Plutonium Residue Recovery (PuRR) Project Quarterly Progress Report April-June 1989

D. W. Gregg, R. G. Hickman, J. H. Landrum,
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October 20, 1989

Received by OSTI

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Manuscript date: October 20, 1989

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Foreword

The Plutonium Residue Recovery (PuRR) project addresses the recovery of weapons-grade Pu from intractable residues that are currently stored at several Department of Energy (DOE) sites. More than 2 metric tonnes of Pu have accumulated in intractable residues since the 1950s, and the amount of intractable Pu residue continues to increase by about 50 to 100 kg per year.

This project is a joint effort by Lawrence Livermore National Laboratory (LLNL) and Argonne National Laboratory (ANL), and has two primary objectives:

- Efficient Pu recovery from feedstocks that currently cannot be processed.
- Rejection of tramp elements in a waste form that contains <100 nCi/g of Pu (<1.6 ppm Pu), i.e., non-transuranic ("non-TRU") waste.

If this project is successful, the results will be a lessening of potential hazards to the environment, cleanup of vault overloading with no need for enlarging national vault capacity, and the return of usable Pu to the pipeline.

Due to other considerations and commitments, the Defense Systems Program at LLNL could only fund PuRR through June 1989. There are plans to resume the effort in FY90 under the sponsorship of the Isotope Separation and Materials Processing Program at LLNL. The original goals and objectives will be reexamined for viability against other processes that are being developed at various DOE contractor sites.

This report is the final PuRR Quarterly Progress Report under the sponsorship of Defense Systems Program, LLNL. Special thanks are due G.H. Miller for initial funding, R.E. Clough for continued funding and moral support, and R.M. Alire for enthusiastic initial leadership. We also thank Donna Lee Paquette for editing the reports and preparing the manuscripts.

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Plutonium Residue Recovery (PuRR) Project Quarterly Progress Report April–June 1989

Abstract

A material-balance flowsheet for ash-heel processing has been prepared. The major process features are (1) reduction of Pu into a calcium-zinc alloy and selective electrolytic recovery of the Pu from the alloy, (2) removal of americium as a waste, (3) concentration of nontransuranic tramp elements in a zinc waste, (4) removal of oxygen and recovery of calcium by electrolysis of CaO, and (5) zinc recycle by evaporation. Based on this idealized flowsheet, the mass of solid waste is only 62% of that of the original residue. This is accomplished by recycling virtually all the reagents and discarding the oxygen as CO and CO₂.

The pyrochemical recovery of Pu from incinerator ash heel from the Rocky Flats Plant was investigated. During this period, zinc-calcium alloys were used to reduce the PuO₂ in the ash. Reduction of ash heel has been attempted with zinc-calcium alloys containing 2, 6, and 10 wt% calcium after the reduction. These resulted in extractions of 95%, 97%, and 99.5%, respectively, of the Pu from the salt. Following exposure of the reduction alloy to a ZnCl₂-bearing salt, the Pu was removed effectively from the alloy; however, the Pu recovered in the salt did not complete the material balance. A single scrub was performed with each of the reduction salts using fresh zinc-calcium alloy. For the 10 wt% Ca-Zn run, the scrubbed salt contained only 6 ppm of Pu, which is approaching non-TRU levels (~1.5 ppm).

Experiments were made to test a calcium-zinc reference electrode against a Zn-Ca-Mg-Al liquid alloy. The results agreed well with calculated potentials, and such electrodes are promising for application to process monitoring. The electrode used for these tests allowed too much diffusion, resulting in a changing reference alloy composition and a drifting signal.

Graphitic carbon tended to flake when used as a consumable anode at which oxygen is discharged in aqueous solution. Vitreous carbon, on the other hand, retained its structural integrity. Pyrolytic boron nitride was attacked by calcium but not calcium chloride at 900°C.

Calculations were made that verify that most of the americium in the molten salt is present in the divalent state when distributed between liquid Pu and NaCl-KCl. The AmCl₂ activity coefficient is about 10 times that of PuCl₃ in the salt mixture.

Plutonium Residue Recovery (PuRR) Project Quarterly Progress Report April-June 1989

I. Introduction

The PuRR process was conceived as a project in mid-1987. Motivations for the project were to recover as much as 3 tons of weapons-grade Pu and to reduce the amount of transuranic (TRU) residues now stored at DOE facilities. These residues may eventually have to be placed in a permanent high-level waste disposal site. Either of the motivations should provide sufficient incentive for developing the process and implementing it on a production scale.

The intractable residues that are feedstock for the PuRR process are some of the streams produced by conventional (aqueous) Pu production processes. Consequently, from the outset it was recognized that nonaqueous chemistry (pyrochemistry) would have a dominant role to play in PuRR.

The project is being conducted jointly with ANL because many of the pyrochemical and electrochemical processes expected to be used have been or are being developed there as part of nuclear reactor fuel reprocessing cycles. LLNL, too, is using pyrochemical and electrochemical processes, but rather as an integral part of the Special Isotope Separation Program. In addition, LLNL has a Class I

Plutonium Facility with space available to accommodate larger-scale experiments and processes that are expected to be part of this project in its later stages.

