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TREATMENT OF HIGH-LEVEL WASTES FROM THE IFR FUEL CYCLE*

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T. R. Johnson, M. A. Lewis, A. E. Newman, and J. J. Laidler

Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

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Argonne National Laboratory
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ABSTRACT

The Integral Fast Reactor (IFR) is being developed as a future commercial power source that promises to have important advantages over present reactors, including improved resource conservation and waste management. The spent metal alloy fuels from an IFR will be processed in an electrochemical cell operating at 500°C with a molten chloride salt electrolyte and cadmium metal anode. After the actinides have been recovered from several batches of core and blanket fuels, the salt and cadmium in this electrorefiner will be treated to separate fission products from residual transuranic elements. This treatment produces a waste salt that contains the alkali metal, alkaline earth, and halide fission products; some of the rare earths; and less than 100 nCi/g of alpha activity. The treated metal wastes contain the rest of the fission products (except T, Kr, and Xe) small amounts of uranium, and only trace amounts of transuranic elements. The current concept for the salt waste form is an aluminosilicate matrix, and the concept for the metal waste form is a corrosion-resistant metal alloy. The processes and equipment being developed to treat and immobilize the salt and metal wastes are described.

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INTRODUCTION

The Integral Fast Reactor (IFR) [1] is an advanced power reactor concept sponsored under the U.S. Department of Energy's reactor development program [2]. The IFR features on-site reprocessing using pyrochemical methods to recover actinides from the U-Pu-Zr core and U-Zr blanket fuels, separate fission products, and produce suitable high-level waste forms. More than 99% of the transuranic (TRU) elements are recovered and separated from fission products by an electrorefining process at about 500°C [3]. The electrorefiner (Fig. 1) is a steel vessel with a pool of liquid cadmium that serves as an anode in some operations and a liquid LiCl-KCl electrolyte. Spent fuel elements are chopped, placed in steel baskets, and immersed in the electrolyte, where the fuel is anodically dissolved away from the cladding. A major fraction of the uranium from the fuels is electrochemically deposited on steel cathode rods, and the rest of the uranium and the TRU elements is deposited in liquid cadmium cathodes. These cathodes are treated to produce metal ingots for use as new core and blanket fuels.

The fission products, with the exception of T, Kr and Xe, accumulate in the electrorefiner during processing. The alkali metal, alkaline earth, rare earth, and halide fission products collect in the salt, and noble metal fission products collect in the cadmium pool along with the zirconium from the fuel alloys. After several batches of core and blanket fuels are processed, the salt and cadmium in the electrorefiner are treated in a series of steps to recover residual TRU elements and to concentrate the fission products for conversion to high-level waste forms, which will be placed in a geologic repository. The steps to treat and immobilize the high-level wastes for permanent disposal are described in this paper.

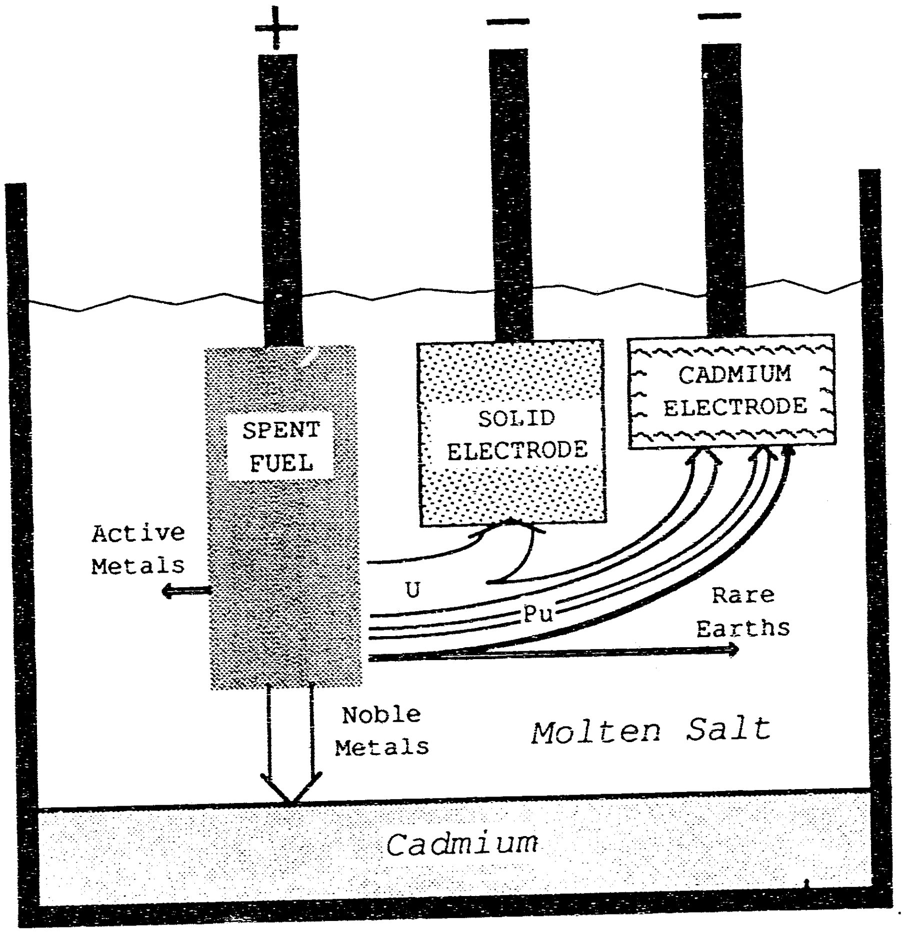

Fig. 1. The IFR Electrorefining Process

The processes being developed for treating the spent salt and metal from the electrorefiner, and the techniques considered for immobilizing the treated salt and metal wastes for permanent disposal are discussed in this paper. The emphasis is on the recovery of TRU elements and the removal of actinides and rare earths from spent salt; the chemistry of these steps has been demonstrated and engineering-scale process equipment is being assembled. Some of the initial results on the ion exchange between zeolites and molten chloride salts are summarized. The use of zeolites to concentrate the fission products remaining in the treated salt appears to be a very promising technique that facilitates immobilization in an aluminosilicate matrix. Concepts for treating and immobilizing the metal wastes in metal alloy matrices are also discussed.

TREATMENT OF SPENT SALT AND CADMIUM FROM ELECTROREFINER

After an electrorefining campaign during which several batches of core and blanket fuels are processed, operations are performed to prepare for the removal of salt and cadmium containing the accumulated fission products. The first operation entails removing all of the actinides from the cadmium pool and most of the actinides from the salt. Then the salt and cadmium are pumped through a steel filter to remove any insoluble impurities (e.g., oxides, nitrides, and carbides) and undissolved noble metals (Zr, Mo, Tc, Ru, and Rh). The filter element retains some cadmium so that a fraction of the soluble noble metals (Pd, Ag, Sn, and Sb) can be removed from the pool. The filter and most of the salt are then removed from the electrorefiner. The estimated amounts of spent salt and metal, based on processing 500 kg of actinides from core and blanket fuels with an overall average burnup of 60,000 MWd/T of actinides, are shown in Table I.

