

NONAQUEOUS PROCESSING METHODS

by

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ABSTRACT

A high-temperature process utilizing molten salt extraction from molten metal alloys has been developed for purification of spent power reactor fuels. Experiments with laboratory-scale processing operations show that purification and throughput parameters comparable to the Barnwell Purex process can be achieved by pyrochemical processing in equipment one-tenth the size, with all wastes being discharged as stable metal alloys at greatly reduced volume and disposal cost. This basic technology can be developed for large-scale processing of spent reactor fuels.

I. INTRODUCTION

Pyrochemical processing methods offer the potential of large cost reductions over traditional aqueous chemical processes proposed for fissile material recovery. The recovery techniques that we propose require no cooling period for iodine decay prior to processing and do not generate volatile species during the processing steps. These processes conserve expensive shielded cell space by using highly compact process hardware. In many steps the process reagents can be recycled because pyrochemical reagents, unlike aqueous reagents, are highly radiation resistant. The minimal amount of wastes arising from these processes is generated as solid materials and rarely requires additional processing prior to packaging for ultimate disposal.

This report is a result of our discussions at the EPRI Workshop on Fission-Fusion Hydride Fuel Cycle Risks in La Jolla, California, April 25-30, 1982. One small working group dealt with the reprocessing of the spent fuel and blanket

material. Since the primary hybrid was suppressed fission of either a metal Be-Th or a metal Be-U blanket to 0.2-0.6% burnup, the molten metal/molten salt processing is particularly promising. The process is based on the salt transport process and metal processing performed in the 1960s and can be extended to include spent power reactor fuels. However, small-scale demonstration and considerable engineering will be required before the process could be adopted.

The nonaqueous methods discussed here are proven chemical processes which have been demonstrated in laboratory-scale operations. In spite of this, we anticipate that a significant engineering effort will be required to design and manufacture the operating hardware needed for reliable, trouble-free remote operations in the hostile environments encountered within shielded process modules.

Pyrochemical processes are, in many ways, similar to the more traditional solvent extraction systems in that separations are accomplished by extracting a chemical family, such as the actinides, out of a solvent with an extractant. The great difference is that in pyrochemical systems the solvent is typically a molten alloy, the extractant is a mixture of molten salts, and the operating temperature is about 800°C. Common solvent alloys contain magnesium, copper, zinc, or bismuth; common extraction salts are various combinations of alkali or alkaline earth halides, commonly chloride salts (NaCl, KCl, MgCl₂, CaCl₂). Fluoride salt melts, which are especially corrosive, can occasionally be used to great advantage in processes where the product elements can be volatilized from the process as hexafluoride gas (UF₆, PaF₆, PuF₆).

Process extractions may be carried out in batches, in counter-flow columns,¹ or in mixer-settler extractors.² Because of the corrosive nature of molten salts, process equipment must be constructed from metals that are highly resistant to chemical attack. Process equipment designed for use with fluoride-bearing salts is commonly made from molybdenum or Hastelloy-N^R, and equipment intended for use with chloride salts can be made from tantalum, tungsten, and, in certain cases, titanium and zirconium. Because the oxides of these refractory metals are volatile at elevated temperatures, pyrochemical process equipment must be contained in inert atmospheres such as argon or helium. The technology of operating inert-atmosphere cells with master-slave manipulators has been successfully demonstrated.³

Process temperatures in pyrochemical separations range from 400°C to 900°C, depending on the salts selected for optimum separation characteristics. The solubility of elements such as uranium, plutonium, and the fission products is at least as large in molten salts and alloys as in common aqueous solvents (nitric or

hydrochloric acids) and, in many cases, is an order of magnitude larger. The net heavy-metal density in typical pyrochemical processes is a factor of 10 greater than in comparable aqueous systems. Therefore, pyrochemical processes equipment can be small in physical size and yet match the throughput capability of much larger aqueous process hardware.

The reaction kinetics of pyrochemical systems is extremely fast.* In experimental evaluation of a counter-current extractor at ANL, the rate-limiting step was the time needed for dissolved metal to diffuse from the center of a solvent droplet to the surface. The equilibrium extraction time for the unit was related to the size of the droplet generated by the distributor plate for the solvent metal. Therefore, the mass throughput of such a column is limited only by physical "flooding" of the extractor plates. Since the specific gravity ratio of molten salts to liquid metals is large, the mass throughput per unit area is much greater than for organic extractant systems.