The PuRR feedstock is mostly compounds of "tramp" metals, with only a few percent of Pu being present on the average. Because of the large number of other elements and compounds of them that are present, several different process flowsheets were considered initially, as mentioned. Experience has now shown that being open to alternative approaches was prudent. Some of the earliest concepts have been eliminated in favor of others that now appear to be the more promising.¹⁻³ However, nothing has been discovered that shows a PuRR process cannot work well.

The process flowsheet has been revised several times based on experimental measurements made by ANL. The earlier versions are presented in earlier quarterly reports. The current flowsheet, which continues to emphasize waste minimization, is presented in Fig. 1 with a material balance presented in Table 1. The material balance is in weight units, and is for a unit weight of Pu.

Figure 1. The current LLNL-ANL baseline Plutonium Residue Recovery (PuRR) project.

Table 1. PuRR material balance for current process.

Stream #	1	2	3	4	5	6	7	10	11	12	13	15	17	18	19	20	21	22
PuO ₂	1.13	0	0	1.13	0	0	0	1.13	0	0	0	0	0	0	0	0	0	0
O ₂	0	0.0267	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ag ₂ O	0.03	0	0	0.03	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0
Al ₂ O ₃	1.45	0	0	1.45	0	0	0	0.29	0	0	0	0	0	0	0	0	0	0
Am ₂ O ₃	0.00818	0	0	0.00818	0	0	0	0.00818	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3.75	0	0
CO ₂	0	0	0.0367	0	0	0	0	0	0	0	0	0	0	0	0	2.95	0	0
CaO	0.4	0	0	0.4	0	0	0	12	0	0	0	0	0	15	0	0	0	0
Cr ₂ O ₃	0.33	0	0	0.33	0	0	0	0.066	0	0	0	0	0	0	0	0	0	0
CuO	0.07	0	0	0.07	0	0	0	0.014	0	0	0	0	0	0	0	0	0	0
Fe ₂ O ₃	1.5	0	0	1.5	0	0	0	0.3	0	0	0	0	0	0	0	0	0	0
MgO	0.08	0	0	0.08	0	0	0	0.016	0	0	0	0	0	0	0	0	0	0
Ni ₂ O ₃	0.18	0	0	0.18	0	0	0	0.036	0	0	0	0	0	0	0	0	0	0
PbO	0.07	0	0	0.07	0	0	0	0.014	0	0	0	0	0	0	0	0	0	0
SiO ₂	3.38	0	0	3.38	0	0	0	0.676	0	0	0	0	0	0	0	0	0	0
SnO ₂	0.03	0	0	0.03	0	0	0	0.006	0	0	0	0	0	0	0	0	0	0
TiO ₂	0.05	0	0	0.05	0	0	0	0.01	0	0	0	0	0	0	0	0	0	0
CaCl ₂	0	0	0	0	0	113	0	113	0	0	0	0	0	113	0	0	0	113
PuCl ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CaF ₂	0	0	0	0	0	37.5	0	37.5	0	0	0	0	0	37.5	0	0	0	37.5
Ag	0	0	0	0	0	0	0.0223	0	0	0.00559	0.00559	0	0	0	0	0	0	0
Al	0	0	0	0	0	0	0.614	0	0	0.154	0.154	0	0	0	0	0	0	0
Am	0	0	0	0	0	0	0	0	0	0.00744	0	0.00744	0	0	0	0	0	0
Ca	0	0	0	0	8.31	0	0	0	2.41	0	0	0	0	0	0	0	10.7	0
C	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	2.41	0	0	0
Cr	0	0	0	0	0	0	0.181	0	0	0.0452	0.0452	0	0	0	0	0	0	0
Cu	0	0	0	0	0	0	0.0447	0	0	0.0112	0.0112	0	0	0	0	0	0	0
Fe	0	0	0	0	0	0	0.84	0	0	0.21	0.21	0	0	0	0	0	0	0
Mg	0	0	0	0	0	0	0.0384	0	0	0.0096	0.0096	0	0	0	0	0	0	0
Ni	0	0	0	0	0	0	0.102	0	0	0.0256	0.0256	0	0	0	0	0	0	0
Pb	0	0	0	0	0	0	0.0520	0	0	0.0130	0.0130	0	0	0	0	0	0	0
Pu	0	0	0	0	0	0	0	0	0	1	0	1	1	0	0	0	0	0
Si	0	0	0	0	0	0	1.26	0	0	0.315	0.315	0	0	0	0	0	0	0
Sn	0	0	0	0	0	0	0.0189	0	0	0.00473	0.00473	0	0	0	0	0	0	0
Ti	0	0	0	0	0	0	0.024	0	0	0.006	0.006	0	0	0	0	0	0	0
Zn	0	0	0	0	160	0	160	0	90.4	90.4	90.4	0	0	0	250	0	250	0
Sum	8.72	0.0267	0.0367	8.71	168	150	163	165	92.8	92.2	91.2	1.01	1	165	253	6.70	261	150

Table 1. PuRR material balance for current process. (cont.)

