or otherwise recovering actinides from the sediment. Several options were identified and evaluated, which included both in situ (i.e., rechlorination of sediment within the electrorefiner) and ex situ (i.e., rechlorination of sediment outside the electrorefiner) techniques. Thermodynamic stability analyses were performed on select options along with Gibbs energy minimization, which modeled the sediment and salt phases of the subject electrorefiner based on the provided elemental and isotopic analysis results. An evaluation of the sediment re-chlorination options identified a baseline approach (oxide reduction in an oxide reduction vessel), which primarily uses existing equipment in the Hot Fuel Examination Facility. Other options (oxide reduction in the electrorefiner, chlorination, and hydrogen chloride) were dismissed for various deficiencies. Three options (carbon tetrachloride, zirconium tetrachloride, and uranium trichloride) were recommended for further investigation.

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## ACRONYMS

ER	electrorefiner
GEM	Gibbs energy minimization
HFEF	Hot Fuel Examination Facility
ICP-MS	inductively coupled plasma – mass spectroscopy
ICP-OES	inductively coupled plasma - optical emission spectroscopy
INL	Idaho National Laboratory
IRT	integrated recycling test
LCC	liquid cadmium cathode
LWR	light water reactor
OR	oxide reduction
RDS	remote distillation system
RSD	relative standard deviation
U/TRU	uranium/transuranium
XRD	x-ray diffraction

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# Study of Electrorefiner Sediment Re-Chlorination Options

#### 1. OBJECTIVE

The objective of this study was to survey, evaluate, and recommend options for re-chlorinating recently identified sediment in a kg-scale uranium electrorefiner (ER) at Idaho National Laboratory's (INL's) Hot Fuel Examination Facility (HFEF).

#### 2. BACKGROUND

During the final operations of a kg-scale uranium ER for an integrated recycling test (IRT) with used Dresden light water reactor (LWR) fuel at INL's HFEF, researchers identified a bed of sediment at the bottom of the ER's salt pool. Specifically, a liquid cadmium cathode (LCC) assembly was lowered into the pool to recover uranium and transuranium (U/TRU) metal from the ER salt phase. Instead of the assembly's top plate resting on the ER vessel head, which is the normal position suspending the LCC crucible in the salt pool, the top plate stood above the vessel head approximately 2 cm (see Figure 1), indicating the bottom of the assembly was standing on material at the bottom of the ER salt crucible. After completing the first of two U/TRU recovery runs and removing the LCC assembly, the bottom of the crucible was raked with a stainless-steel rod to displace any perceived solid component (e.g., a broken ceramic tube) that might have precluded the complete insertion of an LCC assembly. The same assembly was then reinserted into the ER salt pool using the same port for a second U/TRU recovery operation, and the assembly's top plate stood approximately 0.6 cm above the ER vessel head, indicating the assembly was again standing on material at the bottom of the crucible. After completing the first of two using the same port for a second U/TRU recovery operation, and the assembly's top plate stood approximately 0.6 cm above the ER vessel head, indicating the assembly was again standing on material at the bottom of the crucible. After completing the second U/TRU recovery operation, and the assembly was removed from the ER vessel head, indicating the assembly was removed from the ER salt pool.



Figure 1. First LCC assembly standing on material on bottom of ER salt crucible.

After the two U/TRU recovery runs, researchers performed a cleanup run to remove any remaining uranium metal from the anode basket used in the U/TRU recovery operations and from the ER crucible. This required an addition of uranium trichloride to the salt pool. After the cleanup run, ER salt samples were taken and placed in sealed storage containers. A tool was then transferred into the HFEF main cell and used to scrape along the bottom of the ER salt crucible, revealing sediment shown in Figure 2. Sediment was removed through three rectangular ports in the ER vessel head. A total of 862 g of salt-occluded sediment was removed from the bottom of the ER salt crucible that was accessible from the three ports. Later, another 1,404 g of salt-occluded sediment was removed from the bottom of the ER salt crucible. Based on diminishing returns from scraping the bottom of the ER crucible, the majority of the sediment was removed; however, some sediment inevitably remained in the crucible. The origin of the sediment and its rate of formation have yet to be determined.



Figure 2. ER sediment before (left) and after (right) distillation.

Samples of the ER sediment were placed in sealed storage containers. Then, 763 of the initial 862 g of ER sediment was subjected to reduced pressure and elevated temperature to remove occluded salt. The distillation apparatus was unloaded, revealing 458 g of separated distillate material (presumably all salt) and 305 g of solids, the latter of which is shown in Figure 2. Samples of the distilled ER sediment solids were placed in sealed storage containers.

Researchers analyzed three ER salt samples prior to sediment removal and three ER sediment samples after distillation. Specifically, the salt samples were subjected to elemental and isotopic analyses via inductively coupled plasma – optical emission spectroscopy (ICP-OES), inductively coupled plasma – mass spectroscopy (ICP-MS), and gamma spectroscopy. The ER sediment samples after distillation were first separated into oxide and metal fractions via an ethyl acetate – bromine dissolution technique. The separated oxide and metal phases were subsequently subjected to ICP-OES, ICP-MS, and gamma spectroscopy. Consolidated analytical results for the ER salt samples, including their relative standard deviations (RSDs), are shown in Table 1, and those for the ER sediment samples after distillation are shown in Tables 2, 3, and 4.

ppm	L	Sample 1	Sample 2	Sample 3	Average	% RSD
	<sup>133/137</sup> Cs, <sup>135</sup> m/z	27.1	26.8	26.7	26.9	0.775
	Ва	158	163	161	161	1.57
	<sup>136/137/138</sup> Ba	123.5	124.7	123.9	124.0	0.493
<u>e</u>	Sr	43.3	45.2	<50	44.3	3.04
[dul]	<sup>86/88</sup> Sr, <sup>90</sup> m/z	25.9	24.0	23.5	24.5	5.18
-So	<sup>85/87</sup> Rb	10.75	10.80	10.16	10.57	3.37
Salt	<sup>125/128/130</sup> Te	<14	<15	<17		
	Nd	3,940	3,290	3,330	3,520	10.3
	<sup>143/144/145/146</sup> Nd, <sup>148/150</sup> m/z	4,245	3,452	3,454	3,717	12.3
	Се	<2.000	<2.000	<2.000		
	<sup>140/142</sup> Ce	1.893	1.588	1.590	1,690	10.3
	La	1,450	1.320	1.290	1,353	6.28
	<sup>139</sup> La	1.350	1.200	1.200	1.250	6.93
	Pr	974	807	825	869	10.6
s	<sup>141</sup> Pr	974	804	801	860	11.5
arth	Sm	1,050	848	848	915	12.7
e E	<sup>147/149/152</sup> Sm, <sup>151/154</sup> m/z	501	402	401	435	10.8
Rar	Y	568	440	430	479	13.1
	234/235/236/238U	45,100	27,000	26,400	32,800	32.4
	<sup>235</sup> U (iso %)	0.541	0.601	0.533	0.549	
	<sup>239/240</sup> Pu	12,560	9,820	9,830	10,740	14.7
	<sup>237</sup> Np	334	242	242	273	19.5
	<sup>241</sup> m/z	898	723	717	779	13.2
les	<sup>242</sup> m/z	481	369	367	406	16.1
tinic	<sup>243</sup> m/z	71.7	56.8	56.9	61.8	13.9
Ac	<sup>244</sup> m/z	3.39	2.61	2.62	2.87	15.6
	Zr	<25	<25	<30		
	$^{91}$ Zr, $^{92/93/94/96}$ m/z	<9	<10	1.32	1.32	
	<sup>95/97/98/100</sup> Mo	<4	<5	2.29	2.29	
tals	<sup>101/102/104</sup> Ru	<1.9	<2.2	<3		
Me	<sup>99</sup> m/z	<0.4	<0.5	<0.5		
ble	<sup>105/108/110</sup> Pd, <sup>106/</sup> m/z	12.4	5.9	33.7	17.3	83.9
2°2	<sup>103</sup> Rh	<0.8	<0.9	<1		
	K	246,000	246,000	244,000	245,000	0.471
	Li	70,500	71,600	74,300	72,100	2.71
	Fe	<230	<260	1,050	1,050	
	Cr	<20	<10	<25		
ler	Ni	<590	<590	<660		
Otł	Cd	<35	<40	281	281	

