

Conf-930905--4

PARTITION OF ACTINIDES AND FISSION PRODUCTS  
BETWEEN METAL AND MOLTEN SALT PHASES -  
THEORY, MEASUREMENT, AND APPLICATION TO  
IFR PYROPROCESS DEVELOPMENT\*

by

John P. Ackerman and Terry R. Johnson  
Chemical Technology Division  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, Illinois 60439

OCT 01 1993  
OSTI

To be presented at

ACTINIDES-93  
International Conference  
Santa Fe, New Mexico  
September 19-24, 1993

The submitted manuscript has been authored  
by a contractor of the U. S. Government  
under contract No. W-31-109-ENG-38.  
Accordingly, the U. S. Government retains a  
nonexclusive, royalty-free license to publish  
or reproduce the published form of this  
contribution, or allow others to do so, for  
U. S. Government purposes.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

\*Work supported by the U. S. Department of Energy, Office of Nuclear Energy Research & Development, Contract W-31-109-Eng-38.

**MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

# Partition of Actinides and Fission Products between Metal and Molten Salt Phases – Theory, Measurement, and Application to IFR Pyroprocess Development\*

JOHN P. ACKERMAN and Terry R. Johnson

Chemical Technology Division,  
Argonne National Laboratory, Argonne, IL 60439 (U.S.A.)

## Abstract

The chemical basis of Integral Fast Reactor fuel reprocessing (pyroprocessing) is partition of fuel, cladding, and fission product elements between molten LiCl-KCl and either a solid metal phase or a liquid cadmium phase. The partition reactions are described herein, and the thermodynamic basis for predicting distributions of actinides and fission products in the pyroprocess is discussed. The critical role of metal-phase activity coefficients, especially those of rare earth and the transuranic elements, is described. Measured separation factors, which are analogous to equilibrium constants but which involve concentrations rather than activities, are presented. The uses of thermodynamic calculations in process development are described, as are computer codes developed for calculating material flows and phase compositions in pyroprocessing.

---

\*Work supported by the U.S. Department of Energy, Nuclear Energy Research and Development Program, under Contract W-31-109-Eng-38.

## 1. Introduction

Pyrochemical processing of metallic nuclear fuel is a key element of the Integral Fast Reactor (IFR) concept [1,2]. In the IFR concept, fuel is removed from the reactor and reprocessed, either at the reactor site or at a central reprocessing location. The transuranic (TRU) metals (mostly Pu, but also Np, Am, and Cm) in the spent fuel are essentially completely returned to the reactor as fresh fuel, and fission-product wastes are converted to forms suitable for geologic disposal.

IFR spent fuel is entirely metallic, except for minor amounts of noble gas, halogen, and chalcogen fission products. There are two kinds of spent fuel: blanket fuel, which is made up of uranium with 10 wt% zirconium plus a few wt% of fission product and TRU metals, and core fuel, which is similar except that TRU metals replace about 1/4 of the uranium, and the fission product content is greater. Neither core nor blanket fuel contains actinides having lower atomic number than uranium, and the ratio of all other TRU elements to plutonium is somewhat less than 1/100.

The spent fuel is treated in a pyrochemical process at a temperature near 775 K to recover the actinides [3]. This process has three key requirements. First, the fuel elements must be separated into two streams. A stream containing nearly TRU-free uranium is used to fabricate new blanket elements, and a stream that is TRU-rich (> 25% TRU) is used to fabricate new core fuel. Second, most, but preferably not all, of the fission products must be separated from the reprocessed fuel. Radioactivity from residual fission products supplements that due to TRU elements in the reprocessed fuel, and makes it even less attractive for diversion. Third, fission products and other waste must exit the process in a form suitable for preparation of satisfactory waste forms. In particular, the TRU content of waste streams should be small or nil.

In the IFR pyroprocess, spent metal fuel inside its stainless steel cladding is chopped into short (~1/4") segments and placed in a metal basket. The basket is lowered into molten LiCl-KCl inside the process vessel, which is called an "electrorefiner."