The sodium in the spent salt shown in Table I arises when the bond sodium in the chopped fuel elements fed to the electrorefiner is converted to chloride by the addition of $CdCl_2$. Yttrium, samarium, and europium are included with the alkaline earths, because these rare earths behave like alkaline earths and remain in the salt during the salt treatment steps.

TABLE I. Spent Salt and Cadmium Discharged from Electrorefiner after Processing 500 kg Actinides

Salt	Weight of Chloride (kg)	Metal	Weight of Metal (kg)
LiCl-KCl-NaCl	445	Cd	87
RbCl-CsCl	20	Zr	2
$SrCl_2$-$BaCl_2$[a]	16	Noble Metals	11
(Rare Earth)Cl_3	15		
UCl_3	1	U	~0
(TRU)Cl_3	3	TRU	~0
Totals	500		100

[a] Includes YCl_3, $SmCl_2$, and $EuCl_2$.

The amounts of alkali metal, alkaline earth, and rare earth fission products in the salt exceed those fed with the 500 kg of actinides, because salt treatment removes only a fraction of these elements and returns the rest to the electrorefiner with recycled salt. The amount of zirconium in the spent metal shown in Table I is the amount of the fission product; the zirconium in the fuel alloy is recovered during electrorefining and reused.

Figure 2 illustrates the process steps used to recover TRU elements, salt, and cadmium for return to the electrorefiner, and to prepare high-level waste forms for the remaining salt and metal [4]. Spent salt from the electrorefiner flows through an extraction train, which consists of several countercurrent stages, where it is contacted with a Cd- 2 wt % U solution. This step extracts more than 99% of the TRU elements and leaves more than 70% of the rare earths in the salt. Actinides and rare earths in the product cadmium solution are separated from the cadmium by retorting and returned to the electrorefiner; the cadmium is recycled to the extractor after the addition of uranium.

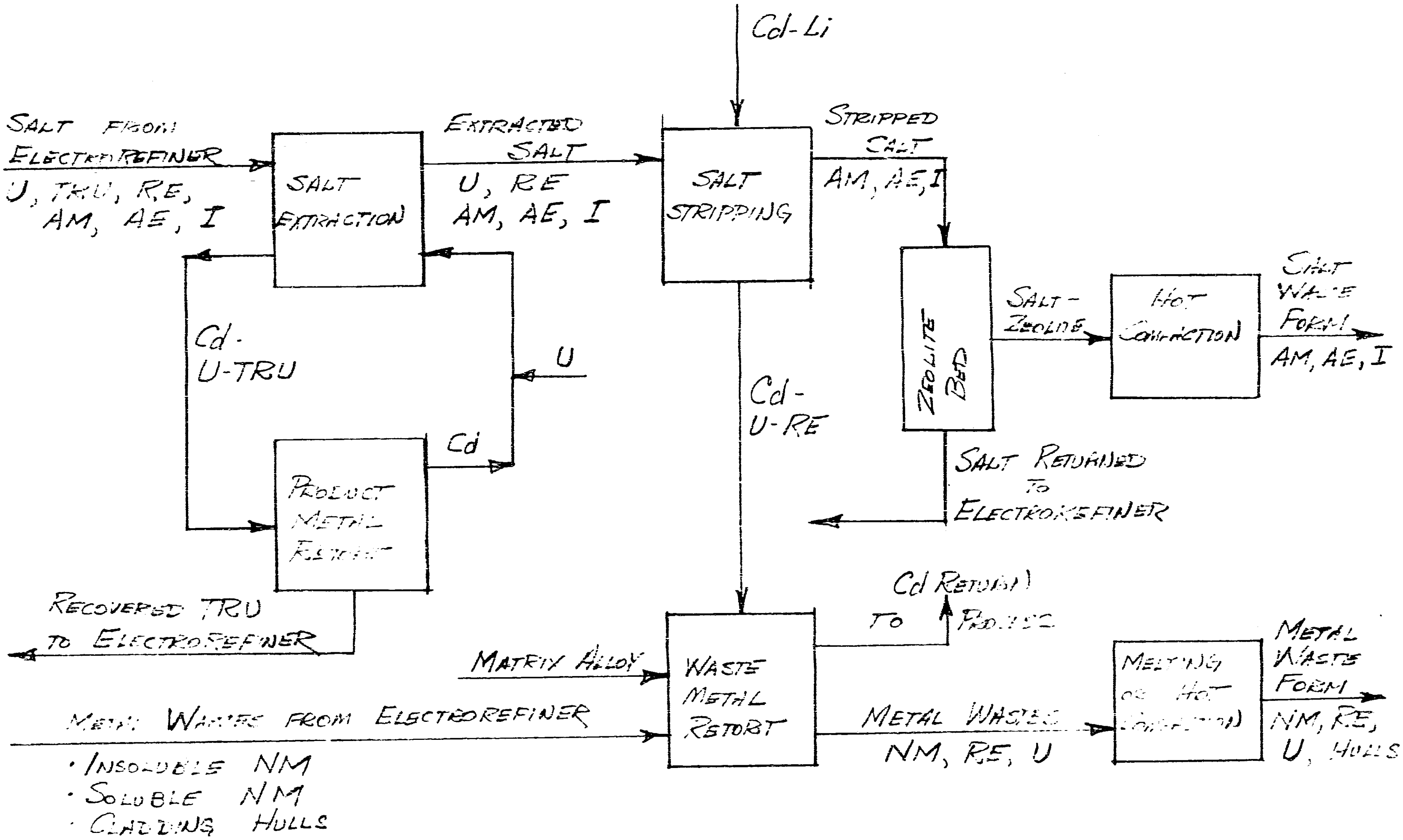

Fig. 2. Reference Process for Treating and Containing Salt and Metal Wastes (TRU = Np, Pu, Am, Cm; RE = Rare earth fission products; AM = Rb, Cs; AE = Sr, Ba; NM = Noble metals)

The product salt from the extractor, which contains fission products, uranium, and very small amounts of TRU elements, is sent to the salt stripper, where it is contacted with a liquid Cd-Li alloy to reduce essentially all of the actinides. With the exception of Y, Sm, and Eu, more than 99% of the rare earth elements will also be transferred to the cadmium solution. In addition to those three rare earths, the stripped salt contains nearly all of the alkali metal, alkaline earth, and halide fission products, but only trace amounts of actinides.