Table 1. Consolidated analytical results of ER salt samples prior to sediment removal.

ppr	n	Oxide Fraction	Metal Fraction	Oxide & Metal	% Metal
	<sup>133/137</sup> Cs, <sup>135</sup> m/z	0.734	0.00865	0.743	1.18
	Ва	<20	<60	<80	
	<sup>136/137/138</sup> Ba	3.73	<20	3.73	
e	Sr	<35	<65	<100	
[dul	<sup>86/88</sup> Sr	6.32	<10	6.32	
-So	<sup>85/87</sup> Rb	<6	<8	<14	
Salt	<sup>125/128/130</sup> Te	12.4	<31	12.4	
	Nd	2,650	<100	2,650	<4
	143/144/145/146Nd,148/150m/z	4,190	69.5	4,260	1.66
	Ce	2,080	<170	2,080	<8
	<sup>140/142</sup> Ce	2,100	35.8	2,140	1.68
	La	1,450	<75	1,450	<5
	<sup>139</sup> La	1,500	42.1	1,540	2.73
	Pr	1,310	<590	1,310	<31
s	<sup>141</sup> Pr	1,050	18.3	1,070	1.71
arth	Sm	847	<150	847	<16
е E	<sup>147/149/152</sup> Sm, <sup>151/154</sup> m/z	517	5.65	523	1.08
Rai	Y	658	<55	658	<8
	234/235/236/238U	779,000	33,900	813,000	4.17
	<sup>235</sup> U (iso %)	0.806	indeterminate		
	<sup>239/240</sup> Pu	17,200	478	17,700	2.70
	<sup>237</sup> Np	390	24.2	414	5.84
des	<sup>241</sup> m/z	1,050	24.8	1,070	2.31
tini	<sup>242</sup> m/z	454	12.2	466	2.62
Ac	<sup>243</sup> m/z	66.8	<2	66.8	<3
	Zr	573	<65	573	<11
	<sup>91</sup> Zr, <sup>90/92/93/94/96</sup> m/z	892	92.0	984	9.35
	<sup>95/97/98/100</sup> Mo	370	15.45	386	4.00
tals	<sup>101/102/104</sup> Ru	5.97	<4	5.97	<41
Me	<sup>99</sup> m/z	7.45	<2	7.45	<22
ble	<sup>105/108/110</sup> Pd, <sup>106/</sup> m/z	3.67	<7	3.67	
<u>~</u>	<sup>103</sup> Rh	<2	<3	<5	
	К	1,460	<570	1,460	<29
	Li	<210	<390	<600	
	Fe	7,130	32,500	39,600	82.0
	Cr	4,090	1,350	5,440	24.8
ler	Ni	<480	3,960	3,960	>89
Of	Cd	<95	<180	<275	

Table 2. Consolidated analytical results of ER sediment samples after distillation, Sample 1.

ppr	n	Oxide Fraction	Metal Fraction	Oxide & Metal	% Metal
	<sup>133/137</sup> Cs, <sup>135</sup> m/z	0.0630	0.00448	0.0675	6.64
	Ba	<20	<25	<45	
	<sup>136/137/138</sup> Ba	16.8	2.86	19.7	14.5
<u> </u>	Sr	<25	<55	<80	
[dul	<sup>86/88</sup> Sr	<4	<10	<14	
-So	<sup>85/87</sup> Rb	<6	<5	<11	
Salt	<sup>125/128/130</sup> Te	7.64	<3	7.64	<29
	Nd	2,120	<140	2,120	<7
	<sup>143/144/145/146</sup> Nd, <sup>148/150</sup> m/z	2,496	47.5	2,543	1.87
	Ce	1.130	<270	1.130	<20
	<sup>140/142</sup> Ce	1,152	23.7	1,176	2.02
	La	843	<65	843	<8
	<sup>139</sup> La	862	25.2	887	2.84
	Pr	629	<460	629	<43
s	<sup>141</sup> Pr	590	12.3	602	2.04
arth	Sm	896	<95	896	<10
е E	<sup>147/149/152</sup> Sm, <sup>151/154</sup> m/z	431	7.36	439	1.68
Ra1	Y	576	<45	576	<8
	234/235/236/238U	732,000	26,200	758,000	3.46
	<sup>235</sup> U (iso %)	0.776	0.680	0.773	
	<sup>239/240</sup> Pu	10,340	308	10,650	2.89
	<sup>237</sup> Np	240	13.6	254	5.36
des	<sup>241</sup> m/z	630	16.2	646	2.51
tini	<sup>242</sup> m/z	252	7.76	260	2.99
Ac	<sup>243</sup> m/z	38.7	<2	38.7	<5
	Zr	561	<150	561	<22
	<sup>91</sup> Zr, <sup>90/92/93/94/96</sup> m/z	809	112.2	921	12.2
	<sup>95/97/98/100</sup> Mo	434	85.1	520	16.4
tals	<sup>101/102/104</sup> Ru	1.61	<4	1.61	
Me	<sup>99</sup> m/z	3.29	<3	3.29	
ble	<sup>105/108/110</sup> Pd, <sup>106/</sup> m/z	10.69	<7	10.69	
_ <u>_</u> 2	<sup>103</sup> Rh	<1	<1	<2	
	К	892	<580	892	<40
	Li	<230	<340	<570	
	Fe	12,200	48,200	60,400	79.8
	Cr	4,250	4,600	8,850	52.0
ler	Ni	<730	7,630	7,630	>91
Oth	Cd	<65	<140	<205	

Table 3. Consolidated analytical results of ER sediment samples after distillation, Sample 2.