All the alkali and alkaline earth elements in the spent fuel are oxidized into the salt, along with most of the rare earth elements. This oxidation occurs by reaction with actinide chlorides, which are maintained at a concentration of about 2 mol% in the molten salt by periodic addition of an oxidant such as  $\text{UCl}_3$  or  $\text{CdCl}_2$ . The oxidation of the active metals occurs when they are exposed to the electrolyte, either immediately or in the subsequent electrotransport steps. The alkali, alkaline earth, and most of the rare earth chlorides remain in the salt until they are removed during salt purification (see below); halides and chalcogenides also remain in the salt phase. Cladding elements and "noble" metal (those less readily oxidized than zirconium) fission products are never perceptibly oxidized; they are removed from the electrorefiner as unreacted metal. All actinide and rare

earth elements (except Sm, and Eu, which behave like alkaline earth elements) partition between the salt and metal. Control of this partition allows electrotransport to be used for separate recovery of the pure uranium product and the TRU-rich product.

Next, a potential is applied between the basket and a product-collection cathode that is also inserted into the salt. The basket is made positive; it becomes an anode. When current flows, the actinide elements in the fuel are oxidized to chlorides and electrotransported through the salt phase. At the same time, an equivalent amount of actinide chloride is reduced to metal at the cathode. Actinides chlorides must exist in the salt for electrotransport to occur. The total amount of actinide chlorides does not change during electrotransport, but the amounts of individual actinide chlorides can increase or decrease.

Two kinds of cathodes are used: solid-mandrel cathodes and cathodes that comprise liquid cadmium in a ceramic crucible. Over a range of salt compositions that is much wider than would be required by the pyroprocess, only uranium deposits on solid-mandrel cathodes, because uranium metal is relatively stable toward reaction with the chlorides of the other actinides [4]. The TRU content of the solid cathode product is low, as required for fabrication of blanket fuel; more importantly, removal of uranium (only) is used to control the TRU- $\text{Cl}_3/\text{UCl}_3$  ratio in the salt, and, hence, the TRU/U ratio in the TRU-rich product, which is recovered in cadmium cathodes. Typically, a 20 kg (actinide content) batch of spent fuel is electrotransported through an electrolyte salt containing about 45 kg of actinide chlorides. From 13 to 20 kg of pure uranium is removed on solid cathodes, depending on the feed composition; the balance of the batch is removed as TRU-rich product using liquid cadmium electrodes.

Purification of the salt is required after several dozen batches of fuel have been processed so that fission product decay heating in the electrorefiner does not become excessive. Reactions between molten salt and liquid cadmium solutions will be used in a continuous salt purification cycle. Special high temperature centrifugal contactors, called "pyrocontactors," are being developed for the purpose [5]. They can be used wherever molten salt and liquid metal can be reacted without formation of solid phases. Pyrocontactors are very small, but they have enormous throughput; they are also expected to give excellent phase separations.

In the first step of the proposed purification cycle, the bulk of the actinide elements are reduced from the salt into a cadmium stream containing a controlled amount of lithium. Next, all but a few ppm of the remaining TRU elements are extracted from the salt by contact with excess uranium in cadmium. About 90% of the rare earths remains in the salt. A multi-stage pyrocontactor bank is selected for this step; use of countercurrent flows of metal and salt greatly enhances the selectivity of the extraction process. In a third step, the rare earth (and uranium) chlorides are removed from the salt, again by reduction with lithium in cadmium. In the fourth step, alkali and alkaline earth fission products are removed from the salt in a zeolite bed; a small fraction of the salt accompanies

the used zeolite bed to waste form fabrication. Finally, oxidant (cadmium chloride or uranium chloride) is added to the majority of the salt, and the TRU elements are oxidized back into the salt by contacting it with the cadmium from steps 1 and 2. The salt is returned to the electrorefiner purified of rare earth chlorides, yet its quantity and composition (U and TRU content) are such that it is ready for immediate use.

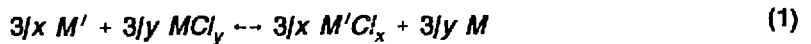
Because the distribution of rare earths and actinides among the product and waste streams is largely determined by partition between salt and metal phases, knowledge of partition behavior is essential for design, development, and operation of the pyrochemical fuel recovery process. Adequate thermodynamic information exists to predict compositions of anode, cathode, salt, and extraction streams with acceptable accuracy, and codes have been developed to facilitate the large number of complex calculations that are required for process development.