The stripped salt passes through a zeolite bed that removes Cs, Sr, and Ba by ion exchange. Excess salt is removed from the bed by a final purge with argon gas, but the bed retains a considerable amount of salt occluded in the zeolite cavities and adhering to the zeolite surface. Most (~90%) of the salt, with its fission product content reduced by about 10 to 20%, passes through the zeolite bed and is returned to the electrorefiner. The salt-laden zeolite is then mixed with an inorganic matrix material and hot pressed to form a high-level waste form consisting of salt dispersed in a dense ceramic matrix.

The combined metal wastes are retorted to recover cadmium, which is returned to the process. A matrix metal, e.g., a copper alloy, is added during the retorting process to disperse and immobilize the residue, which consists of the noble metal and rare earth fission product, small amounts of uranium, trace amounts of TRU elements, and cladding hulls.

CHEMICAL BASIS OF SALT EXTRACTION AND STRIPPING

Salt extraction and stripping, as well as the electrorefining process itself, are based on the distribution of metallic elements dissolved in cadmium and their chlorides dissolved in a mixture of stable alkali metal and alkaline earth chlorides [3]. Equilibrium among the elements that distribute between the phases is achieved by exchange reactions between cations in the salt and metal atoms in the cadmium. Equilibrium among elements that form trivalent chlorides can be represented by exchange reactions between any pair of elements, for example,

$$UCl_3 + Pu = U + PuCl_3, \text{ and} \tag{1}$$

$$UCl_3 + Ce = U + CeCl_3. \tag{2}$$

Uranium, TRU elements, and most rare earth fission products form only trivalent chlorides under IFR process conditions. Samarium and europium form divalent chlorides and tend to behave like alkaline earths in this process. Exchange reactions involving cadmium metal and chlorides of the alkali metals, alkaline earths, and the rare earths Y, Sm and Eu, can be ignored under most IFR process conditions. The equilibrium constant, K, for Reaction 1 is

$$K = \frac{[U][PuCl_3]}{[UCl_3]\ [Pu]} = \exp\left(-\Delta G°/RT\right), \tag{3}$$

where $[U]$ = activity of uranium in cadmium,
$[UCl_3]$ = activity of UCl_3 in salt,
$\Delta G°$ = standard free energy of formation of a chloride,
R = gas constant, and
T = absolute temperature.

This leads to an expression for the plutonium-uranium separation factor,

$$SF_{Pu} = \frac{D_{Pu}}{D_u} = K \left\{ \frac{\left(\gamma_{Pu}\right)\left(\gamma_{UCl_3}\right)}{\left(\gamma_{PuCl_3}\right)\left(\gamma_U\right)} \right\}, \tag{4}$$

where γ = activity coefficient
= (activity)/(mole fraction metal cations or metal atoms), and
D = distribution coefficient
= (mole fraction in salt)/(atom fraction in metal).

The activity coefficient term in Eq. 4 is constant if the salt-and metal-phase activity coefficients are independent of phase composition. This appears to be the case for the concentration ranges and conditions of interest for the IFR fuel cycle processes. Similar expressions between any other pair of elements that form trivalent chlorides result in the following equation:

$$D_U = \frac{D_{Pu}}{SF_{Pu}} = \frac{D_{Np}}{SF_{Np}} = \frac{D_{Am}}{SF_{Am}} = \frac{D_{Ce}}{SF_{Ce}} \cdots \tag{5}$$

where the separation factors are relative to uranium. (The choice of uranium as the reference element is arbitrary; any trivalent element could be chosen.) This relationship can be extended to an element (A) that forms a monovalent or trivalent chloride if the separation factor is defined as:

$$SF_A = [(D_A)^{3/n}]/D_U, \tag{6}$$

where n = valence of chloride formed by element A. Process calculations are greatly simplified through the use of these separation factors because they have been found to be constant over wide ranges of redox conditions in the IFR salt/cadmium systems. Equation 5 also illustrates that the distribution coefficients of all elements can be calculated once the coefficient of one element is known.

As indicated by Eq. 4, separation factors can be calculated from thermodynamic properties, but calculated factors are generally not reliable because some of the required data are inaccurate or have not been measured. For the IFR program, it has been necessary to measure the actinide and rare earth separation factors. Distribution data for uranium, TRU elements, and some rare earths, which were collected by several researchers during the development of the electrorefining and waste treatment processes, were analyzed by Koyama et al. [5]. Results for the LiCl-KCl eutectic at 500°C are shown in Fig. 3. The distribution coefficients in this figure are the ratios of weight fractions rather than mole fractions.

Ackerman and Settle measured distribution coefficients for several rare earths and related these data to the actinide coefficients [6, 7]. To overcome the experimental difficulties of determining separation factors larger than about 50, they made measurements with several pairs of elements that are progressively more salt-philic. Table II gives a set of distribution coefficients derived from these data for conditions where the uranium distribution coefficient is 1.0. The values of the distribution coefficients for the trivalent elements are the same as the separation factors relative to uranium. Because samarium and europium form divalent

Table II. Distribution Coefficients of Some Actinides and Rare Earths
(Where Uranium Coefficient Is 1.0)
(LiCl-KCl eutectic/Cd at 500°C)

Element	Distribution Coefficient[a]	Ref.	Element	Distribution Coefficient[a]	Ref.
Np	2.12	5	Ce	6.1E+1	7
Pu	1.88	5	La	1.2E+2	7
Am	3.08	5	Gd	2.1E+2	7
Cm	3.52	5	Y	4.9E+3	7
Pr	43.1	6	Sm	6.1E+7	7
Nd	44.0	6	Eu	1.6E+9	7