ppr	n	Oxide Fraction	Metal Fraction	Oxide & Metal	% Metal
	<sup>133/137</sup> Cs, <sup>135</sup> m/z	0.968	0.00659	0.975	0.676
	Ba	<15	<45	<60	
	<sup>136/137/138</sup> Ba	12.05	<14	12.05	
<u> </u>	Sr	<25	<45	<70	
[dul	<sup>86/88</sup> Sr	6.37	<5	6.37	
-So	<sup>85/87</sup> Rb	<4	<5	<9	
Salt	<sup>125/128/130</sup> Te	15.8	<17	15.8	
	Nd	3,640	<80	3,640	<3
	143/144/145/146Nd,148/150m/z	4,030	59.2	4,080	1.45
	Ce	1,920	<120	1,920	<6
	<sup>140/142</sup> Ce	1,822	30.2	1,852	1.63
	La	1,090	<50	1,090	<5
	<sup>139</sup> La	1,130	33.6	1,160	2.89
	Pr	1,090	<400	1,090	<27
SI	<sup>141</sup> Pr	988	16.4	1,004	1.63
arth	Sm	492	<100	492	<17
е Н	<sup>147/149/152</sup> Sm, <sup>151/154</sup> m/z	340	7.80	347	2.25
Rai	Y	621	<40	621	<7
	234/235/236/238U	733,000	26,300	759,000	3.46
	<sup>235</sup> U (iso %)	0.842	indeterminate		
	<sup>239/240</sup> Pu	17,900	423	18,300	2.31
	<sup>237</sup> Np	417	18.6	436	4.27
des	<sup>241</sup> m/z	1,060	20.9	1,080	1.93
tini	<sup>242</sup> m/z	504	11.0	515	2.14
Ac	<sup>243</sup> m/z	67.1	1.44	68.5	2.10
	Zr	452	<45	452	<10
	<sup>91</sup> Zr, <sup>90/92/93/94/96</sup> m/z	795	79.4	874	9.08
	<sup>95/97/98/100</sup> Mo	336	29.6	365	8.11
tals	<sup>101/102/104</sup> Ru	5.0	<3	5.0	
Me	<sup>99</sup> m/z	3.62	<1	3.62	
ble	<sup>105/108/110</sup> Pd, <sup>106/</sup> m/z	11.72	<4	11.72	
_ <u>_</u> 2	<sup>103</sup> Rh	0.998	<2	0.998	
	К	2,260	<400	2,260	<16
	Li	<140	<260	<400	
	Fe	5,740	19,200	24,900	77.0
	Cr	3,220	1,440	4,660	30.9
ler	Ni	<310	2,650	2,650	>89
Oth	Cd	<60	<120	<180	

Table 4. Consolidated analytical results of ER sediment samples after distillation, Sample 3.

#### 3. APPROACH

The approach for this study was to survey the literature for information regarding the chlorination of actinide oxides or techniques to otherwise recover actinides from the ER sediment. Researchers supporting this study discussed the survey results to identify applicable options to ER sediment rechlorination and recovery. As applicable, they further evaluated identified options that could be performed on the sediment at the bottom of the ER crucible (i.e., in situ) and those that could be performed on the sediment after its removal from the crucible (i.e., ex situ). They also conducted thermodynamic stability analyses, as applicable, for each of the options using thermochemical database software. [1] A summary of identified options (or chlorinating agents), and variations thereof, for rechlorinating or otherwise recovering actinides from the ER sediment is shown in Table 5. Each option is discussed further in subsequent subsections.

Table 5. Summary of options, and	l variations the	ereof, for re-ch	lorinating or of	herwise recovering	; actinides
from the ER sediment.					

No.	Option (or chlorinating agent)	In Situ	Ex Situ
1	Oxide reduction (OR) in OR vessel		Х
2	Oxide reduction in ER vessel	Х	
3	Chlorine	Х	Х
4	Hydrogen chloride	Х	Х
5	Carbon tetrachloride	Х	Х
6	Zirconium tetrachloride	Х	Х
7	Uranium trichloride	Х	Х

#### 4. Discussion

The ER salt sample analytical results near the time of the ER sediment removal (see Table 1), along with those preceding them, identified an expected gradual accumulation of rare earths and salt-soluble constituents (i.e., Cs, Ba, Sr, Rb) following each electrorefining run with reduced oxide fuel; however, the relative concentrations of the salt-soluble constituents were lower, as they primarily accumulated in the OR vessel with a small fraction carrying over to the ER vessel from incomplete OR salt removal. As such, the rare earth concentration in the ER salt was roughly 8,000 ppm while the salt-soluble fraction was ~200 ppm. TRU constituents also accumulated in the ER salt from reduced oxide fuel electrorefining; however, their concentrations, along with those of uranium, varied following U/TRU recovery operations in the ER. In the subject samples, the U/TRU concentrations were 3.3 and 1.1 wt%, respectively. Notably absent in the ER salt phase were noble metals, stainless-steel constituents (Fe, Cr, and Ni), and cadmium.

The analytical results for ER sediment samples (see Tables 2–4) revealed uranium as the primary constituent. Specifically, uranium constituted roughly 90% of the analyte mass (metal + oxide) measured for these samples, followed by 6% stainless-steel constituents (i.e., Fe, Cr, and Ni), 2% TRU constituents, and 1% rare earths. The analysis results did not include oxygen, which was expected to contribute significantly to the balance of mass for these samples. Chlorine was another constituent not measured in these analyses that could have contributed significantly to the balance of mass for these samples. The ethyl acetate – bromine dissolution enabled the separation of metal and oxide phases in the ER sediment, revealing metal fractions in the uranium at 3–4 wt%, TRU at 2–6 wt%, and rare earths at 1–3 wt%. However, the ethyl acetate – bromine dissolution technique has only been validated with uranium and plutonium metal and oxide phases. The technique should be applicable to rare earth and other TRU constituents as well; nevertheless, without validating each specific metal and oxide combination, the results for rare earth and other TRU constituents can only be considered approximations.

Aside from metal and oxide phase distinction, no other analyses have been performed on the ER sediment to identify possible compound formations. For the purpose of this study, we assumed that the U, TRU, and rare earths are in standard oxide forms under reducing conditions. Accordingly, the uranium is present as uranium dioxide, while the TRU and rare earths are likely sesquioxides. The formation of uranium dioxide in ER salt is consistent with a recent study by Volkovich et al., who introduced oxygen gas into LiCl-KCl-UCl<sub>3</sub> at 550°C, revealing precipitates of UO<sub>2</sub> as a major phase and mixed lithium-uranium oxide and mixed potassium-uranium oxide as minor phases via x-ray diffraction (XRD). [2] The presence of oxychlorides in the ER sediment is possible, particularly among the TRU and rare earth constituents, which were not included in the Volkovich study. Consequently, additional analyses of the ER sediment to speciate its compounds is under consideration.

#### 4.1 Oxide Reduction in OR Vessel

One option to recover actinides from the ER sediment involves removing it from the ER vessel, distilling away the ER salt, and subjecting the material to oxide reduction in the kg-scale OR vessel at HFEF. The reduced material would then be subjected to OR salt distillation to remove OR salt prior to electrorefining the material in the ER vessel. A simplified flow diagram of this approach is shown in Figure 3.