## 2. Chemical Basis

The thermodynamics of partition of actinides and lanthanides between metal and salt phases has been discussed previously [3,6-8]. The partition of the elements is largely determined by the stability of their chlorides [9] and the activity coefficients of the chlorides in LiCl-KCl and of the metals in cadmium solution. The activity coefficients of the rare earth and TRU actinide metals in cadmium tend to be small [10-13] and to differ considerably from each other. They may also be affected by interactions among the metals in multi-solute cadmium solutions. Activity coefficients of the salts, on the other hand, tend to have values closer to one and to be less variable [14].

The redox reaction can be written in general form as:

Reaction 1



The corresponding equilibrium constant expression is:

$$K = \frac{a_{M'Cl_x}^{3/x} a_M^{3/y}}{a_{M'}^{3/x} a_{MCl_y}^{3/y}} = \frac{\gamma_{M'Cl_x}^{3/x} \gamma_M^{3/y}}{\gamma_{M'}^{3/x} \gamma_{MCl_y}^{3/y}} \cdot \frac{X_{M'Cl_x}^{3/x} X_M^{3/y}}{X_{M'}^{3/x} X_{MCl_y}^{3/y}} \quad (2)$$

Here,  $a$  denotes activity,  $\gamma$  signifies activity coefficient, and  $X$  indicates mole fraction.

The integer 3 appears in Reaction 1 and eqn. (1) because the actinides and rare earths are the elements whose concentrations can be significant at equilibrium under IFR pyroprocessing conditions, and the +3 oxidation state is by far the most common (Sm and Eu notably excepted) for these elements and conditions. For species in the +3 and 0 oxidation states, each term of eqn. (1) reduces to a simple and convenient form.

The second term of the right hand side of eqn. (1) is called the "separation factor;" unlike equilibrium constants, separation factors are not necessarily constant over wide composition ranges unless the product of the activity coefficients (the first term on the right hand side of eqn. (1) is constant. The individual activity coefficients in eqn. (1) can be far from unity, especially in the metal phase. In homogeneous solution, however, the separation factors appear to be approximately constant over the concentration ranges of interest, as if the solutes obeyed Henry's law and each solute had only one oxidation state. Constant separation factors can be multiplied and divided in the same way that equilibrium constants are combined when the corresponding chemical equations are added and subtracted. For process development, the concentrations, rather than the activities, are often what is needed.

Each measurement of a separation factor requires the values of four concentrations: two metals in molten cadmium and two chlorides in liquid salt. When separation factors become large, one (where the metal is a constituent of the salt) or (usually) two of the four concentrations become very small, and difficult to measure with precision, especially at relatively oxidizing or reducing conditions. Thus, separation factors are measured for similar pairs of metals to achieve maximum precision. Separation factors for unlike pairs are then derived by combination. For practical purposes, the exact value of large separation factors is not important.

A considerable body of data regarding separation factors is available from evaluation of chemical analyses taken in the course of other work [8] and from experiments designed for the purpose [6, 7]. These factors were combined to form the following series, which is expressed as separation factors relative to uranium: U, 1 (basis); Pu, 1.88; Np, 2.12; Am, 3.08; Cm, 3.52; Pr, 43.1; Nd, 44.0; Ce, 49; La, 130; Gd, 150; Dy, 500; and Y, 6000. Separation factors for Eu and Sm are thought to be very much larger ( $\geq 10^{10}$ ), and those of the alkali and alkaline earth metals are generally larger yet. We use (see Sec. 3 and 4) separation factors when only homogeneous liquids are in equilibrium, and methods based on equilibrium constants when the presence of solid phases is important, but this is just a convenience for calculation.