[a] mole fraction in salt/atom fraction in cadmium

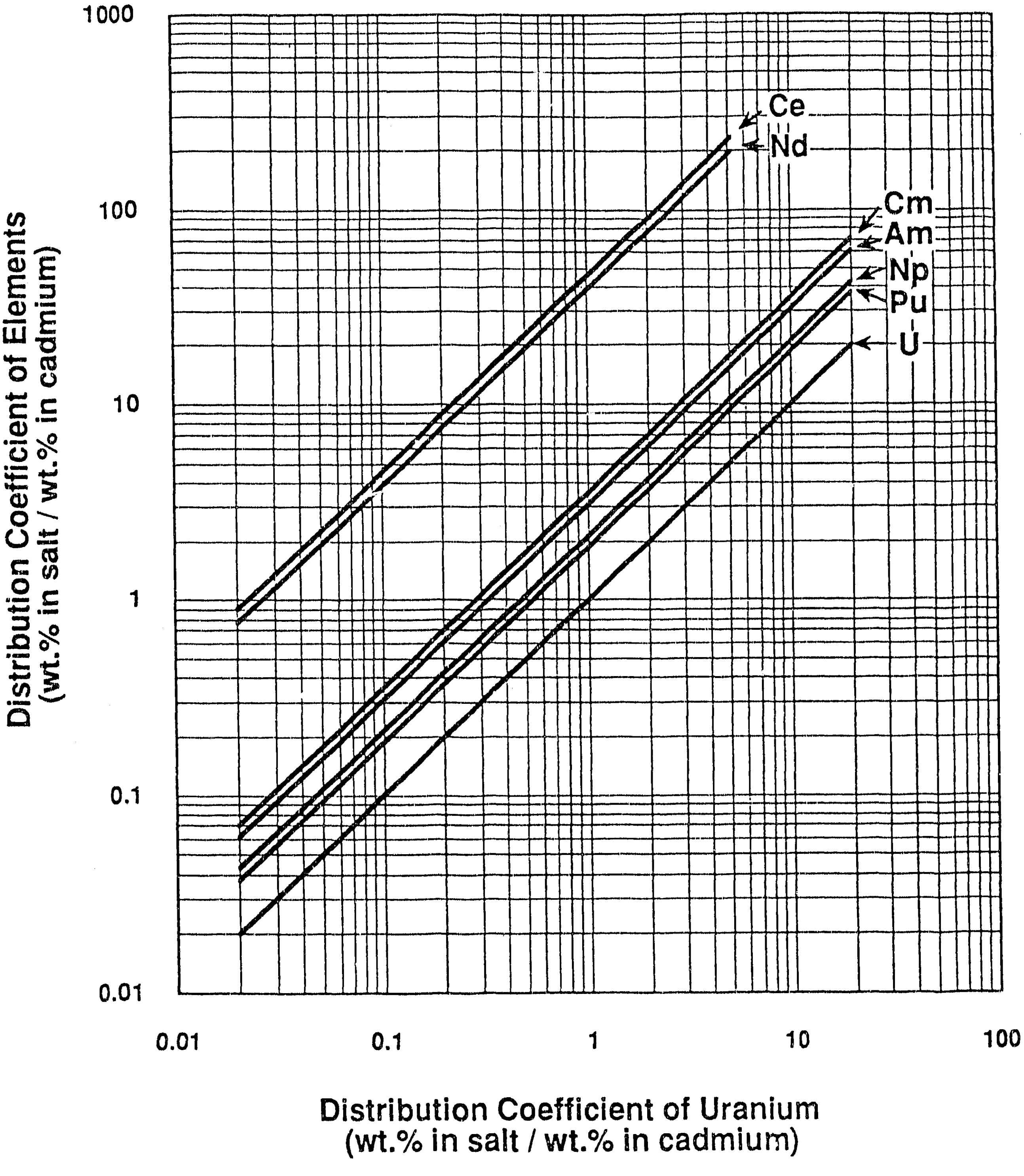

Fig. 3. Distribution Coefficients of TRU Elements and Some Rare Earths in Alkali Metal-Rich Salt/Cadmium Systems at 773 K

chlorides, their distribution coefficients vary nonlinearly with the uranium coefficient as indicated in Eq. 6. Measurements by Ackerman and Settle [7] of the distribution of several alkali metals and alkaline earths have confirmed that Na, K, Cs, Sr, and Ba will remain almost completely in the salt phase during the IFR fuel recovery process.

The large separation factors between rare earths and actinides show that these element groups can be effectively separated by liquid salt-metal extractions. The small separation factors among the actinides are a distinct advantage for the IFR concept, because it would be difficult to separate uranium and the minor actinides from plutonium to produce high purity plutonium in an IFR facility. The basis of the extraction process can be illustrated by considering the following: When a salt containing uranium, TRU elements, and rare earths is contacted with cadmium containing only uranium, the elements will redistribute by means of exchange reactions to satisfy the equilibrium relationship of Eq. 5. The net result is that TRU elements and rare earths in the salt exchange with uranium in the metal, but a larger fraction of the TRU elements transfer than rare earths. Uranium replaces TRU elements in the salt and eventually becomes part of the high-level metal waste. This uranium loss, which is less than 1% of the actinides fed to the electrorefiner, is not a serious penalty because it is depleted uranium.

Calculations [8] using the measured separation factors have shown that adequate TRU recoveries and rare earth separations can be achieved by use of four to seven countercurrent, equilibrium stages with roughly equal volumes of metal and salt phases. Typical results are shown in Fig. 4, where the fractions of TRU elements and "extractable" rare earths remaining in the product salt are shown as functions of the metal/salt weight ratio and the number of equilibrium stages. The extractable rare earths do not include Y, Sm, and Eu, which remain almost completely in the salt phase during extraction. With four theoretical stages and a metal/salt weight ratio of 4.0, 99.8% of the plutonium and 99.0% of the minor actinides (Np, Am, and Cm) are recovered from the spent electrorefiner salt. The percentage of extractable rare earths remaining in the salt is about 80%.