Figure 3. Simplified flow diagram of actinide recovery from ER sediment via oxide reduction.

This option is an ex situ approach, requiring the removal of ER sediment from the ER vessel prior to subsequent actinide recovery operations. The sediment would be subjected to an elevated temperature (around 1000°C) and reduced pressure (below 200 mTorr) to distill away ER salt. The ER salt distillation could be performed with existing equipment, a remote distillation system (RDS), in the HFEF main cell, and the distilled ER salt could be returned to the ER vessel. The distilled ER sediment would be similar in form to the 305 g, which has already been prepared and described (see Section 2). ER salt distillation could also contribute to the possible decomposition of uranium (III) oxychloride, forming uranium metal, uranium trichloride, and uranium oxide, as follows.

$$6 \text{ UOCl} \rightarrow \text{U} + 3 \text{ UO}_2 + 2 \text{ UCl}_3$$

(1)

The above reaction has a negative Gibbs energy of reaction ( $\Delta G_{Rx}$ ) above 1194°C under ideal mixing and with unit activities. [1] However, the forward promotion of this reaction at a lower temperature could be enabled by the continual removal of uranium trichloride in a gaseous state.

Based on observations from previously distilled ER sediment, the material consisted of fine particulates. Consequently, the distilled sediment would best be loaded into an OR basket that would contain such fines (e.g., an existing basket with a nominal 10- $\mu$ m porosity). The basket would then be immersed in the OR salt (LiCl-Li<sub>2</sub>O) at 650°C and configured as a cathode between adjacent anodes. Polarization of this system would drive the actinide oxides, and to a certain extent rare earth oxides, to metal, while the liberated oxygen ions would simultaneously diffuse through the salt phase (i.e., electrolyte) and become oxidized to gaseous oxygen at the anodes, where it would be discharged from the system.

Once reduced, the OR basket would be removed from the OR vessel, while allowing OR salt to drain away. The basket would then be subjected to an elevated temperature (around 700°C) and reduced

pressure (below 200 mTorr) in an existing RDS to distill away occluded OR salt.

The basket would then be introduced into the ER vessel and configured as the anode between adjacent cathode assemblies. Electrorefining the reduced sediment would collect uranium metal at the cathodes, while TRU and rare earths would partition to the ER salt as chlorides. Thus, the uranium in the ER sediment would be recovered as uranium metal, while the TRU and rare earth constituents would accumulate in the ER salt, just as they do with the baseline pyrochemical process for uranium oxide fuels. Consequently, the recovery of actinides from ER sediment via oxide reduction in the OR vessel is a baseline approach, as it primarily uses existing equipment and proven operations. The primary drawback to this approach is the number of operating steps with its accompanying material handling requirements, particularly the need to first remove the sediment from the ER vessel.

#### 4.2 Oxide Reduction in ER Vessel

To obviate the need for ER sediment removal and subsequent ex situ actinide recovery, an in situ approach has been proposed by reducing the oxidized sediment within the ER vessel. Although, the practicality of actinide recovery using this approach is questionable.

Converting the oxidized ER sediment to metal in the ER vessel would require suitable reducing conditions in the system, which could be accomplished electrolytically or chemically. An electrolytic approach could be accomplished by configuring the ER crucible as the cathode with inert anodes suspended in the ER salt. Polarization of this cell configuration would initially drive uranium in the salt phase to deposit as metal on the crucible surfaces. Chlorine gas would initially form at the inert anodes, which would be discharged from the cell and require some type of off-gas capture system to preclude chlorine gas from escaping into the HFEF main cell atmosphere.

Once the ER salt approached the depletion of uranium under a continued polarization of the cell, TRU constituents would then be reduced to metal on the crucible surfaces, followed by rare earth constituents. Once the ER salt was depleted of U/TRU and rare earths under continued polarization, the cell would move towards reduction of the LiCl/KCl eutectic salt, creating the conditions for electrolytic reduction of actinide oxides in the ER sediment. Accordingly, U/TRU oxides, and to a certain extent rare earth oxides, would be reduced to metal, while the liberated oxygen ions would simultaneously diffuse through the salt phase and become oxidized to gaseous oxygen at the anodes.

Once all the ER sediment was reduced to metal by this approach and the salt was presumably depleted of oxygen ions, the crucible would be configured as an anode and existing cathode assemblies would be suspended in the ER salt pool. The polarization of this electrochemical cell would progressively oxidize rare earth metals, TRU metals, and uranium metal in contact with the crucible to the salt phase as chlorides, while simultaneously depositing and eventually recovering uranium metal at the cathode assemblies.

A chemical reduction variation of this approach would include an incremental introduction of lithium metal to the ER salt in lieu of an electrochemical reduction. Such a variation would theoretically yield similar results in terms of reducing the uranium, TRU, and rare earth chlorides in the ER salt to their respective metals that would precipitate within the crucible. Additional lithium metal introduction would then convert the U/TRU, and to a certain extent rare earth oxides, in the sediment to metal, forming oxygen ions within the salt phase. An electrolytic removal of the oxides would then be necessary with an inert anode, as described previously to deplete the salt of oxygen ions. The rare earth metals, TRU metals, and uranium metal in contact with the crucible could then be progressively oxidized to the salt phase as chlorides, as described previously.

A primary concern with the reduction of sediment oxides in the ER vessel is the entire depletion of uranium trichloride, as well as all fuel constituents more active than uranium trichloride, from the ER salt phase in order to effect the subsequent in situ reduction of the ER sediment oxides. Furthermore, given the limited ability of a lithium-based reducing system to completely reduce rare earth oxides, the presence

of some sediment composed of rare earth oxides would persist at the bottom of the ER crucible.

Another primary concern with this approach is the formation of TRU and rare earth metals on the stainless-steel crucible, due to intermetallic formations between the reduced metals and stainless-steel components. This is of particular concern with plutonium metal formation, which can form a low melting point eutectic with iron at 410°C, [3] well below the normal ER operating temperature at around 500°C. To address this concern, a separate step could be introduced into this approach to electrolytically deposit and completely remove TRU and rare earth metals onto dedicated and removable cathodes. Afterwards, converting the ER sediment oxides to metal could proceed as previously described.

Another primary concern with this approach is the formation of fuming potassium metal upon reduction of the ER sediment. It has long been understood that oxide reduction is not plausible in a LiCl/KCl eutectic system, as both an electrolytic reduction and lithium metal addition would generate potassium metal, which is highly volatile at the normal ER operating temperature. Given the above concerns, the practically of reducing ER sediment oxides in situ is doubtful.

