

# **Theoretical Considerations on an Electrolytic Reduction Process for Reducing Spent Oxide Fuel**

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## **ABSTRACT**

A metal product obtained from an electrolytic reduction process, possesses less volume and radioactivity than those of the unprocessed spent oxide fuels. The chemical composition of the metal product varies according to the process condition. In this work, a basic study was performed to evaluate the chemical forms of the spent oxide fuel components in an electrolytic reduction process with the operation conditions. One of the most important operation conditions is the cell potential applied for the reduction cell. It is expected that  $\text{Pu}_2\text{O}_3$  is difficult to reduce even though the cell potential is negative enough to reduce the lithium oxide when the activity of  $\text{Li}_2\text{O}$  exceeds 0.003. The reduction of actinide oxides via the reduction of  $\text{Li}_2\text{O}$  is assumed to have a greater reduction yield than a direct reduction of the actinide oxides.

## **INTRODUCTION**

The advanced spent fuel conditioning process (ACP) has been developed to reduce the radioactivity and the heat load as well as the volume of spent oxide fuels by converting the oxides to metals. This pyrochemical separation process has been given

much attention as a promising option in the nuclear fuel cycle. In an electrolytic reduction process which is a main part of the ACP, the oxygen ions released from a cathode travel to the anodes leaving behind the metal elements and then they are oxidized to gas [Hur et al., 2003]. Uranium and transuranic elements (TRU) are recovered after being reduced to their corresponding metals and the high heat-generating elements are selectively separated from the product by being dissolved in the molten salt.

Metallization of the spent oxide fuels is accomplished in an electrolytic reduction cell where a molten LiCl is adopted as an electric medium and Li<sub>2</sub>O is added to increase the initial activity of the oxygen ion in the system [Gourishankar et al., 2002; Hur et al., 2003]. The operation conditions such as the initial Li<sub>2</sub>O concentration and the cell potential should be determined based on theoretical considerations. In this study, a thermodynamic approach is performed for the electrolytic reduction process so that a fundamental process analysis may be undertaken and a distribution of the nuclides may be evaluated in perspective. This work will draw a baseline for the experimental approaches and for an improvement of the linkages between the unit processes.

## **ELECTRODE REACTIONS**

The reactions on a cathode in an electrochemical reduction process can be categorized into a series of reductions and a direct electrochemical reduction process. In the series process [Hur et al., 2003], the electrochemical reduction of lithium ion from the dissolved Li<sub>2</sub>O and the chemical reaction between the reduced lithium metal and the metal oxides in the cathode take place in series and simultaneously as follows.





On the other hand, in the direct electrochemical reduction process [Gourishankar et al., 2002; Li et al., 2003], the metal species in the metal oxides are reduced by an electric force



At the anode, the produced oxygen ions from the cathode are oxidized to gas by releasing electrons to the anode for both reduction processes when an inconsumable material is used as the anode.



The overall reaction for the series of reductions is the same as the direct electrochemical reduction. However, the reaction conditions are somewhat different for the electrochemical reductions which are represented as Eqs.(1) and (3). In the following section, the reduction potentials for the metal oxides and the chemical reactions between the metal oxides and the lithium metal will be surveyed briefly.

## **CHEMICAL REACTIONS AND DECOMPOSITION POTENTIALS**

The chemical reactions denoted as Eq.(2) are the same as those of a lithium reduction process [Battles et al., 1994; Usami et al., 2002]. However, the amount of lithium metal is controllable in the electrolytic reduction process since the lithium metal

is produced in the same reaction cell by the electric current, unlike the lithium reduction process and the concentration of  $\text{Li}_2\text{O}$  in the melt cannot exceed the initial concentration for the electrolytic reduction process while that of the lithium reduction cell increases as the reductions of the metal oxides proceed.

The reactions between actinide oxides and lithium metal in a molten  $\text{LiCl}$  cell are listed in the Table 1 with the activity of  $\text{Li}_2\text{O}$ . As summarized in Table 1, most of the actinide oxides will be reduced into their corresponding metals and not metal chlorides in the cell. However,  $\text{AmO}_2$  is supposed to be  $\text{AmCl}_3$  by reacting with  $\text{Li}$  and  $\text{LiCl}$  when the activity of  $\text{Li}_2\text{O}$  is lower than 0.1631 and it is difficult to reduce  $\text{Pu}_2\text{O}_3$  by the lithium metal when the activity of  $\text{Li}_2\text{O}$  is higher than 0.003.

A combination of Eqs.(1) and (4) is the decomposition potential of  $\text{Li}_2\text{O}$  and that of Eqs.(3) and (4) is the decomposition potentials of the metal oxides, which are listed in Table 2. In the case of the direct electrochemical reduction, the cell potential is maintained between -2.39 and -2.47 V in order to reduce  $\text{UO}_2$  and not to reduce  $\text{Li}_2\text{O}$ . Accordingly, some actinide oxides such as  $\text{Am}_2\text{O}_3$ ,  $\text{PuO}$ , and  $\text{Pu}_2\text{O}_3$  will not be reduced to their metal forms and the lanthanide oxides except for  $\text{Eu}_2\text{O}_3$  will remain in the form of oxides. However, for the series of reductions, it is possible to reduce  $\text{PuO}$  and  $\text{Am}_2\text{O}_3$  into their metals by producing lithium metal and controlling the  $\text{Li}_2\text{O}$  activity as shown in Table 1.

