Equilibrium calculation for the electrolytic reduction process of the ACP

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The electrolytic reduction process is the most critical process of the advanced spent fuel conditioning process (ACP) since most of the chemical reactions take place during this reduction process in a molten salt bath. However, it is very difficult to observe the behavior of all the spent fuel elements by experiments. Therefore, a perspective calculation is required to predict how much the chemicals are distributed between the phases and which forms are stable in each phase.

Chemical equilibria take place during the electrolytic reduction process. The reduction process uses a porous magnesia filter and the materials to be reduced are loaded into the filter, which means the filter, the cathode of the electrolytic reduction cell, acts as a packed-bed reactor. The reductions of the metal oxides in the filter take place as follows.

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

$$M_xO_y + 2yLi = xM + yLi_2O \tag{2}$$

Lithium metal is produced by an electrolytic reaction in a molten Li_2O-LiCl cell and the reaction is denoted as Eq.(1). In this work, attention has been paid to the chemical reactions of Eq.(2) since an electrochemical reaction is controlled easily by the supplied current and the extents of the chemical reactions are determined by considering many candidates species. Uranium oxides, for example, can be reduced to U_4O_9, UO_2, and/or U when U_3O_8 is fed to the electrolytic reduction process. Therefore, the chemical reaction of U_3O_8 should be extended by considering all of the possible products as follows.

$$4U_3O_8 + 10Li = 3U_4O_9 + 5Li_2O \tag{2-1}$$

$$U_3O_8 + 4Li = 3UO_2 + 2Li_2O \tag{2-2}$$

$$U_3O_8 + 16Li = 3U + 8Li_2O \tag{2-3}$$

The amounts of the three uranium oxides and uranium metal are determined by minimizing the Gibbs free energy of the above system. The amount of lithium metal participating in reactions (2-1) to (2-3) is controlled by the current and the electrochemical reaction time for Eq.(1). Therefore, the amounts of the uranium oxides and the metal are also calculated with respect to the current and time.

In this work, the amounts of SF components during the electrolytic reduction process are calculated with respect to the reaction time under an assumption that the produced lithium metal is uniformly spread throughout the cathode and each metal-oxide system (e.g. U-O, Am-O, and Pu-O) behaves as a separated system.