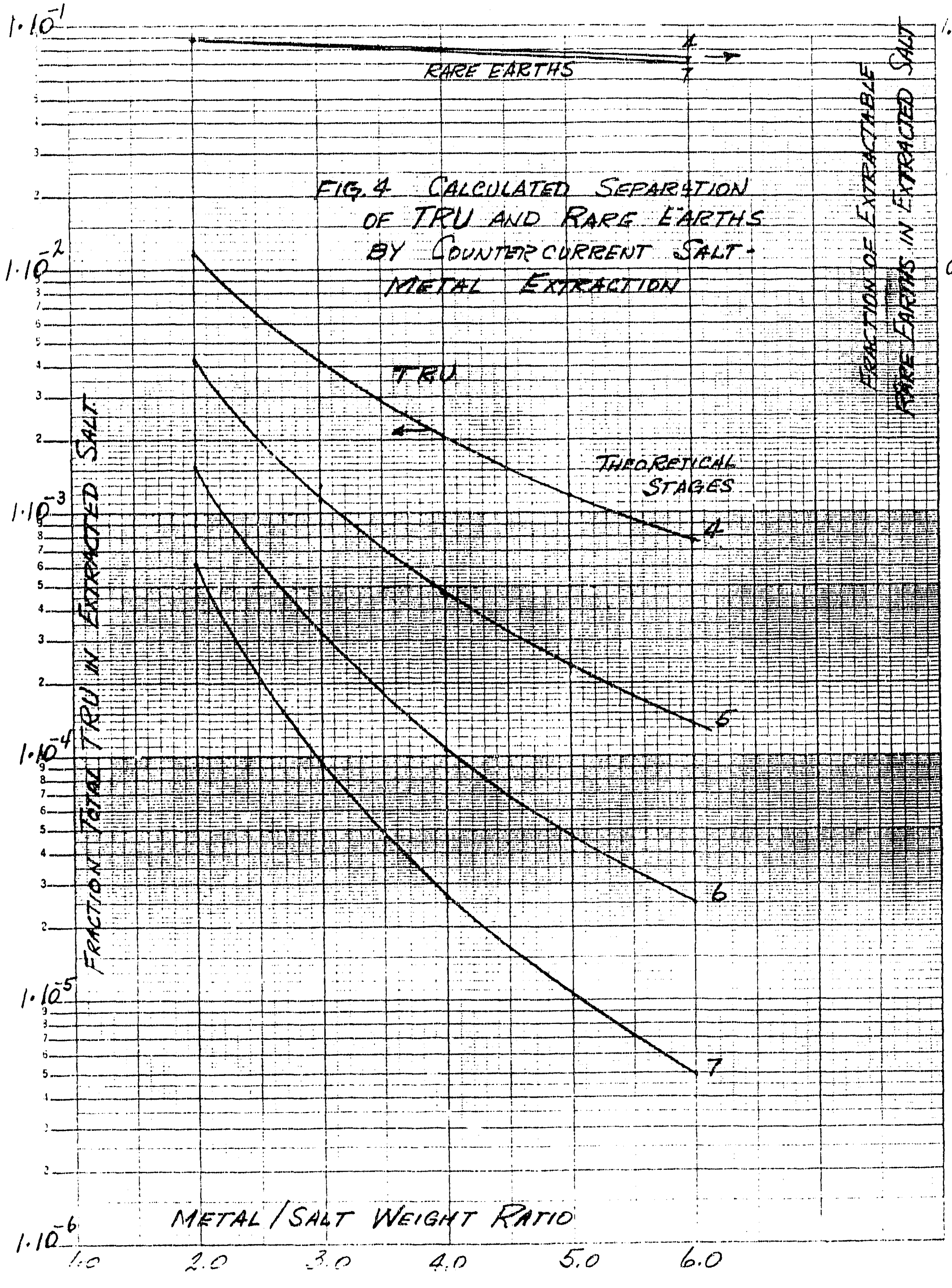

FIG. 4 CALCULATED SEPARATION OF TRU AND RARE EARTHS BY COUNTERCURRENT SALT-METAL EXTRACTION

The chemistry of the salt stripper is based on the same distribution behavior of actinides and rare earths between salt and cadmium as the extractor, but the system is made highly reducing by the addition of sufficient lithium metal to reduce essentially all of the actinides and extractable rare earths from the salt and produce a final metal solution with 0.01 to 0.1 wt % Li. The uranium distribution coefficient at this condition is estimated to be less than $1 \cdot 10^{-6}$. As a result, the TRU distribution coefficients calculated from the measured separation factors are less than $4 \cdot 10^{-6}$, and the coefficients for the extractable rare earths range from roughly $4 \cdot 10^{-5}$ for Pr and Nd up to $3 \cdot 10^{-4}$ for gadolinium.

The production of low-TRU salt by this stripping technique has been confirmed in several tests using one-kilogram batches of salt discharged directly from a laboratory-scale electrorefiner [9]. The salt contained 0.2 wt % U and 1 wt % total rare earths (Y, Ce, Nd, and Sm), which are approximately the expected levels in salt from the IFR extraction step, and 1.2 wt % Pu and 33 ppm Am, which exceed the expected levels. After a single contact with a cadmium solution having a final lithium content of about 0.1 wt %, the U, Ce, and Nd contents of the salts were below detectable limits of 0.01 wt %. The plutonium activity in the salt was less than 1 nCi/g corresponding to a distribution coefficient of less than $1 \cdot 10^{-6}$, but the americium coefficient was about $1 \cdot 10^{-3}$ rather than the less than $2 \cdot 10^{-6}$ calculated from the plutonium coefficient. There is some experimental evidence for the formation of $AmCl_2$ under very reducing conditions. This could explain the higher-than-expected americium content in the stripped salt. Even with an americium distribution coefficient of $1 \cdot 10^{-3}$, the stripped salt in an IFR process would have a total alpha activity of less than 10 nCi/g.

During these experiments [9], it was found that direct contact of the salt with a Cd-Li alloy produced intermetallic compounds of cadmium with actinides and rare earths that collected on the crucible walls and did not dissolve readily in the metal phase. Evidently, the chloride reduction rate exceeded the rate at which the metal reduction product could be dissolved by the cadmium. The result was the formation at the salt-metal interface of solid intermetallic compounds that were swept to the sides of the vessel by the agitator. Some means of limiting the reduction rate, such as controlling the lithium addition rate, must be developed.

ION EXCHANGE WITH ZEOLITES IN MOLTEN SALTS

As shown in Fig. 2, the stripped salt passes through a bed of zeolites that preferentially removes a fraction of the Sr, Cs, Ba, and rare earths from the salt by cation exchange. Most of the salt passes through the bed and is returned to the electrorefiner, but some is retained in the bed as salt occluded in the molecular cages of the zeolite and as salt adhering to the surfaces of zeolite particles.

Preliminary experiments with various zeolites showed that zeolite A has desirable ion exchange and salt occlusion properties for removing alkali metal and alkaline earth fission products from molten LiCl-KCl solutions [10]. Ion exchange between the molten salt and zeolite A was demonstrated in two batch experiments through changes in the composition of the zeolite before and after equilibration with LiCl-KCl eutectic salt containing $SrCl_2$, CsCl, $BaCl_2$, and NaI. Initially, the zeolite contained 16.2 wt % sodium and essentially no Cs, Sr, Ba, or I.

After equilibration at 400°C in the first batch experiment, the zeolite was washed with water to remove the surface or non-occluded salt. Table III gives the analyzed composition of the washed, salt-occluded zeolite as well as the salt composition calculated from a mass balance. In the second batch experiment, more than 80% of the molten salt was separated from the zeolite by pressure filtration. Table III also gives the analyzed composition of the separated salt and the composition of the salt-occluded zeolite calculated by a material balance. After both experiments, the sodium content of the zeolite had decreased from about 16 wt % to less than 1 wt % and the sodium content of the salt had increased.