## CONCLUSIONS

The reaction considerations are surveyed according to the reduction conditions on the basis of the calculated data for an electrolytic reduction of spent oxide fuel. The electrolytic reduction process is considered as a promising option among the pyrometallurgical technologies for treating spent oxide fuel due to its simplicity of not

handling an active reduction reagent such as lithium metal. The reduction of each oxide depends on the operation condition of the electrochemical reduction process. When the cell potential is controlled to within the range of -2.39 to -2.47 V for the purpose of reducing metal oxides while keeping the lithium oxide stable in the melt, named the direct electrochemical reduction, various actinide oxides will be reduced into their corresponding metals but  $\text{Am}_2\text{O}_3$ ,  $\text{PuO}$ , and  $\text{Pu}_2\text{O}_3$  are expected to be stable and remain in the form of an oxide. In the series of reductions process in which the reductions of metal oxides take place by way of a reduction of the lithium oxide, the cell potential is controlled enough to reduce the lithium oxide to lithium metal and the actinide oxides but for  $\text{Pu}_2\text{O}_3$  are supposed to be reduced to their metal forms. However, lanthanide oxides excluding  $\text{Eu}_2\text{O}_3$  are considered to maintain their oxide forms during the electrolytic reduction process in both conditions.

## REFERENCES

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Table 1. Actinides Reactions in an Electrolytic Reduction Reactor at 650 °C

Reaction	$\Delta G^*$	$a_{Li_2O}$	Reaction	$\Delta G^*$	$a_{Li_2O}$
$U_3O_8 + 16Li \leftrightarrow 3U + 8Li_2O$	107.0742	1	$AmO_2 + 4Li \leftrightarrow Am + 2Li_2O$	-96.9479	1
$U_3O_8 + 7Li + 9LiCl \leftrightarrow 3UCl_3 + 8Li_2O$	20.3502	$5.847 \times 10^{-2}$	$AmO_2 + Li + 3LiCl \leftrightarrow AmCl_3 + 2Li_2O$	20.3091	0.1631
$U_4O_9 + 18Li \leftrightarrow 4U + 9Li_2O$	-54.1543	1	$Am_2O_3 + 6Li \leftrightarrow 2Am + 3Li_2O$	10.6516	0.2496
$U_4O_9 + 6Li + 12LiCl \leftrightarrow 4UCl_3 + 9Li_2O$	96.8672	$2.287 \times 10^{-5}$	$Am_2O_3 + 6LiCl \leftrightarrow 2AmCl_3 + 3Li_2O$	166.9942	$8.389 \times 10^{-7}$
$UO_2 + 4Li \leftrightarrow U + 2Li_2O$	-14.7619	1	$PuO_2 + 4Li \leftrightarrow Pu + 2Li_2O$	-37.1980	1
$UO_2 + Li + 3LiCl \leftrightarrow UCl_3 + 2Li_2O$	155.1373	$1.770 \times 10^{-6}$	$PuO_2 + Li + 3LiCl \leftrightarrow PuCl_3 + 2Li_2O$	86.5883	$5.411 \times 10^{-4}$
$NpO_2 + 4Li \leftrightarrow Np + 2Li_2O$	-43.9893	1	$PuO + 2Li \leftrightarrow Pu + Li_2O$	6.9734	0.4031
$NpO_2 + Li + 3LiCl \leftrightarrow NpCl_3 + 2Li_2O$	107.1502	$9.076 \times 10^{-5}$	$Pu_2O_3 + 6Li \leftrightarrow 2Pu + 3Li_2O$	44.5364	$3.019 \times 10^{-3}$
			$Pu_2O_3 + 6LiCl \leftrightarrow 2PuCl_3 + 3Li_2O$	209.5849	$1.895 \times 10^{-8}$

\*(kJ/g-mol O)

Table 2. Decomposition Potentials of Metal Oxides at 650 °C

Reaction	E(V)	Reaction	E(V)	Reaction	E(V)
$Li_2O \rightarrow 2Li + 1/2O_2$	2.4728	$Ce_2O_3 \rightarrow 2Ce + 3/2O_2$	2.6492	$Nd_2O_3 \rightarrow 2Nd + 3/2O_2$	2.6705
$UO_2 \rightarrow U + O_2$	2.3963	$Dy_2O_3 \rightarrow 2Dy + 3/2O_2$	2.7458	$Pr_2O_3 \rightarrow 2Pr + 3/2O_2$	2.6641
$U_4O_9 \rightarrow 4U + 9/2O_2$	2.1921	$Er_2O_3 \rightarrow 2Er + 3/2O_2$	2.8128	$Sc_2O_3 \rightarrow 2Sc + 3/2O_2$	2.8255
$U_3O_8 \rightarrow 3U + 4O_2$	1.9179	$Eu_2O_3 \rightarrow 2Eu + 3/2O_2$	2.3791	$Sm_2O_3 \rightarrow 2Sm + 3/2O_2$	2.6834
$AmO_2 \rightarrow Am + O_2$	1.9704	$Gd_2O_3 \rightarrow 2Gd + 3/2O_2$	2.6962	$Tb_2O_3 \rightarrow 2Tb + 3/2O_2$	2.7629
$Am_2O_3 \rightarrow 2Am + 3/2O_2$	2.5279	$Ho_2O_3 \rightarrow 2Ho + 3/2O_2$	-2.7860	$Tm_2O_3 \rightarrow 2Tm + 3/2O_2$	-2.7749
$NpO_2 \rightarrow Np + O_2$	2.2448	$La_2O_3 \rightarrow 2La + 3/2O_2$	2.6408	$Y_2O_3 \rightarrow 2Y + 3/2O_2$	2.8263
$PuO_2 \rightarrow Pu + O_2$	2.2800	$Lu_2O_3 \rightarrow 2Lu + 3/2O_2$	2.7760	$Yb_2O_3 \rightarrow 2Yb + 3/2O_2$	2.6796
$Pu_2O_3 \rightarrow 2Pu + 3/2O_2$	2.7036				
$PuO \rightarrow Pu + 1/2O_2$	2.5089				