II. SALT TRANSPORT PROCESS

We believe the ANL Salt Transport Process (STP) would be a superior method for performing fissile material recovery and providing a suitable decontamination from fission products. The process utilizes the difference in distribution coefficients between two metal phases and a common transport salt. Alloys containing a common alloying element are used to prevent contamination of the phases with foreign solvents. For example, binary alloys of magnesium can be used with magnesium chloride as the bridge between two halves of a simple Redox process. The following information from Process Chemistry, Series III, Volume 4 presents an insight into the chemistry of the Salt Transport method of chemical purification.⁴

Many factors enter into the selection of liquid metal solvent systems, such as melting point, vapor pressure, and solubility relationships. Of particular interest in a process involving separations by salt-metal extraction methods are the effects of metal phase composition upon the distribution behavior of uranium, plutonium, and the fission-product elements. The distribution coefficients of individual elements and the separation factors between elements can both be changed markedly by varying the composition of the metal phase.

*Information provided by R. D. Pierce, Argonne National Laboratory, November 4, 1980.

In Fig. 1, the distribution behavior of praseodymium between a 50 mol% $MgCl_2$ -30 mol% $NaCl$ -20 mol% KCl salt phase and various binary alloys of magnesium is shown. Much of the experimental work on salt-metal extraction methods has been done with tracer-level radioactive praseodymium because it behaves as a typical rare-earth fission product and is a convenient element for radiochemical analysis. As may be seen in Fig. 1, the praseodymium distribution coefficient is about 10^5 times larger for a Cu-67 wt% Mg alloy than it is for an Al-20 wt% Mg alloy. This pronounced effect is due to the large differences in the activities of praseodymium and magnesium in these two alloys.

The composition of the metal phase has a strong effect, not only on the distribution coefficients, but also on the separation factors that can be obtained for various solutes. Because of the importance of the plutonium/rare-earth separation in pyrochemical processes, several experiments have examined the effect of separations. The praseodymium/plutonium separation factor depended upon the magnesium content of the liquid alloy, the other constituent of the alloy, and the temperature. The effects of these three factors are illustrated in Fig. 2, where the praseodymium/plutonium separation factor is plotted against the magnesium content of the alloy phase for binary alloy of magnesium with copper, zinc, and cadmium at 600°C. In all cases, the salt phase composition was the ternary system, 50 mol% $MgCl_2$, 30 mol% $NaCl$, and 20 mol% KCl . The effect of temperature may be seen by comparing the curves for the copper-magnesium system at 600°C and 800°C. The effect of magnesium concentration is in qualitative agreement with the prediction from the activity coefficients of praseodymium and plutonium in the four pure solvents. At 600°C, these values indicate that the separation factors in the pure metals should differ by the following factors: 1.6 for magnesium and cadmium, 3.4 for magnesium and zinc, and 490 for magnesium and copper. These predicted values agree with the values estimated from Fig. 2.

Largely because of the data shown in Fig. 2, a 33 wt% Cu-67 wt% Mg is often selected as the liquid metal solvent for the reduction and rare-earth extraction steps of the STP flowsheet. This alloy has the highest observed rare-earth/plutonium separation factor, and its relatively low melting point ($\sim 590^\circ C$) permits operation at a reasonable temperature.

Salt transport separations are based upon selective transfer of a solute from one liquid metal alloy (donor) to another (acceptor) by contacting the two alloys either alternately or simultaneously with the same molten salt. This method can be used to separate plutonium from uranium and the noble-metal fission products.