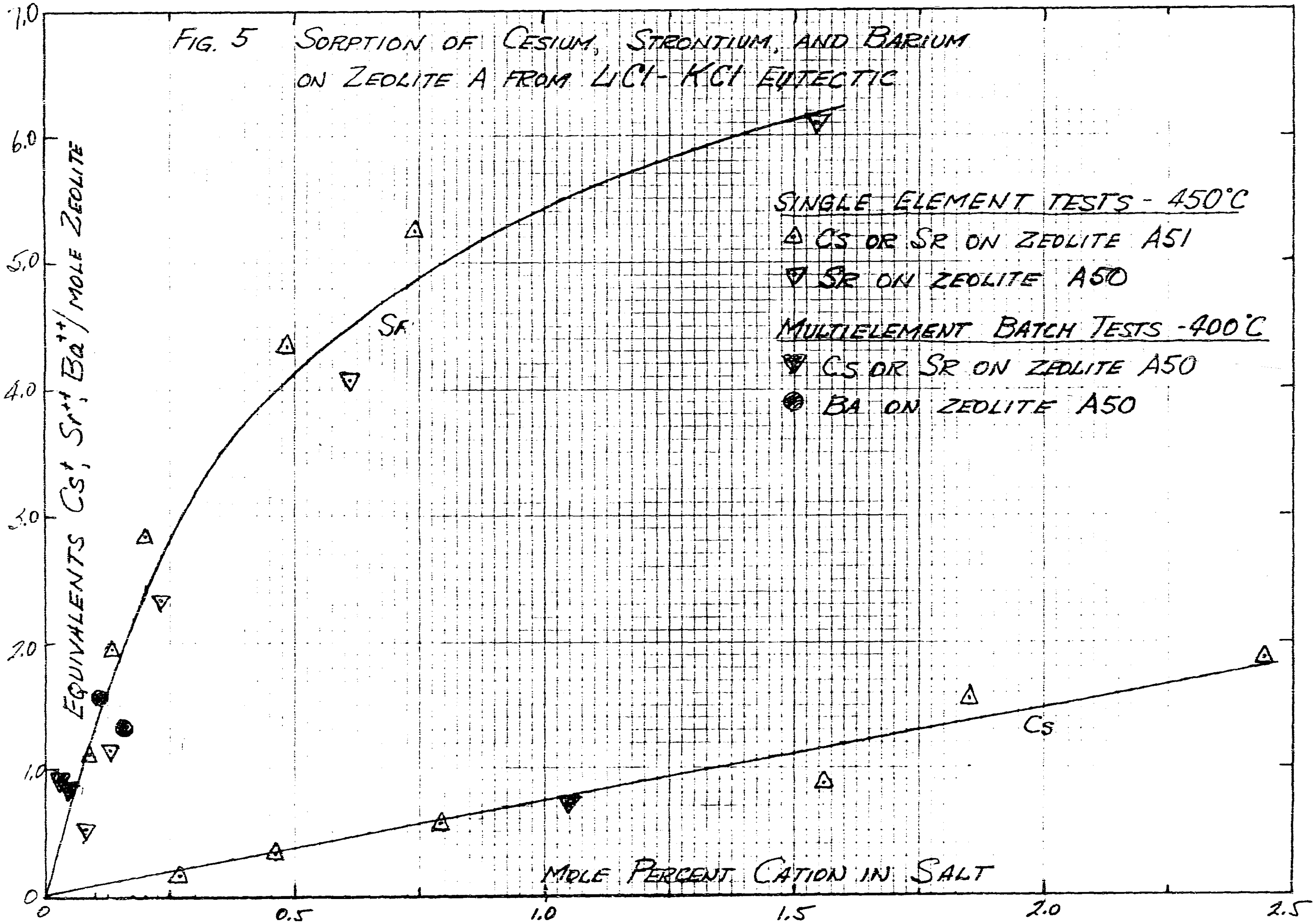

Fig. 5 Sorption of Cesium, Strontium, and Barium on Zeolite A from LiCl-KCl Eutectic

TABLE III. Compositions of Salt and Zeolite in Batch Experiments
Salt: LiCl- KCl; Zeolite: Na-A50;
Temperature: 400°C

		Batch #1		Batch #2	
Salt/Zeolite (g/g):		5.2		6.1	
		Compositions after Equilibration			
Component	Initial Salt (wt %)	Molten Salt[a] (wt %)	Salt-Zeolite[b] (wt %)	Molten Salt[c] (wt %)	Salt-Zeolite[a] (wt %)
Sr	0.41	0.021	1.5	0.034	1.7
Cs	4.1	2.5	6.7	2.9	6.2
Ba	1.40	0.24	4.5	0.27	5.1
I	0.40	0.39	0.13	0.36	0.2

[a] Calculated from material balance.
[b] Analyses of salt-occluded zeolite.
[c] Analyses of filtered salt samples.

The data in Table III demonstrate that ion exchange occurred between molten salt and zeolite A. The salt-occluded zeolite contained significant amounts of Sr, Cs, and Ba while the concentrations of these elements in the salt decreased. More complete analyses of the salt-occluded zeolite showed that between 10 and 12 salt molecules were occluded in the zeolite cavity. It was not possible to distinguish between the occluded cations and the ion exchanged cations. The iodide content of the molten salt phase was lowered slightly by contact with the zeolite indicating that the salt in the zeolite cavities was enriched in iodide compared to the molten salt.

Other data for cesium and strontium adsorption on zeolite A at 450°C are shown in Fig. 5 [11]. The ordinate is the cation equivalent sorbed per mole of zeolite with a unit cell represented by $Na_{12}[(AlO_2)(SiO_2)]_{12}$. These data were obtained by adding increments of cesium or strontium chloride to a mixture of LiCl-KCl and zeolite particles, stirring for several hours, and taking filtered samples of the salt solution. Then the amount of the cation adsorbed by ion exchange with sodium in the zeolite was determined from the amount lost from the salt solution as calculated by mass balance.

The ion exchange step in the process flowsheet has been demonstrated in experiments in which zeolite A (sodium form) was mixed with 30 g of LiCl-KCl solution containing 0.44 wt % Sr, 3.9% Cs, 1.3% Ba, and 0.42% I. With a salt/zeolite weight ratio of 6/1 and a temperature of 400°C, these values were reduced to 0.06 wt % Sr, 3.0% Cs, 0.37% Ba, and 0.39% I. Based on the results in Table III, the reduction of the iodide anion was attributed to iodide enrichment of the occluded salt. After passing through either a 5- or 20-μm steel filter, the salt contained less than 10 ppm Al and 50 ppm Si. A filtered salt with these low impurity contents, could be returned to the electrorefiner. The adsorption data for Sr, Cs, and Ba obtained in the filtration tests are plotted in Fig. 5 along with the data obtained with only Sr or Cs present. Although the temperatures were different, there is fair agreement between the two sets of data.

Process calculations based on the above results show that the removals of Sr, Ba, Cs, and I obtained by ion exchange and salt occlusion provide adequate decontamination of the salt so that the effluent salt from a zeolite column can be returned to the electrorefiner. In addition, the fission product concentration by zeolite is more than sufficient to minimize waste form volume.

SALT WASTE FORM DEVELOPMENT

The salt remaining in the zeolite column is expected to contain negligible amounts of actinides and trivalent rare earths. However, the salt-zeolite mixture is a high-level waste because it contains large amounts of several relatively short-lived nuclides, namely Sr-Y-90, Cs-Ba-137, Sm-151, Eu-154, and Eu-155. The heat produced by these radionuclides must be considered in the design of a waste form. The presence of several long-lived nuclides (I-129, Cs-135, and perhaps Se-79) requires that the waste salt be converted to a form that limits radioactive releases for thousands of years.

