

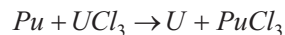
Thermodynamic Modelling of Molten Salt Electrorefining Process

EXECUTIVE SUMMARY

Molten salt electrorefining is the pyrochemical process for reprocessing metallic fuels. Modelling plays an important role in the development of the electrorefining process. A computer code, PRAGAMAN, has been developed for the simulation of the electrotransport behaviour of the various metal constituents during the electrorefining process. The code is based on the thermodynamic equilibria among the metals and chlorides of actinides, minor actinides and fission products in the anode/cathode and electrolyte salt respectively. The code enables incorporation of various combinations of anodes and cathodes such as liquid cadmium anode/cathode and solid anode/solid cathode and the possible conditions with respect to saturation of a given element in liquid cadmium.

OUTLINE

Modelling the molten salt electrorefining process is an integral part of the development programme for the process. Various types of models for the electrorefining have been developed around the world using equilibrium thermodynamics, finite element method and fluid mechanics based methods. The approach using equilibrium thermodynamics takes into consideration mass balance requirements and at the Gibbs energy of formation of various species in the molten salt and the anode/cathode. A typical equilibrium reaction taking place in the electrorefining cell among a pair of elements, say, U and Pu and their chlorides is as shown below



Similar reactions could be envisaged among the pairs of elements encountered in the spent fuel and their chlorides. Under the special restricted equilibrium conditions prevailing in the cell, the ratios of the activities of two elements in two phases in equilibrium are equal rather than the activities themselves being equal as in classical equilibrium. The equilibrium constant relationship is evaluated which involves activity coefficients of UCl_3 and $PuCl_3$ in the molten salt and in liquid cadmium. The total amount of solute metal at any step of electrotransport will remain constant even though the composition at the anode and cathode will change as equilibrium is established. Mass balance equations are established for various solute elements present in the electrorefiner. The equations are solved for the unknown compositions of U, Pu and other elements at anode, cathode and in the salt phase. In case of only U and Pu electrotransport, PRAGAMAN code has 16 different subroutines to solve the different sets of nonlinear equations depending on the conditions that could be encountered during the electrorefining cell. At each step of electrotransport, the condition at the anode and cathode can be any of the 16 different possibilities. The subroutines are called into an electrotransport loop which subsequently solves the nonlinear equations depending on the composition of the solute elements and salt phase at anode and cathode.

The computations have also shown that when both the liquid cadmium anode and cathode are unsaturated with respect to both U and Pu, then both get electrotransported at equal rates. That is, Pu/U ratios at the anode and cathode remain constant and equal under these conditions. However, when saturation with respect to one element in any one of the phases occurs, predominant transport of that element prevails.

As an example, a typical Pu profile is shown in Figure 2 where the feed conditions are such that U is initially saturated at the Cd anode. Therefore the rate of electrotransport of U or depletion rate from the Cd anode is faster than that for Pu. At around 16% electrotransport, U gets saturated at the cathode and this condition of saturation with respect to U at both anode and cathode prevails until 71% electrotransport. Until 71% electrotransport, there is no Pu electrotransport and therefore the amount of Pu at anode and cathode remains constant. After 71% electrotransport when U gets unsaturated at the anode, Pu again gets electrotransported to the Cd cathode.

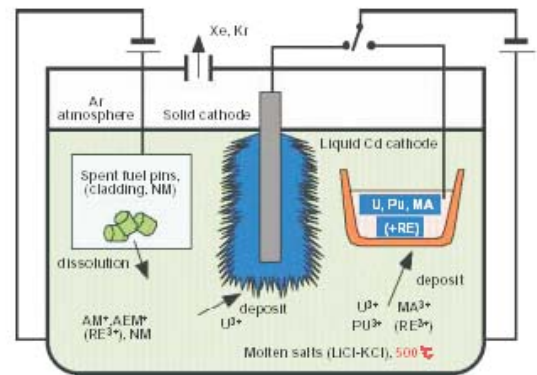


Fig. 1 : Schematic diagram of molten salt electrorefining process

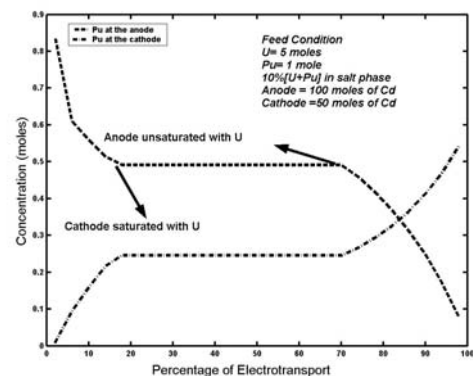


Fig. 2 : Simulated profile of Pu electrotransport from liquid Cd anode to liquid Cd cathode

■ ADDITIONAL INFORMATION ABOUT THE NUMERICAL METHODS USED IN THE MODEL

In the case of U and Pu only, there are 16 possible conditions with respect to the different possible combinations of liquid cadmium as anode/cathode and solid mandrel anode/cathode. All the different possibilities lead to different sets of nonlinear equations the degree of nonlinearity of which varies depending on the number of unknowns. The saturation conditions of U and Pu at both liquid cadmium anode/ cathode lead to sets of linear equations involving solution of sparse matrices. Conjugate Gradient method and Nelder Mead optimization method are some of the numerical methods used in the solution of nonlinear equations.