### 3. Equilibria involving solid phases

#### 3.1 Solid electrodes

At the solid cathode, the reaction of TRU with  $UCl_3$  determines the maximum allowable TRU- $Cl_3/UCl_3$  ratio

in the salt before significant TRU deposits along with U. For example, a TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratio of about 5 is calculated to put 1 ppm of TRU in solid solution in the uranium of the solid cathode at 775 K. This value is based on the observation that plutonium dissolves in uranium to a maximum of 15% [15] and the assumption that the activity of TRU in U varies linearly from 0 to 1 as the atom fraction in solid solution varies from 0 to 0.15. A ratio of activity coefficients (UCl<sub>3</sub> /PuCl<sub>3</sub>) of 0.67 was derived from the work of Johnson, et al. [10-13] and Koyama, et al. [8]. The free energy for the reaction of Pu with UCl<sub>3</sub> is -90270 J/mole [9]. These latter two values are taken to be typical of all TRU elements in the PYRO codes, as explained in Sec. 5.1.

Experimentally, small morphology changes in uranium deposits attributable to TRU were seen in electrotransport at or above a TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratio of 13, even though the concentrations of Pu and Am were too small to measure with available analytical methods [4]. For comparison, the maximum desired TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratios do not exceed 5. The solid cathode is therefore quite "robust" in that nearly pure uranium is deposited over a wide range of TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratios in the salt.

Identical calculations apply to the compositions of anode metals in contact with the salt. With desired process TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratios, essentially all of the TRU in the feed stock will react with UCl<sub>3</sub> in the salt as the surfaces of the fuel segments are removed and fresh metal is exposed. During steady-state operation of the electrorefiner, the TRU-Cl<sub>3</sub>/UCl<sub>3</sub> ratio thus rises gradually during electrotransport to a solid cathode, because only uranium is removed from the salt.

In the presence of UCl<sub>3</sub>, rare earth metals are not stable at solid surfaces (electrodes) because the rare earth chlorides are very much more stable than the actinide chlorides.

### 3.2 Cadmium electrodes

The TRU-rich product from the cadmium electrode is blended with (depleted) uranium to make core fuel; the minimum required TRU/U ratio is about 0.25 in the TRU-rich feed used for blending. In practice, much larger TRU/U ratios (typically 2 to 5) are desired in the cadmium cathode product to avoid formation of metallic uranium dendrites while still removing an adequate amount of plutonium; these dendrites tend to grow out of the crucible and induce short circuits. The TRU-U equilibrium at the cadmium cathode is strongly influenced by the activity coefficients of the metals in cadmium. The activity coefficient of uranium in cadmium is approximately 80 [13], and that of plutonium is  $2.1 \times 10^{-4}$  [11]. Thus, Pu/U ratios in homogeneous Cd solution are 0.53 times the PuCl<sub>3</sub>/UCl<sub>3</sub> ratio in the salt in equilibrium with the cadmium. (This is equivalent to saying that the Pu-U separation factor is 1.88.)

In practice, the cadmium electrode comprises a homogeneous metal solution at the beginning of electrotransport only. It is normally operated until a solids loading of 25 vol% or more<sup>1</sup> is achieved, and most of the plutonium is present as solid PuCd<sub>6</sub>. Thus, the amounts of the various actinide metals are primarily determined by the quantity of solid phases containing those actinides. If an actinide deposits as a solid (is saturated), then the activity of that actinide becomes essentially independent of the amount of material transported, and it will be the primary element electrotransported to the cathode until its cation is significantly depleted from the electrolyte or until all transportable material is exhausted from the anode. Should solid solutions be deposited (if, for example, PuCd<sub>6</sub> and NpCd<sub>6</sub> co-deposit because of very similar structure) similar behavior would be expected for the co-depositing elements. Table 1 shows the solubilities and precipitating phases for some important elements in cadmium at 775 K.

Rare earth metals are stabilized by formation of intermetallic compounds with cadmium in the same way that plutonium is stabilized [10]. However, because of the great stability of the rare earth chlorides, only relatively small amounts of rare earth metals exist in homogeneous solution in the cadmium cathode.

Table 1. Solubilities and precipitating phases in cadmium at 775 K\*

Element	Solubility (at %)	Precipitating Phase	Element	Solubility (at %)	Precipitating Phase
Uranium	0.0112	Metal	Lanthanum	0.31	LaCd <sub>11</sub>
Neptunium	0.021	NpCd <sub>6</sub>	Cerium	0.7	CeCd <sub>11</sub>
Plutonium	0.0180	PuCd <sub>6</sub>	Praseodymium	1.0	PrCd <sub>11</sub>
Americium	†	†	Neodymium	1.5	NdCd <sub>11</sub>
Curium	†	†	Samarium	2.1	SmCd <sub>6</sub>

\* References 9, 10, 12,14

† Unknown. Precipitation is unlikely because of very small quantities. Behavior is very similar to plutonium.