Work to develop techniques for consolidating the salt-zeolite mixture into a suitable waste form has begun. Encapsulation of chlorides in an aluminosilicate matrix appears to be a promising technique, which has the advantages of being compatible with pyroprocesses and not requiring steps for converting chlorides into other compounds. It has yielded reasonably leach-resistant compacts in preliminary laboratory tests [12, 13]. A form made by directly compacting the salt-zeolite mixture would contain more than 25% salt and have an excessively high fission product heat rate. Diluting the salt-zeolite mixture with an aluminosilicate matrix so that the waste form contain 5 to 10% salt yields a high-level waste form with a heat rate suitable for disposal in a geologic repository.

Leaching tests [12] on unconsolidated particles of salt-occluded zeolites have shown that the Sr, Ba, and Cs contained in the molecular cage of the zeolite have resistances to water leaching (expressed as grams per day per square centimeter of particle surface) comparable to those for waste glass. Irradiation of salt-occluded zeolites by a Co-60 source at total doses up to 1000 Mrad did not measurably change their leach resistance [10].

METAL WASTE TREATMENT AND IMMOBILIZATION

Four metal waste streams are treated to separate cadmium for return to the process and to produce a metal waste form [4]: (1) the cadmium solution from salt stripping, which contains the rare earths and some uranium; (2) a portion of the cadmium pool in the electrorefiner, which contains the noble metals soluble in cadmium (Zr, Pd, Ag, In, Sn, Sb, and Te); (3) a steel filter element, which contains the insoluble noble metals and impurities removed from the electrorefiner; and (4) cladding hulls, which have been washed with cadmium to remove adhering actinide-laden electrolyte. In the current concept for treating these streams, they are combined in a retort, and essentially all of the cadmium is vaporized. A matrix metal, such as copper or a copper alloy, may be added during retorting to aid in dissipating fission product heat and to begin the process of forming a metal waste form. After retorting has been completed, additional matrix alloys may be added to disperse and immobilize the wastes. A dense metal ingot is formed by melting or hot pressing.

Initial investigations suggest that metal alloy waste forms have considerable promise for immobilizing noble metal and rare earth fission products and small amounts of actinides that will be present in the combined metal wastes. The metal wastes could be made less susceptible to reaction with repository groundwater by dissolving them in a corrosion-resistant matrix alloy that forms stable intermetallic compounds with the fission products. Possible matrix alloys include copper or stainless steel, which could be obtained from the fuel cladding and reactor assembly. It seems advantageous to contain technetium as a metallic alloy, because the reducing conditions surrounding a metal waste form should slow the formation of the water-soluble pertechnetate anion. However, the waste form is likely to be highly heterogeneous. Even if the alloy is melted, a large number of intermetallic compounds and insoluble metal phases will precipitate as this highly complex mixture is cooled. The grain size and degree of phase separation will depend, to a large extent, on the cooling rate. The waste form can be encapsulated in a thick-walled container of a corrosion-resistant material to provide nearly complete containment for several hundred years, but long-term resistance to releases into the near-field environment must be provided by the waste form itself. Work has been started to determine fission product release rates from candidate metal alloys.

DEVELOPMENT STATUS AND PLANS

The Fuel Cycle Facility (FCF) of the Experimental Breeder Reactor-II (EBR-II) in Idaho is being readied for a large-scale demonstration of a prototype IFR fuel cycle, which should start in 1993. The primary objective of this demonstration is to obtain information for the design of a commercial IFR power plant and an estimate of its cost. The equipment to disassemble spent EBR-II fuel assemblies, chop fuel elements for feeding to the electrorefiner, consolidate electrorefiner products, and manufacture new fuel assemblies from the recovered actinides have been built and are being installed in the FCF. The chemical and engineering feasibilities of the electrorefining process have been established in tests with unirradiated materials [14]. An electrorefiner capable of handling 20-kg batches of spent EBR-II fuels has been built and should be operational in the FCF early in 1993. It is planned that the equipment to demonstrate treatment and packaging of the high-level process wastes will be in operation by 1995, when sufficient volumes of spent salt and metal will have been accumulated.

The basic flowsheet for treating and packaging process wastes has been designed, as described in this paper, but laboratory development of several important steps is ongoing. The chemical feasibility of spent salt treatment has been established, and engineering-scale prototypes of the pyrocontactor and salt stripper will be in operation soon with uranium and nonradioactive fission products.

The extraction equipment being developed for liquid salt and cadmium is similar to a centrifugal contactor used for aqueous/organic extractions. The pyrocontactor (see Fig. 6) consists of a hollow rotor spinning at speeds up to 2000 rpm in a stationary housing [15]. Liquid salt and cadmium are fed into the annulus where they are stirred vigorously, and are then drawn into the bottom of the rotor, which acts as both a pump and phase separator. The two liquids are separated by underflow-overflow weirs at the top of the rotor, leave the contactor, and flow to the adjacent contactors in the countercurrent flow train.

A salt stripping system, which is a prototype of equipment for the FCF, has been fabricated and has successfully completed shake-down tests [16]. To test this equipment, about 120 kg of salt, which contains a total of about 1 wt % U, Ce, Nd, and Y, will be pumped from a large-scale electrorefiner into the stripper. The stripper is a well-stirred vessel, 40-cm in diameter, with several ports for instruments, sampling, and