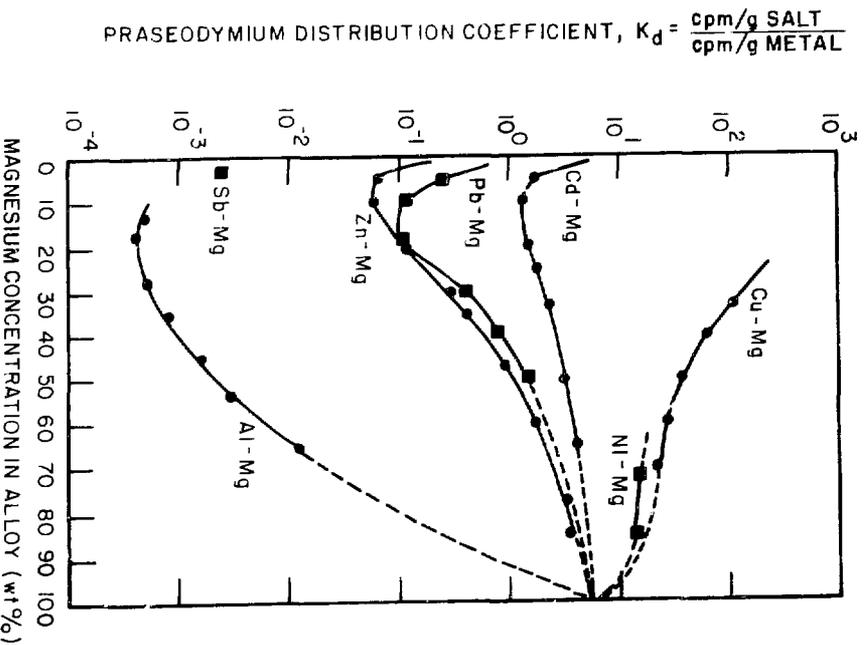


Fig. 1. Effect of metal phase composition on the distribution of praseodymium. Temperature: 600°C; salt phase: 50 mol% MgCl_2 -30 mol% NaCl-20 mol% KCl.

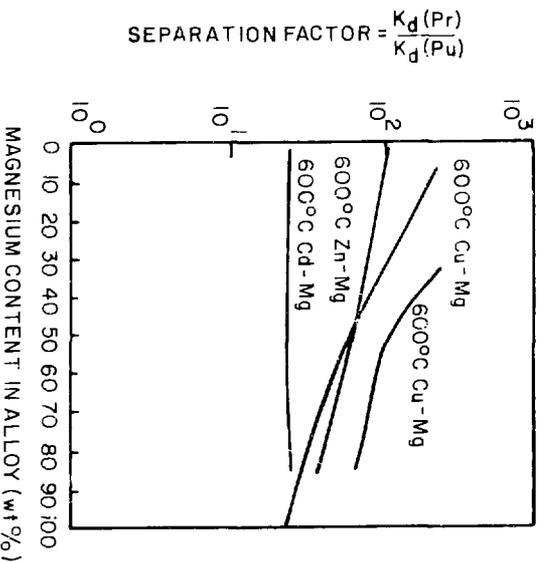


Fig. 2. Praseodymium/plutonium separation factors for various binary magnesium alloys. Salt phase; 50 mol% MgCl_2 -30 mol% NaCl-20 mol% KCl.

The donor and acceptor alloys contain the same metal that is the weaker reducing agent (Mg), and the salt contains the complementary oxidizing agent (MgCl₂). The alloys also contain one or more solvent metals that are weaker reducing agents than magnesium, e.g., zinc, cadmium, copper. The magnesium concentrations in the alloys and the solvent metal are selected so that the thermodynamic properties of the system will favor the desired separation. The salt transport step for plutonium recovery and purification employs a 33 wt% Cu-67 wt% Mg donor alloy, a Zn-5 wt% Mg acceptor alloy, and a 50 mol% Cl₂-30 mol% NaCl-20 mol% KCl salt phase.

The salt transport of plutonium is illustrated schematically in Fig. 3. The plutonium in the donor alloy is oxidized by MgCl₂ and extracted into the salt:

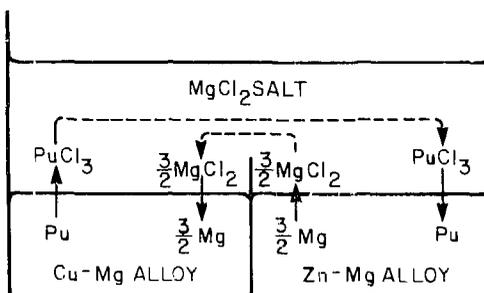
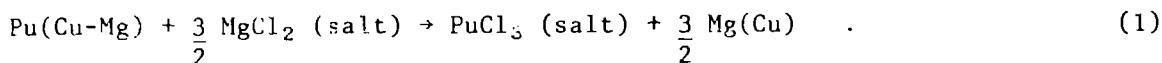
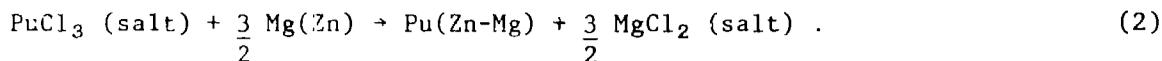
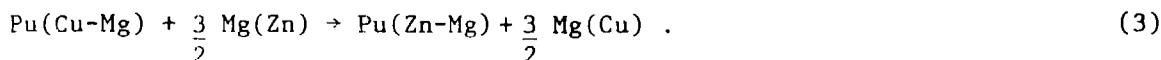


Fig. 3. Schematic illustration of salt transport step for plutonium.

The salt containing the PuCl₃ is then contracted with the zinc-magnesium acceptor alloy, where the reverse reaction takes place:



The overall reaction is



For each mole of plutonium transferred from the donor to the acceptor, 1.5 moles of magnesium move in the opposite direction. The depletion of magnesium in the

acceptor alloy and its increasing concentration in the donor alloy must be taken into account in the practical application of a salt transport separation.