#### 4. Equilibria between homogeneous liquids

The same chemistry governs the homogeneous and heterogeneous equilibria, but a simpler mathematical description (the separation factor formalism) can be used to calculate mass flows and element distributions in the homogeneous case. This is fortunate, because it becomes practical to calculate the behavior of a large number of elements individually and with greater precision. Greater precision is necessary because the critical separation

<sup>1</sup>Vol% solids is defined as volume solids/(volume solids + volume liquid).



of TRU elements occurs in the countercurrent extractor, and because simulation of countercurrent flow magnifies any errors in the fundamental equilibrium calculation. The distributions of more than a dozen discrete elements are calculated by "simultaneous" solution of all pairs of separation factors.

Extraction with uranium in cadmium is chosen for the critical separation of TRU chlorides from rare earth chlorides. The TRU-U separation factors are larger than one; reaction between TRU chlorides and uranium is therefore not favored, but this can be overcome by the use of excess uranium. Because the rare earth-uranium separation factors are much larger than the TRU-U factors, little rare earth is reduced by uranium while a much higher fraction of TRU chloride is reduced. In this way, rare earth chlorides are separated from the TRU chlorides (but not from uranium chloride) so that the rare earths sent to waste have a very low TRU content. The (depleted) uranium in the waste is not a concern.

## 5. Computer codes

Based on the way equilibrium is calculated, we distinguish two different kinds of codes. In PYRO and TRANSPORT, the equilibration routines account for the effects of solid phases, but they deal only with the three major element groupings (uranium, TRU, and rare earth). In XTRACT, the distribution of many elements between two homogeneous liquids is calculated.

### 5.1 PYRO and TRANSPORT

PYRO is actually a family of programs; a library module called PYRO contains EQUILIBRATE and a number of other routines that describe pyroprocessing. A user-written "driver" program invokes the routines in the library module in the order desired. A template file contains sets of user-provided constants that control the execution of the driver. Results are accumulated in immense detail in a random-access file of records; various text files describe feedstocks and process fluids. Several utility programs fetch desired data from the output file and modify the input files. The ELECTROPORT procedure describes electrotransport in the PYRO family of programs. It is also used in a somewhat simpler shell, called TRANSPORT, to model electrotransport.

The heart of PYRO and TRANSPORT is a chemical equilibrium procedure, called EQUILIBRATE, that calculates the equilibrium concentrations in a molten salt phase and the solid and liquid metal phases that are in contact with it. This routine will be described first, then the rest of the code built on it will be described in lesser detail. The codes do not treat kinetic effects.

### 5.1.1 Equilibration procedures

When EQUILIBRATE is called, all the TRU elements in a metal and in a salt are added together, as are all the rare earth elements. The last step in the EQUILIBRATE procedure is to separate them out again. EQUILIBRATE brings the three element groups (U, TRU, and rare earth) into equilibrium by iteratively equilibrating each of the three possible pairs of groups. Any two pairs would suffice, but there is a minor speed and moderate robustness advantage to dealing with all three pairs. A separate procedure is invoked to deal with each pair (again for speed), but all three procedures are essentially identical.

EQUILUPU, the procedure that calculates the U-Pu equilibrium, is typical. The composition of a metal and a salt are fed to this procedure; it returns new metal and salt compositions wherein the uranium and plutonium (only) are in equilibrium. First, it determines the difference between the appropriate equilibrium constant and a corresponding mass action expression. The mass action expression is identical in form to the equilibrium constant, but it replaces equilibrium activities of four species (uranium, plutonium, and their chlorides) with the existing, non-equilibrium activities of the same four species. The non-equilibrium activities are calculated from the existing metal and salt compositions. The difference between the mass action expression and the equilibrium constant is a measure of how far the system is from U-Pu equilibrium. Next, some quantity of the two species on the right (or the left, depending on the sign of the mass action-equilibrium constant difference) of the chemical equation are removed ("reacted"), and an equivalent amount of material is added to the two species on the left (or the right). Finally, activities of all species and the difference between mass action expression and the equilibrium constant are recalculated. This process is repeated until the absolute value of the relative difference between the mass action expression and the equilibrium constant is sufficiently small. At that point, the activities and amounts of uranium and plutonium metal and chlorides are sufficiently close to their equilibrium values.