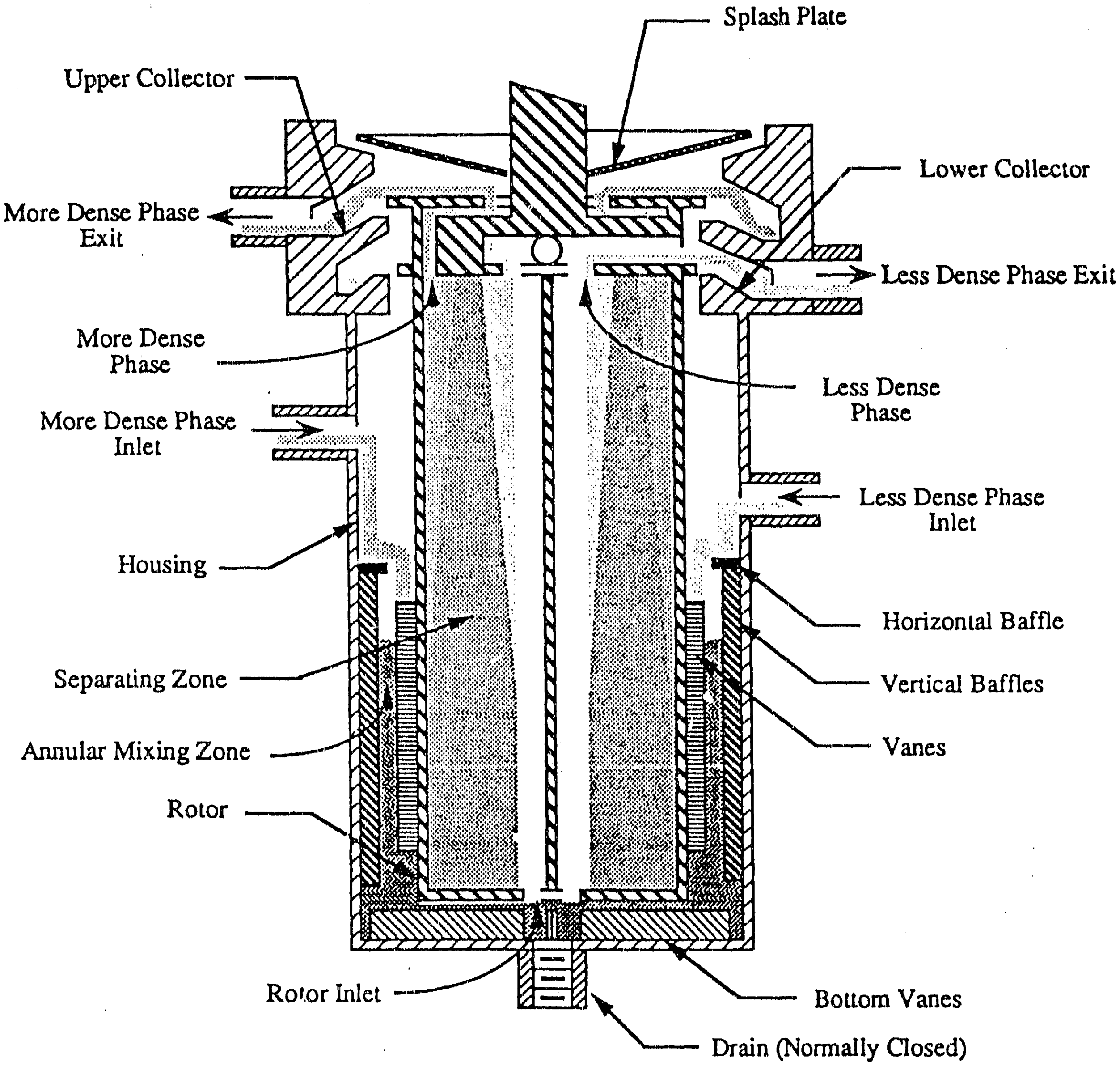

Fig. 6. Pyrocontactor

transferring salt or cadmium. Measurements of the rate and extent of uranium and rare earth transfer will be made. Techniques will be investigated for avoiding the formation of difficult-to-dissolve intermetallic compounds by controlling the lithium metal addition rate to the cadmium so that the chloride reduction rate does not exceed the metal dissolution rate. In addition, the capability of a sintered metal filter for removing insoluble materials from the salt and metal in the stripper and electrorefiner will be evaluated.

Development of suitable salt and metal waste forms is at an early stage. Laboratory experiments have shown that adequate fission product removals from salt can be achieved with zeolites, but quantitative data are needed to select the best zeolite and to design the process. Particles of salt-occluded zeolite appear to have good resistance to water leaching, but techniques must be developed to consolidate salt-zeolite mixtures into monolithic waste forms. Efforts to select suitable metal waste forms and develop the fabrication processes are just beginning.

The dauntingly arduous work of qualifying salt and metal waste forms for disposal lies ahead. An important objective of the IFR Program is to develop a data base on waste form performance that will be the foundation of the regulatory qualification process for wastes from a future commercial IFR. Prototype forms will be made from the FCF wastes and tested to obtain the data needed for predictions of repository performance. Qualification of IFR wastes may be somewhat less arduous than the qualification of vitrified defense waste, because of their lower TRU content and the ongoing work to qualify high-level wastes for disposal at Yucca Mountain.

The ultimate aim of the IFR Program is to lay the groundwork for the construction of future IFRs. A key part of this demonstration program is the development of practical waste treatment techniques and acceptable waste forms.

REFERENCES

1. C. E. Till and Y. I. Chang, "Evolution of the Liquid Metal Reactor: The Integral Fast Reactor (IFR) Concept," in Proceedings of the American Power Conference, Chicago, IL, April 1989, Vol. 51, pp 688-691.

2. C. E. Till, W. H. Arnold, and J. D. Griffith, "The U.S. Liquid Metal Reactor Development Program," Presented at American Nuclear Society Topical Meeting -- Safety of Next Generation of Power Reactors, 1988.

3. J. P. Ackerman, "Chemical Basis for Pyrochemical Reprocessing of Nuclear Fuel," I&EC Research 30(1), 141 (1991).

4. T. R. Johnson and J. E. Battles, "Waste Management in IFR Fuel Cycle," Proceedings of Waste Management '91, Vol. 1, p 815, Arizona Board of Regents (1991).

5. T. Koyama, T. R. Johnson, and D. F. Fischer, "Distribution of Actinides in Molten Chloride Salt/Cadmium Metal Systems," J. of Alloys and Compounds, to be published in 1992.

6. J. P. Ackerman and J. L. Settle, "Partition of Lanthanum and Neodymium Metals and Chloride Salts between Molten Cadmium and Molten LiCl-KCl Eutectic," J. of Alloys and Compounds 177, 129-141 (1991).

7. J. P. Ackerman and J. L. Settle, Argonne National Laboratory, private communication, 1992.

8. J. P. Ackerman, "PYRO - A System for Modeling Fuel Reprocessing," presented at American Nuclear Society Winter Meeting, San Francisco, CA, November 26-30, 1989.

9. Y. Kobayashi and D. F. Fischer, Argonne National Laboratory, private communication, June 1991.

10. M. A. Lewis and L. J. Smith, Argonne National Laboratory, in preparation.

11. M. A. Lewis, Argonne National Laboratory, private communication, March 1992.

12. M. A. Lewis, J. J. Laidler, and D. F. Fischer, "Immobilization of High-Level Chloride Salt Waste," Argonne National Laboratory, in preparation.

13. T. Koyama and D. F. Fischer, Argonne National Laboratory, private communication, June 1991.

14. Z. Tomczuk, J. P. Ackerman, R. D. Wolson, and W. E. Miller, "Uranium Transport to Solid Electrodes in Pyrochemical Reprocessing of Nuclear Fuel," to be published in J. of Electrochem. Society.

15. L. Chow, R. A. Leonard, T. R. Johnson, and G. F. Vandegrift, "Development of a Centrifugal Contactor for Pyrochemical Processing," presented at Pu/U Recovery Conference, Oak Ridge, TN, October 24-26, 1989.

16. R. Blaskovitz and E. Carls, Argonne National Laboratory, private communication, June 1992.

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