A. Typical Process

A typical STP is diagrammed in Fig. 4. The process equipment consists of three counter-current vertical extraction columns arranged in parallel. A salt pump is used to circulate the molten transport salt through all three columns. The process material, probably consisting of uranium with plutonium and fission products, is placed in the donor alloy (33 wt% Cu-67 wt% Mg) and into the first column. The uranium is dissolved at the rate that is transported across the salt bridge to the acceptor reservoir. The transition and noble-metal fission products will remain in the donor loop. A small side stream from the donor column effluent is shunted to a distillation unit to remove the fission-product residues from this stream. Eventually the transition and noble-metal products will be discharged to waste as a copper alloy with no additional waste solidification treatment.

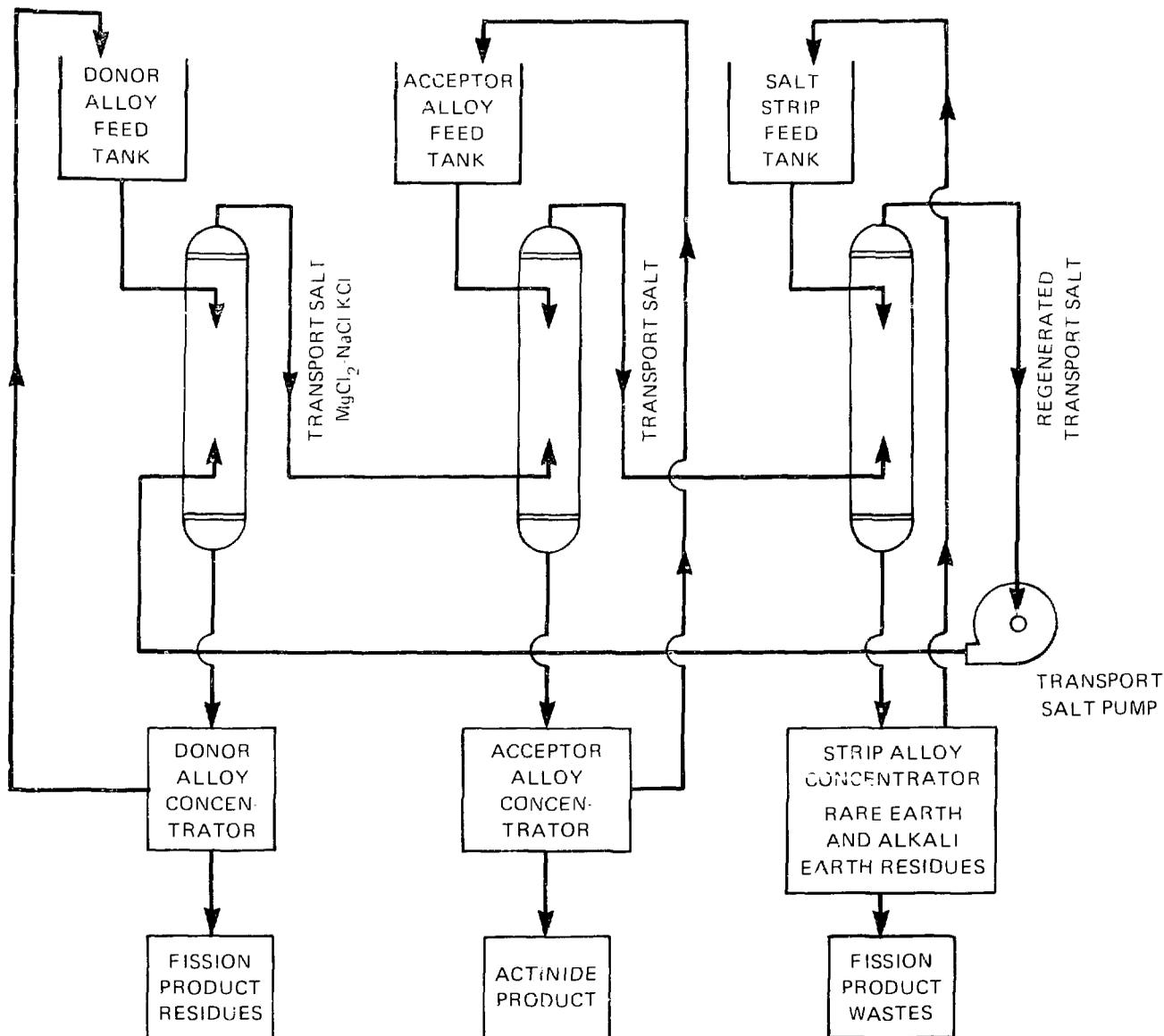
The actinide and rare-earth elements will be extracted into the transport salt, 50 mol% $MgCl_2$ -30 mol% NaCl-20 mol% KCl, but only the actinides will be re-extracted into the acceptor alloy (95 wt% Zn-5 wt% Mg). The small mass of rare-earth fission products can build up in the transport loop for a considerable time or can be removed in the third column by a stripping alloy (50 wt% Al-50 wt% Mg). The rare earths can be disposed of as alloys in a metallic aluminum matrix with no further waste treatment.