When EQUILUPU is entered initially, the quantity of material "reacted" is taken to be half of the least of the four species. If the sign of the mass action-equilibrium constant difference has not changed on recalculation, the amount of material is left unchanged, and the "reaction" is repeated. If the sign has changed, the number of moles of material "reacted" is halved, and the "reaction" is repeated, but in the opposite direction. Thus, the relative amounts of the four species are adjusted in the appropriate direction by progressively smaller amounts, while the mass of each element is conserved, until uranium and plutonium are sufficiently close to being in equilibrium.

To evaluate the mass action expression, ACTIVITIES is called to translate the amounts of each of the metal species (and of any other metal involved, such as cadmium) into the appropriate activities, based on concentrations in solution or the presence of solid phases. ACTIVITIES calls the recursive procedure FINDEM to evaluate the amounts, if any, of solid intermetallic compounds that may exist.

EQUILIBRATE is called as the last step in the REDOX procedure. In PYRO, 48 elements are ordered from the least reducing (bromine) to the most reducing (barium). REDOX selects a test element, beginning with bromine. If possible, REDOX calculates a complete reaction of the test element with all the elements that are more reducing than itself, beginning with barium and proceeding back to the test element. The next (more reducing) element in the list is made the test element, and the process is repeated until there are no elements that are more reducing than the test element. REDOX then calls EQUILIBRATE. Thus, all the "quantitative" reactions, e.g., the reaction of lithium with cadmium chloride, are rapidly and correctly accounted for prior to equilibration.

### 5.1.2 Electrotransport

The algorithm for modeling electrotransport in ELECTROPORT is conceptually simple. A fraction of the transportable material (U, TRU, and rare earth) in the anode is placed in the cathode. The composition of this fraction is not important. Next, anode and cathode are alternately equilibrated with the electrolyte salt until the salt composition is sufficiently constant. ELECTROPORT yields a description of electrotransport of one fraction of the anode contents; the electrotransport process can be described in as much detail as desired by repeatedly calling ELECTROPORT with varying values of the fraction transported.

Because the anode and cathode must both come to equilibrium with the salt, the relative amounts of cadmium, actinide and rare earth elements at the anode and cathode, and rare earth and actinide chlorides in the electrolyte all act together to determine the composition (amounts of each element in each phase) of each phase. Thus, electrotransport calculations can become quite extensive, especially when many cases are studied.

In PYRO, ELECTROPORT is usually invoked with only one value of the fraction of material transported, because only the result of the whole electrotransport step is needed. TRANSPORT is a stand-alone program that calls ELECTROPORT repeatedly, using a text input file to define the conditions and the parts of the electrotransport run to be modeled; it is used for studying the electrotransport process *per se*. TRANSPORT has been used to study electrotransport to both solid and liquid cathodes from cadmium pools [4,16]. In every case, the predicted compositions agreed with measured values within experimental uncertainty.

### 5.1.3 Other procedures and programs in PYRO

Each individual step in pyroprocessing (addition of spent fuel, retorting of cadmium from the cathode product, etc.) is modeled with a separate procedure. These procedures call the electrotransport and equilibration routines as needed. By stringing together these procedures, complete pyroprocessing campaigns can be modeled, and the effects of operating conditions and strategic choices can be studied.

The user names the procedures in the driver program to model pyroprocessing of as many batches of fuel as desired. A status record describes the condition of the electrorefiner; each modeling procedure reads the current status record, then generates a new one and stores it in the indexed file of status records. Each modeling procedure also reads a "template" record in which the user has stored the necessary conditions or parameters to govern the modeling; several procedures commonly use the same template. A random-access file contains the collection of template records, and a special procedure is invoked in the driver program to select template records.