#### 4.3 Chlorine

Recovering actinide oxides from ER sediment via reaction with gaseous chlorine has been proposed, which could include both in situ and ex situ approaches. An in situ approach would involve sparging chlorine gas into the ER salt pool such that the gas contacts and reacts with oxides in the sediment. A thermodynamic stability analysis was performed using a Gibbs energy minimization (GEM) model to assess the outcome of this approach. [1] Inputs to the model included a nominal 12-kg loading of ER salt and a nominal 1-kg loading of sediment, each at concentrations listed in Tables 1–4. The model also assumes ideal mixing and unit activities. To limit the number of constituents in the model, the makeup of the input salt and sediment compounds were constrained to the major species (i.e., LiCl, KCl, and Ar) and select species of interest, including U, Pu (representing TRU constituents), Nd (representing rare earth constituents) metals, their oxides (including UO<sub>2</sub>, Pu<sub>2</sub>O<sub>3</sub>, and Nd<sub>2</sub>O<sub>3</sub>), and their chlorides (including UCl<sub>3</sub>, PuCl<sub>3</sub>, and NdCl<sub>3</sub>). An excess of gaseous chlorine in this system over a temperature range of 0–500°C produced an outcome of possible compounds based on GEM and available compounds in the software's database, as shown in Figure 4.

Results of the GEM model for an in situ chlorination of sediment in the ER salt pool identify the chlorination of trivalent plutonium and neodymium oxides to their respective trivalent chlorides, as substantiated by the following favored reactions. [1]

$2 \operatorname{Pu}_2\operatorname{O}_3 + 6 \operatorname{Cl}_2(g) \to 4 \operatorname{Pu}\operatorname{Cl}_3 + 3 \operatorname{O}_2(g)$	$\Delta G_{Rx,500C} = -200 \text{ kJ}$	(2)
$2 \operatorname{Nd}_2\operatorname{O}_3 + 6 \operatorname{Cl}_2(g) \rightarrow 4 \operatorname{NdCl}_3 + 3 \operatorname{O}_2(g)$	$\Delta G_{Rx,500C} = -235 \text{ kJ}$	(3)

The resultant oxygen gas from the above reactions would likely participate in other reactions within the system, particularly with uranium compounds. The presence of trivalent plutonium chloride in this system, as opposed to the tetrachloride, is notable.



Figure 4. Equilibrium content of gaseous chlorine with ER salt with sediment.

In contrast, the uranium compounds in this system react to form a variety of oxychlorides, as opposed to pure chlorides like plutonium and neodymium exhibited in Equations 2 and 3. Rather, uranium dioxide could react with chlorine directly or in combination with uranium trichloride to form various oxychlorides per the following favored reactions.

$2 \text{ UO}_2 + \text{Cl}_2(g) \rightarrow 2 \text{ UO}_2\text{Cl}$	$\Delta G_{Rx 500C} = -57 \text{ kJ}$	(4)
2 2(8) 2	10,0000	

$$UO_2 + Cl_2(g) \rightarrow UO_2Cl_2$$
  $\Delta G_{Rx,500C} = -45 \text{ kJ}$  (5)

$$2 \text{ UO}_2 + 2 \text{ UCl}_3 + \text{Cl}_2(g) \rightarrow 4 \text{ UOCl}_2$$
  $\Delta G_{\text{Rx},500\text{C}} = -268 \text{ kJ}$  (6)

$$2 \text{ UO}_2 + 2 \text{ UCl}_3 + 3 \text{ Cl}_2(g) \rightarrow 4 \text{ UOCl}_3$$
  $\Delta G_{\text{Rx},500\text{C}} = -308 \text{ kJ}$  (7)

The absence of any uranium dioxide and uranium trichloride in this system due to the above reactions and excess chlorine in the system is notable. Any remaining uranium trichloride would react with excess chlorine to form uranium tetrachloride, as shown in Figure 4 and per the reaction below.

$$2 \operatorname{UCl}_3 + \operatorname{Cl}_2(g) \to 2 \operatorname{UCl}_4 \qquad \qquad \Delta G_{\operatorname{Rx},500C} = -193 \text{ kJ}$$
(8)

A drawback to an in situ chlorination approach is the potential attack of elemental chlorine or uranium tetrachloride on the stainless-steel components of the ER. To avoid contacting the ER system with gaseous chlorine at a temperature around 500°C, an ex situ chlorination route could be taken. Specifically, the ER sediment could be removed from the ER and the adhering salt distilled away in an RDS. The distilled sediment could then be contacted with gaseous chlorine in a separate apparatus to re-chlorinate sediment constituents. Applying an excess of chlorine to a nominal 1 kg of ER sediment in a GEM model produced compounds as a function of temperature per the plot in Figure 5.



Figure 5. Equilibrium content of gaseous chlorine with ER sediment.

Modeling results of an ex situ chlorination of ER sediment reveal the formation of trivalent plutonium and neodymium chlorides and various uranium oxychlorides around 500°C. The ex situ GEM model was extended to 1000°C to encompass a distillation operation to possibly remove the plutonium and neodymium chloride while leaving behind uranium oxide. However, the model revealed the formation of plutonium oxide at elevated temperatures in the presence of uranium oxides and oxychlorides.

Neither the in situ nor ex situ approach to re-chlorinate ER sediment with gaseous chlorine offers any compelling benefit to recovering actinides. While the in situ approach identifies the formation of plutonium trichloride in the ER salt, the uranium trichloride is converted into a variety of possible uranium oxychloride compounds, the solubilities of which in the ER salt are not well defined. Furthermore, any remaining uranium trichloride is converted to uranium tetrachloride, which along with gaseous chlorine can be corrosive to the stainless-steel components within the ER. Thus, using chlorine gas to re-chlorinate and recover actinides within the process does not appear to be a desirable option.

### 4.4 Hydrogen Chloride

Recovering actinide oxides from ER sediment via reaction with gaseous hydrogen chloride has been proposed, which could also include both in situ and ex situ approaches. An in situ approach would involve sparging hydrogen chloride gas into the ER salt pool such that the gas contacts and reacts with the oxides in the sediment. A thermodynamic stability analysis was performed using a GEM model to assess the outcome of this approach. [1] Using the same input parameters and assumptions for a GEM model as for chlorine, an outcome of possible compounds of the GEM for an in situ hydrogen chloride approach to

ER salt and sediment is shown in Figure 6.



Figure 6. Equilibrium content of hydrogen chloride gas with ER salt and sediment.

Results of the GEM model for in situ hydrochlorination of sediment in the ER salt pool identify the conversion of trivalent plutonium and neodymium oxides to their respective trivalent chlorides, as substantiated by the following favored reactions. [1]

$$Pu_2O_3 + 6 HCl(g) → 2 PuCl_3 + 3 H_2O(g)$$
   
ΔG<sub>Rx,500C</sub> = -119 kJ (9)

$$Nd_2O_3 + 6 HCl(g) \rightarrow 2 NdCl_3 + 3 H_2O(g)$$
  $\Delta G_{Rx,500C} = -137 kJ$  (10)

The resultant moisture from the above reactions would likely participate in other reactions within the system, particularly with uranium compounds. Per the GEM model for this system, the initial uranium metal and uranium trichloride likely react with hydrogen chloride to form uranium tetrachloride, which in turn could react with uranium dioxide to form uranium (IV) oxychloride, per the following combined reactions.