The uranium will exceed the solubility of the acceptor alloy and be removed from the process as metallic fines;⁵ plutonium will remain in the acceptor solvent and be recovered by distillation of the solvent metal.

The entire process can be housed in a single argon-atmosphere hot cell of rather small dimensions. For example, all process equipment required could easily be housed in the EBR-II argon-atmosphere hot cell known as HFEF-North.

B. Alternate Processes

Another viable, demonstrated method for the recovery of Pa, U, Np, and Pu from irradiated fuels is the volatilization of the respective hexafluoride gas from a fluidized bed containing alumina and the fuel in the form of oxide, chloride, or tetrafluoride salt.⁶ Either fluorine or another strong fluorinating agent is passed through the bed with an inert carrier gas at temperatures ranging from 300°C to 600°C, and the volatile hexafluoride gases are trapped from the flowing gas stream on NaF or MgF_2 traps operated at temperatures ranging from

NOTES:DONOR ALLOY:

33 wt% Cu, 67 wt% Mg

ACCEPTOR ALLOY:

95 wt% Zn, 5 wt% Mg

SALT REGENERATING ALLOY:

50 wt% Al, 50 wt% Mg

PROCESS CELL ATMOSPHERE:

ARGON GAS, 1 atm

TEMPERATURE:

~ 800° C FOR EXTRACTORS

MATERIAL:

TANTALUM COLUMNS, PIPING

FEED RATE:

~ ½ GPM METAL ALLOY

~ 3 GPM EXTRACTION SALT

Fig. 4. Salt transport process schematic diagram, uranium recovery.

100°C to 400°C. The few volatile fission products can be readily fractionated from the actinide elements on these traps, and after decontamination, the actinides can be recovered by elution off the traps and conversion to the filterable tetrafluoride.⁷ This is done either by thermal decomposition of the hexafluoride or photoreduction with high-intensity light of the proper frequency. Unused fluorinating agents can be recycled back through the process for reuse.

It is also possible to separate actinide elements from each other by the volatility technique. For example, plutonium can be isolated from uranium by first passing BrF_5 through the bed containing $\text{UO}_2 - \text{PuO}_2$ at 300°C. Only UF_6 is volatilized from the bed and is collected on NaF traps; then F_2 is passed through the bed at 550°C and the PuF_6 is collected on a different set of traps.

It is probable that PaF_5 and UF_6 can be isolated from thorium by a similar volatilization technique; the nonvolatile ThF_4 can be reduced to metal with cadmium at 800°C and recycled back to the blanket for reuse.

The utilization of molten fluoride salts as both a reactor coolant and breeding blanket has been thoroughly demonstrated at ORNL during the development of a molten salt power reactor.⁸ Many detailed discussions of both the chemistry and engineering techniques associated with this method exist in the current literature.^{9,10} Since the technology of flowing molten fluoride salts is fully developed and documented, we will not comment further on this method other than to cite potentially serious problems involving neutronic compatibility between the alloys required for corrosion resistance to the salts and those required for optimum breeding characteristics in the blanket. If these problems can be satisfactorily resolved, this technique would be an excellent method for recovering both ^{233}Pa and ^{233}U from circulating molten salts in a hybrid reactor. Warren Grimes has written an excellent discussion of this subject as part of the report on the feasibility of the fission-suppressed tandem mirror hybrid reactor concept.¹¹

After bulk removal of the major constituent of the blanket, a partial separation of fission products can be achieved by melt-refining or electrorefining processes.

In melt refining, the uranium or praseodymium from the blanket would be maintained for several hours with an oxide slag such as magnesia.¹² The melt would then be separated, probably by pouring, from the slag and the purified uranium (or plutonium) separated.

Electrorefining of plutonium has been very successful at Los Alamos and, from 1964 through 1977, about 1570 kg of pure plutonium has been produced from

metal fabrication scrap.¹³ This electrolytic conversion replaced many processing steps required in plutonium recovery by aqueous methods. Electrorefining is a small-scale operation at Los Alamos; however, it is an excellent method for purification of active metals when molten salt electrolytes are employed.

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