Utility programs in the PYRO family inherit all the same definitions and procedures from the library module that the driver program inherits. Some utility programs create the template file and modify input files; the most important utility programs read the output file of status records and convert selected data to text files.

## 5.2 Extraction code

In XTRACT, solution of the separation factor expressions always involves an equation of from order 2 to 5, so the technique described above for EQUILUPU is used to determine equilibrium concentrations. The separation factor expression is solved simultaneously for 23 elements, including cadmium and nine highly reducing elements. Metal and salt are equilibrated in each contactor, then advanced stepwise in a countercurrent fashion until both metal and salt outlet streams have sufficiently constant compositions.

XTRACT is set up so that the user can choose the number of extraction contactors (1 to 16) and the relative flow rates of the metal and salt streams. The compositions of the metal and salt input streams are given in simple text files. The status (metal and salt composition) of each contactor in each step is recorded in an indexed output file of records in the same way that PYRO generates its output.

XTRACT was used to predict the compositions after reduction and oxidation reactions in a "stripping" vessel (effectively, a large, slow single-stage contactor). Agreement with measured values was excellent [17]. Tests to determine the extent to which the contactor will behave as an equilibrium device are underway on single stage units [5] and are planned for multistage units.

## 6. Conclusion

Equilibrium calculations have proven to provide a useful description of the various processes in pyrochemical processing of spent IFR fuel, including electrotransport, oxidations, reductions, and extractions. Much of the fundamental thermodynamic information necessary for these calculations has existed since the 1960s [10-15]; additional data have been acquired in the last few years [4-8]. Because it is useful to be able to conduct

very large numbers of calculations, computer codes have been written to allow parametric studies of pyroprocessing flowsheets.

Processing strategies for spent IFR that increase throughput and decrease waste volume were developed using the calculational methods and tools described herein. These tools and techniques were particularly useful in determining conditions for removing cathodes having desired compositions and for purification of the salt without loss of TRU.

## 7. Acknowledgments

The work described herein would not have been possible without the contributions and cooperation of colleagues too numerous to list, but particular thanks are due to Leslie Burris for his guidance and support, and to Anthony Scandora and John Osudar for their patient guidance and assistance with programming and computer operation.

**References**

1. C. Till and Y. Chang, Proc. Am. Power Conf., Chicago, IL, April 24-36, 1989, Am. Power Conf., Chicago, IL, 1989, Vol. 51, 688-691.
2. L. Burris, R. Steunenberg, and W. Miller, AICHE Symp. Ser., No. 254, 83 (1987) 135-142.
3. J. Ackerman, Ind. Eng. Chem. Res. **29**, (1991) 142-145.
4. Z. Tomczuk, J. Ackerman, and W. Miller, J. Electrochem. Soc., **139** (1992) 3523-3528.
5. L. Chow, J. Basco, J. Ackerman, and T. Johnson. Presented at Global 93, International Conference and Technology Exhibition Seattle Washington, Sept. 12-17, 1993
6. J. Ackerman and J. Settle J. Alloys and Compounds, **177** (1991) 129-141.
7. J. Ackerman and J. Settle J. Alloys and Compounds, In press.
8. T. Koyama, T. Johnson, and D. Fischer, J. Alloys and Compounds, **189** (1993) 37-44.
9. L. Pancratz, United States Department of the Interior, Bureau of Mines, Bulletin 674 (1984).
10. I. Johnson and R. Yonco, Met. Trans., **1** (1970) 905-910.
11. I. Johnson, M. Chasanov, and R. Yonco, Trans. Met. Soc. AIME, **233** (1965) 1408-1414.
12. I. Johnson, K. Anderson, and R. Bloomquist, Trans. ASM, **52** (1966) 352-355.
13. I. Johnson and H. Feder, Trans. Met. Soc. AIME, **224** (1962) 468-473.
14. J. Lumsden, Thermodynamics of Molten Salt Mixtures, (Academic Press, London, 1966).
15. F. Ellinger, R. Elliot, and E. Cramer, J. Nucl. Mater., **3** (1959) 233-243.
16. M. Steindler et al., Argonne National Laboratory Report # ANL-89/15, Chemical Technology Division Annual Technical Report, 1988.
17. Private Communication from E. Carls, Argonne National Laboratory August, 1993.