$$U + UO_2 + 4 HCl(g) \rightarrow 2 UOCl_2 + 2 H_2(g)$$
  $\Delta G_{Rx,500C} = -435 \text{ kJ}$  (11)

$$2 \text{ UCl}_3 + 2 \text{ UO}_2 + 2 \text{ HCl}(g) \rightarrow 4 \text{ UOCl}_2 + \text{H}_2(g) \qquad \Delta G_{\text{Rx},500\text{C}} = -69 \text{ kJ}$$
 (12)

The formation of moisture from the above reactions appears to mitigate the uranium (IV) oxychloride formation by generating uranium dioxide and hydrogen chloride gas per the following reaction.

$$UOCl_2 + H_2O(g) \rightarrow UO_2 + 2 HCl(g) \qquad \qquad \Delta G_{Rx,500C} = -53 \text{ kJ}$$
(13)

Similar to elemental chlorine, this in situ approach does not address the potential attack of hydrogen chloride on the stainless-steel components of the ER. To avoid such conditions, an ex situ approach with

ER sediment could be taken. Specifically, the sediment could be removed from the ER, and the adhering salt distilled away in an RDS. The distilled sediment could then be contacted with gaseous hydrogen chloride to re-chlorinate the constituents within the sediment. Applying an excess of hydrogen chloride to a nominal 1 kg of ER sediment in a GEM model produced compounds as a function of temperature per the plot in Figure 7.



Figure 7. Equilibrium content of hydrogen chloride gas with ER sediment.

Modeling results of an ex situ chlorination of ER sediment reveal the formation of trivalent plutonium and neodymium chloride along with moisture, likely in accordance with Equations 9 and 10. Uranium dioxide remains largely unperturbed in this system as hydrogen chloride is ineffective at displacing oxygen with chlorine to produce uranium chloride and water (see reaction below) as it does for plutonium and neodymium oxides in Equations 9 and 10.

$$UO_2 + 4 HCl(g) \rightarrow UCl_4 + 2 H_2O(g) \qquad \qquad \Delta G_{Rx,500C} = +143 \text{ kJ}$$
(14)

Extending the model to 1000°C to encompass a distillation option for plutonium and neodymium chloride removal from uranium dioxide reveals a partial conversion of these trichlorides to oxychlorides.

An in situ approach to re-chlorinating ER sediment with gaseous hydrogen chloride does not provide a convincing case for actinide recovery. While the in situ approach identifies the formation of plutonium trichloride in the ER salt, the uranium trichloride is entirely consumed in the formation of uranium oxychloride, the solubility of which in the ER salt is not well defined. Thus, uranium oxide and oxychloride would likely remain as sediment in the ER crucible.

An ex situ approach to re-chlorinating ER sediment with gaseous hydrogen chloride identifies the formation of plutonium and neodymium trichlorides that could be distilled away from uranium dioxide

and returned to the ER salt pool. However, the benefit of this approach could be tempered by the possible formation of plutonium and neodymium oxychlorides at distillation temperatures, similar to the outcome exhibited in Figure 7. Thus, an ex situ option with hydrogen chloride would require further study to investigate the extent of plutonium and neodymium oxychloride formation during the distillation step.

#### 4.5 Carbon Tetrachloride

Recovering actinide oxides from ER sediment via reaction with gaseous carbon tetrachloride is another option with both in situ and ex situ approaches. An in situ approach would involve sparging carbon tetrachloride gas into the ER salt pool such that the gas contacts and reacts with the oxides in the sediment. This approach is based on prior work by Rycerz et al., who chlorinated uranium dioxide using carbon tetrachloride. [4] Specifically, uranium dioxide powder was placed in an alumina crucible inside a quartz reactor within an electric resistance furnace. Argon gas saturated with carbon tetrachloride vapor was passed through the uranium dioxide bed at 550°C for 15 hours, forming uranium tetrachloride. Then the argon and carbon tetrachloride gas flow was replaced with pure hydrogen gas to reduce the uranium tetrachloride at 550°C for 20 hours, forming a high purity (99.9%) uranium trichloride. No additional information regarding material mass (i.e., batch size) or gas flow rates were given to assess the efficiency of the reaction, nor was any mechanism proposed for this reaction.

A thermodynamic stability analysis was performed using a GEM model to assess the outcome of this approach. [1] Using the same input parameters and assumptions for a GEM model used for prior options, an outcome of possible compounds for an in situ carbon tetrachloride approach to ER salt and sediment is shown in Figure 8.

Results from the GEM model for the in situ re-chlorination of sediment in the ER salt pool are consistent with the conversion of uranium dioxide to uranium tetrachloride observed by Rycerz et al., likely per the following favored reaction. [1]

$$UO_2 + CCl_4(g) \rightarrow UCl_4 + CO_2(g)$$
  $\Delta G_{Rx,500C} = -252 \text{ kJ}$  (15)

Indeed, the model identified a similar conversion of trivalent plutonium and neodymium oxides to their respective trivalent chlorides, as substantiated by the following favored reactions. [1]

$$2 \operatorname{Pu}_{2}O_{3} + 3 \operatorname{CCl}_{4}(g) \to 4 \operatorname{Pu}Cl_{3} + 3 \operatorname{CO}_{2}(g) \qquad \Delta G_{\operatorname{Rx},500C} = -1424 \text{ kJ}$$
(16)

$$2 \operatorname{Nd}_{2}O_{3} + 3 \operatorname{CCl}_{4}(g) \to 4 \operatorname{NdCl}_{3} + 3 \operatorname{CO}_{2}(g) \qquad \Delta G_{\operatorname{Rx},500C} = -1458 \text{ kJ}$$
(17)

The carbon tetrachloride option yields a desired outcome of driving not only the plutonium and neodymium oxides to their respective trichlorides but also the uranium dioxide to its tetrachloride. However, uranium tetrachloride would require subsequent uranium metal addition or hydrogen gas sparging to drive it to the trichloride. The presence of uranium tetrachloride and carbon tetrachloride also introduce a corrosion concern for the ER stainless-steel components.



Figure 8. Equilibrium content of carbon tetrachloride gas with ER salt and sediment.

A principal concern with the use of carbon tetrachloride is its toxicity, causing it to be highly regulated, if not banned, in industry. Consequently, the capture and decomposition of excess carbon tetrachloride would likely be necessary in the HFEF main cell. What is also troublesome is the possible formation of phosgene gas, as indicated by the GEM model, which would reinforce the likely need for off-gas capture and decomposition systems. The GEM model for this system also suggests the possible decomposition of carbon tetrachloride to carbon and chlorine gas, which could be catalyzed by products of corrosion. [5] Consequently, the possibility of carbon dusting, perhaps from the following decomposition reaction, within the ER salt crucible would need to be addressed.

$$\operatorname{CCl}_4(g) \to \operatorname{C} + 2 \operatorname{Cl}_2(g)$$
  $\Delta G_{\operatorname{Rx},500\mathrm{C}} = -12 \text{ kJ}$  (18)

An ex situ approach could be pursued by first removing the sediment from the ER vessel, distilling away adhering ER salt and separately contacting it with carbon tetrachloride. A GEM model was performed with such an ex situ approach, revealing essentially the same outcome as an in situ approach, albeit with lower uranium, plutonium, and neodymium chloride concentrations, given the headend removal of the ER salt phase from the sediment. Thus, the ex situ approach does not appear to offer any significant benefit over an in situ approach, other than avoiding potential impacts to the ER.