■ TYPICAL ELECTROTRANSPORT BEHAVIOUR TO A SOLID CATHODE

In the electrorefining process, when a solid cathode is used, deposition of U alone takes place due to the higher thermodynamic stability of PuCl_3 compared to UCl_3 . However, when the ratio of PuCl_3 to UCl_3 in the salt increases above 2, then Pu deposition will also occur.

The code enables computations for these cases also. The simulated electrotransport behaviour of U and Pu to a solid cathode is shown in Figure 3. It is seen from the figure that U alone gets transported until 65% of electrotransport. As U alone gets deposited, the ratio of PuCl_3 to UCl_3 increases. When the ratio reaches a value of 2, which is at 65 % electrotransport in this case, Pu also starts getting deposited at the cathode.

This deposition behaviour at solid cathode enables one to process the irradiated U-Zr blanket from a metal fuelled FBR. The blanket contains about 2% of Pu produced by breeding. Processing using a solid cathode removes U selectively, thus enriching the anode with respect to Pu. When the concentration of Pu in the anode reaches a value of 20-25%, roughly that of the core fuel, the processing is stopped and the anode constituents are mixed with spent core fuel from the reactor, for pyroprocessing using a liquid cadmium cathode.

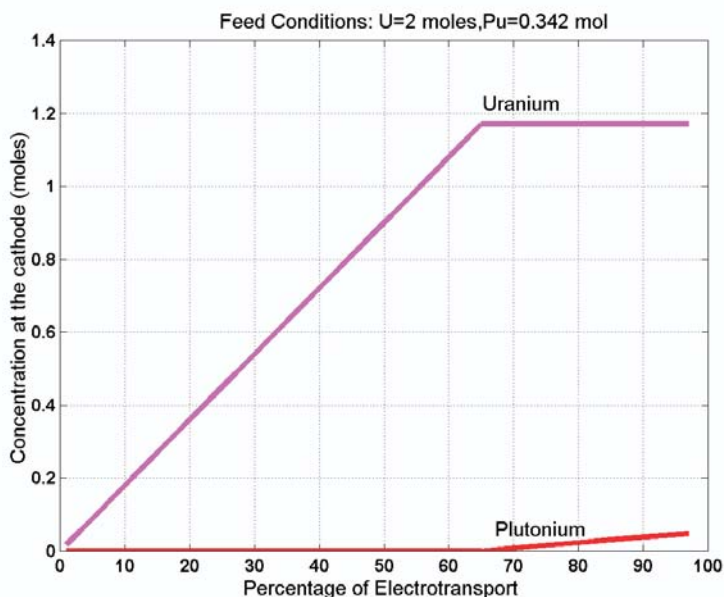


Fig. 3: Simulated electrotransport behaviour of U and Pu to a solid cathode

■ THERMODYNAMIC BASIS FOR THE SEPARATION OF ELEMENTS DURING ELECTRO PROCESS

The separation is achieved by exploiting the difference in the thermodynamic stabilities of the chlorides of U, Pu and the fission products. The highly electropositive alkali, alkaline earth and rare earth elements, whose chlorides are very stable, are easily oxidized but are difficult to reduce. The noble metals whose chlorides are the least stable, do not get oxidized and stay as metals in the anode itself. U and Pu whose chlorides are of intermediate stability are converted to their chlorides, get electro transported to the cathode where they are reduced and deposited as metals.

■ ACHIEVEMENT

Our own simulation code has been developed which can predict the transport behaviour for the various conditions that could be envisaged to prevail during the electro-refining process.

■ PUBLICATIONS ARISING OUT OF THIS STUDY AND RELATED WORK

1. Suddhasattwa Ghosh, B.Prabhakara Reddy and K.Nagarajan, Report No. IGC-278.
2. Suddhasattwa Ghosh, B.Prabhakara Reddy and K.Nagarajan, THERMANS 2006, University of Rajasthan, Jaipur.
3. K.Nagarajan, T.Subramanian, B.Prabhakara Reddy, P.R.Vasudeva Rao and Baldev Raj, *Nucl. Technol.* (In Press).

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