While the application of carbon tetrachloride to ER sediment yields a desirable outcome of rechlorinating actinides and rare earths, it's complicated by the handling of this highly toxic material and its possible byproducts in addition to potential corrosion and carbon dusting concerns. Consequently, in situ and ex situ approaches to the use carbon tetrachloride for ER sediment re-chlorination do not appear to be a reasonable path forward.

#### 4.6 Zirconium Tetrachloride

Recovering actinide oxides from ER sediment via reaction with zirconium tetrachloride is another option, which could be performed in situ or ex situ. An in situ approach would involve the addition of zirconium tetrachloride to the ER salt pool, enabling it to contact and react with the oxides in the sediment. This approach is based on prior work by Sakamura et al., who chlorinated uranium dioxide along with other actinide and rare earth oxides with zirconium tetrachloride. [6] Specifically, zirconium tetrachloride was added to lithium chloride – potassium chloride eutectic salt at 500°C in contact with separate additions of lanthanum, neodymium, and yttrium sesquioxides and cerium, uranium, and plutonium dioxides. The sesquioxides were successfully converted to their respective trichlorides with zirconium tetrachloride; however, the dioxides required zirconium metal in addition to zirconium tetrachloride to effectively convert these oxides to their respective trichlorides. They observed conversion of the dioxides to oxychlorides in the absence of concomitant zirconium metal.

A thermodynamic stability analysis was performed using a GEM model to assess the outcome of this approach. [1] The same input parameters and assumptions for a GEM model used for prior options were applied here with the exception that zirconium metal was input at a 1:3 ratio with excess zirconium tetrachloride to facilitate the conversion of dioxides to trichlorides. An outcome of possible compounds for an in situ zirconium tetrachloride approach to ER salt and sediment is shown in Figure 9.



Figure 9. Equilibrium content of zirconium tetrachloride with ER salt and sediment.

Results of the GEM model for in situ re-chlorination of sediment in the ER salt pool with zirconium tetrachloride and zirconium metal are consistent with the results observed by Sakamura et al. Re-chlorinating sesquioxides likely proceed per the following favored reactions. [1]

$$2 Pu_2O_3 + 3 ZrCl_4 \rightarrow 4 PuCl_3 + 3 ZrO_2 \qquad \Delta G_{Rx,500C} = -802 kJ$$
(19)

$$2 \text{ Nd}_2\text{O}_3 + 3 \text{ ZrCl}_4 \rightarrow 4 \text{ NdCl}_3 + 3 \text{ ZrO}_2 \qquad \Delta G_{\text{Rx},500\text{C}} = -837 \text{ kJ}$$
(20)

Re-chlorinating dioxides likely occurs in accordance with the following favored reaction.

$$4 \text{ UO}_2 + 3 \text{ ZrCl}_4 + \text{Zr} \rightarrow 4 \text{ UCl}_3 + 4 \text{ ZrO}_2 \qquad \Delta G_{\text{Rx},500\text{C}} = -546 \text{ kJ}$$
(21)

Regardless of a sesquioxide or dioxide input for the ER sediment, the outputs for this in situ approach are the respective trichlorides and zirconium dioxide. Per the model, excess zirconium metal is apparently consumed by excess zirconium tetrachloride to form zirconium monoxide per the following reaction.

$$ZrCl_4 + 3 Zr \rightarrow 4 ZrCl$$
  $\Delta G_{Rx \ 500C} = -36 \text{ kJ}$  (22)

It is possible that zirconium monochloride, in combination with zirconium tetrachloride, could act on subsequent uranium dioxide additions, yielding uranium trichloride and zirconium oxide, per the following reaction.

$$3 \text{ UO}_2 + 2 \text{ ZrCl}_4 + \text{ZrCl} \rightarrow 3 \text{ UCl}_3 + 3 \text{ ZrO}_2 \qquad \Delta G_{\text{Rx},500\text{C}} = -401 \text{ kJ}$$
(23)

However, zirconium monochloride in the ER salt could interfere with subsequent uranium electrorefining operations, as the monochloride would likely reduce to zirconium metal on a cathode surface preferential to uranium metal. Thus, the management of zirconium metal and chloride in the ER would need to be considered.

A primary advantage of an in situ re-chlorination with zirconium tetrachloride is converting the oxides in the ER sediment to their respective trichlorides without introducing or generating a significant corrosive compound. Consequently, attack of stainless-steel components in the ER should not be a concern.

A primary disadvantage to this approach is the inability to avoid the need for sediment removal in the ER crucible, as the current U/TRU and rare earth sediment would be replaced with zirconium oxide sediment. Thus, the periodic removal of zirconium oxide particulate would be required.

An ex situ approach could be pursued by first removing the sediment from the ER vessel, placing it within a porous metal basket (e.g., an ER anode basket), and suspending it in the ER salt pool. Zirconium tetrachloride and metal could then be added to the basket to effect the re-chlorination of sediment oxides per reactions shown in Equations 19 –21. An advantage to this ex situ approach is that resultant actinide and rare earth trichlorides could diffuse into the ER salt pool while zirconium oxide particulate should stay in the basket. The basket could then be removed from the ER and subjected to RDS conditions to remove adhering ER salt. The distillate could be returned to the ER salt pool, and the dried zirconium product could be removed and disposed. A disadvantage to an ex situ approach is the possible addition of zirconium monochloride to the ER salt pool, which would require management as previously described.

An in situ or ex situ zirconium tetrachloride approach appears to be promising for actinide and rare earth recovery and could require fewer operations than the baseline approach of oxide reduction in the OR vessel. However, one technical risk associated with a zirconium tetrachloride approach is a likely complication with subsequent actinide removal once a significant bed of zirconium oxide is formed. In other words, if actinides oxides of interest (i.e., TRU oxides) remained in a zirconium oxide particulate, it could be difficult to recover them through a baseline approach of oxide reduction in the OR vessel. These difficulties stem from the electrical insulating properties of zirconium oxide that could preclude electrolytic reduction of sediment oxides and the likely formation of lithium zirconate in the OR vessel. Subsequent contact with lithium zirconate in the ER salt could lead to its reaction with uranium trichloride in the ER salt to form uranium dioxide via the following reaction and contribute to the buildup of sediment in the ER crucible.

$$6 \text{Li}_2 \text{ZrO}_3 + 4 \text{UCl}_3 \rightarrow 12 \text{LiCl} + 4 \text{UO}_2 + 5 \text{ZrO}_2 + \text{Zr} \qquad \Delta G_{\text{Rx},500\text{C}} = -821 \text{ kJ}$$
(24)

Thus, there would need to be assurance that the zirconium oxide product is free from actinides of interest in an in situ or ex situ approach with zirconium tetrachloride.

## 4.7 Uranium Trichloride

Recovering actinide oxides from ER sediment via elevated concentrations of uranium trichloride is another option, which could be performed in situ or ex situ. However, this approach would be limited to re-chlorinating TRU and rare earth oxides and not uranium oxide. Indeed, uranium oxide would be discharged from the ER in this approach, while TRU and rare earth constituents would be returned to the ER salt.

A GEM model of the ER salt crucible prior to sediment removal using the same input parameters as previous options reveals the makeup of constituents shown in Figure 10.



Figure 10. Equilibrium content of ER salt and sediment with current uranium trichloride concentration.

Results of the GEM model of the ER salt and sediment prior to altering the uranium trichloride concentration suggest that the majority of the uranium in the ER sediment is uranium dioxide (~68%) with significant fractions of uranium (III) oxychloride (~24%) and uranium (IV) oxychloride (~8%), assuming the oxychlorides are insoluble in the ER salt phase. The model also suggests that plutonium and neodymium in the ER sediment are predominantly in the trivalent oxychloride state, again assuming these oxychlorides are insoluble in the ER salt phase. The plutonium and neodymium oxychloride concentrations in the ER sediment are affected by uranium trichloride and uranium metal concentrations in the ER sediment. Thus, if uranium metal, which is already at a low concentration in the sediment, was eliminated via anodic dissolution and the uranium trichloride concentration was elevated to 19 wt% uranium as the trichloride (for comparison to related work [7]), a GEM model reveals the change in constituent makeup as shown in Figure 11.



Figure 11. Equilibrium content of ER salt and sediment with elevated uranium trichloride concentration.

Results of the ER salt and sediment with an elevated uranium trichloride concentration reveal a larger uranium oxychloride fraction and smaller plutonium and neodymium oxychloride fractions, which are likely based on the following near-equilibrium reaction at 500°C.

 $PuOCl + UCl_3 \leftrightarrow UOCl + PuCl_3 \qquad \Delta G_{Rx,500C} = +5 \text{ kJ}$ (25)

Accordingly, as the uranium trichloride concentration is elevated, the forward reaction in Equation 25 is promoted. Furthermore, the forward reaction of Equation 25 becomes favored above 901°C. Thus, if the ER sediment were removed from the ER crucible at this point and subjected to ER salt distillation conditions, as previously described, plutonium chloride could be recovered in the distillate and returned to the ER salt pool. Also, uranium oxychlorides would decompose, as noted previously in Equation 1. In the case of neodymium oxychloride, an elevated uranium trichloride concentration promotes the formation of neodymium trichloride via the following reaction.

$$NdOCl + UCl_3 \rightarrow UOCl + NdCl_3$$
  $\Delta G_{Rx,500C} = -10 \text{ kJ}$  (26)

A disadvantage to elevated uranium trichloride concentrations in the ER salt would be the impacts on uranium electrorefining and U/TRU recovery operations. Thus, this approach might be better suited to an ex situ operation. As such, the ER sediment would first be removed and loaded into a porous steel basket (e.g., 10-micron nominal porosity) and suspended in the ER vapor space to drain away as much salt as reasonably achievable. The basket would then be immersed in a separate pool of ER salt with a high concentration of uranium trichloride (e.g., ternary feedstock salt). Mixing the sediment while immersed in ternary salt would likely aid the re-chlorination of TRU and rear earth oxychlorides or oxides to their respective trichlorides. The basket would then be removed from the ternary salt, allowed to drain, and

subjected to ER salt distillation conditions. The distillate would be recovered and returned to the ER salt pool, while the dried solids, which should predominantly consist of uranium dioxide, could be discarded. The ternary salt would be reserved for subsequent re-chlorination operations or for periodic additions to the ER salt pool as needed for uranium trichloride concentration management.

## 5. Summary and Recommendations

A summary of ER sediment re-chlorination options described in this study along with some of their primary considerations is shown in Table 6.

No.	Option (or chlorinating agent)	Considerations
1	Oxide reduction in OR vessel	An ex situ option requiring sediment removal and multiple steps to effect re- chlorination
		A baseline approach, as it uses existing equipment and proven operations
2	Oxide reduction in ER vessel	Results in the entire depletion of U/TRU and rare earths from salt phase
		Material concerns for deposition of TRU and rare earth metals
		Potential for fuming potassium metal
		Not considered a practical option
3	Chlorine	Uranium oxide forms oxychlorides in lieu of chlorides; thus, sediment removal still required for in situ option
		Uranium trichloride converted to uranium oxychlorides
		Concerns with corrosion of ER stainless-steel components
		Neither in situ nor ex situ options offer a compelling benefit
4	Hydrogen chloride	Uranium oxide forms oxychlorides in lieu of chlorides; thus, sediment removal still required for in situ option
		Uranium trichloride is converted to tetrachloride or oxychlorides
		Concerns with corrosion of ER stainless-steel components
5	Carbon tetrachloride	Only option that could potentially re-chlorinate entire sediment in situ
		Uranium trichloride is converted to tetrachloride, requiring subsequent reduction back to the trichloride
		Toxicity of feed (carbon tetrachloride) and possible byproduct (phosgene)
		Concerns with corrosion of ER stainless-steel components
		Possible decomposition of carbon tetrachloride and consequent carbon dusting
6	Zirconium tetrachloride	Chlorinates U/TRU and rare earths to trichlorides
		Forms zirconium oxide particulate requiring removal if performed in situ
		Requires management of excess zirconium chloride in ER salt
7	Uranium trichloride	Does not introduce any new constituents into ER salt system
		Need to address impacts to uranium electrorefining and U/TRU recovery for in situ option
		Uranium in sediment is discarded as oxide as opposed to recovered as chloride

Table 6. Summary of ER sediment re-chlorination options.

As a baseline approach, oxide reduction in the OR vessel (Option 1) is what all other options should be compared to in regard to costs versus benefits. Aside from a suitable ER sediment removal device, no other additional equipment is required. Indeed, a sediment removal device would be common to all other ex situ options. For reasons stated herein, oxide reduction in the ER vessel (Option 2), chlorine (Option 3), and hydrogen chloride (Option 4) lack viability or exhibit sufficient concerns to discourage their advancement.

As the only plausible in situ option, carbon tetrachloride (Option 5) should be explored further from an environmental perspective to assess the practical use and management of this toxic material and its potential byproducts before proceeding with any demonstration of this technique.

Pursuit of an ex situ approach for zirconium tetrachloride (Option 6) is recommended, as it would enable re-chlorination of U/TRU and rare earths without depositing zirconium oxide particulate in the ER crucible. An ex situ approach would also introduce less zirconium chloride into the ER system than an in situ approach.

With perhaps the least contamination of the ER system, pursuit of an ex situ approach with uranium chloride (Option 7) is also a viable option. This option would, however, require ER sediment removal, salt draining, and a separate salt and sediment contacting apparatus (e.g., hot fuel dissolution apparatus).

Given the common need of ER sediment removal for the recommended options, advancing a suitable particulate removal device is also recommended. Such should also be considered for the OR vessel to assess the presence of sediment in its crucible.

#### 6. References

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