Comments and Assumptions

Stream 1: The relative tramp metal composition for ash heels was found at LLNL using an emission spectrograph. Plutonium and americium concentrations were found by gamma ray spectroscopy and calorimetry; carbon by combustion analysis. It is assumed the metals are in the form of oxides.

Stream 2: The amount of oxygen is just enough to burn the carbon to CO_2 .

Stream 3: The CO_2 mass assumes all the carbon is burned.

Stream 4: Contains all the metal oxides

Stream 5: It is assumed that 80% of each of the tramp metal oxides can be reduced before plutonium oxide is. Calcium is added to reduce 80% of the oxides. Zinc is added to remove the metals, assuming a 2% solubility limit.

Stream 6: The amount of salt was calculated assuming a final concentration of 10 wt% CaO after both stages.

Stream 7: All zinc from stream 5 and 80% of the tramp metals

Stream 10: The salt from stream 6, the CaO from the first reduction, the remaining 20% tramp metals, plutonium and americium as oxides

Stream 11: Sufficient calcium to reduce remaining oxides and zinc to dissolve the metals, assuming 2% solubility limit

Stream 12: Zinc from stream 11, remaining tramp metals, plutonium, americium

Stream 13: Tramp metals from stream 12

Stream 15: Plutonium from stream 12

Stream 17: Plutonium from stream 15

Stream 18: Salt from stream 10, CaO produced by reduction, plus a small amount from the original feed

Stream 19: All the zinc from streams 8 and 16; sufficient carbon to carry off the oxygen from the CaO assuming the gaseous product is 50:50 CO and CO_2

Stream 20: CO and CO_2 waste

Stream 21: Zinc from stream 19, and calcium from stream 18, both in the metallic state

Stream 22: Salt from stream 18

II. Process Development Activities

A. Conceptual Design Studies

Residue Calcining

Analysis by x-ray diffraction shows SiC and FeS to be main constituents of our feedstock. Calcining in air converts both to their oxides. The volume change of the iron compound is comparable to that of the silicon compound, which shows a significant increase. Depending on how accurate our chemical analysis is, the charge could nearly double in volume. If the starting material does not remain a free-flowing powder during calcining (and we know it doesn't), the expansion may be more than enough to break the MgO crucible in which the fixed-bed process is conducted.

It seems the fix is to keep the powder free-flowing, i.e., to prevent sintering. This, in turn, means stirring or mixing would be required. One approach is to use a fluidized bed. Advantages of fluidized beds are that they do an excellent job of mixing, have uniform bed temperature, can be staged, and lend themselves to continuous processing. In addition, they have no moving parts. A typical feature is that dust must be controlled. Fluidized beds are often used for calcining in industry, and have been used for chlorinating uranium oxide.

Another approach is to use an almost horizontal rotary kiln. Its bed temperature is less uniform, but depending on the kinetics, that may not be a disadvantage. It has most of the other advantages. Disadvantages are the moving parts, particularly the need for rotating gas seals, and dust control (as with a fluidized bed). A variation on this would be a stationary horizontal cylinder with an internal rotating stirrer having longitudinal helical paddles and brushes. In any case, cyclone or electrostatic separators are not likely to be satisfactory alone, and HEPA filters will be needed.

Gas flow should be provided with induced draft fans to eliminate outward powder leakage through rotating gas seals.

It is essential to know the kinetics of the reactions before we can design a sintering-free calciner. The best method would employ thermogravimetric analysis. The weight gain (SiO_2) and loss (Fe_2O_3) are in ranges easily measured. After the pure compounds' behaviors are determined, appropriate mixtures can be run, so that a calciner may be designed allowing any batch received to be totally reacted. That, of course, implies excess residence times for some batches, but eliminates the need for x-ray diffraction analysis on each batch before processing can begin.

Flowsheet Development

Liquid metals and molten salts at elevated temperature are used as reagents and solvents in the anticipated processes to effect the necessary separations and chemical conversions. Separations are possible because of the differing stabilities of compounds in the molten salt phase in contact with a liquid metal phase. Several residue-recovery flowsheets are under consideration, but all include reduction of PuO_2 in a residue as an initial step. This step is followed by a selective recovery of the Pu by chemical extraction away from the bulk of the tramp elements, which also are reduced. From the large variety of molten-salt and liquid-metal combinations that exist, zinc-magnesium and copper-magnesium-calcium reduction systems were selected to explore initially while considering suitability of other systems. Reference flowsheets, which were prepared based on these systems, formed the basis for the research. Since December 1988, steps based on a

zinc-calcium system have been studied. This system is attractive because it lends itself to recycle of virtually all of the reagents, which minimizes waste volumes. In addition, attention is being given to the application of electrochemical steps to minimize reaction products that must be chemically converted for recycle.

A reference flowsheet for residue processing is summarized in Fig. 2. The major process features are as follows:

- Reduction of the Pu oxide or other compounds into a liquid zinc-calcium alloy (along with most of the tramp elements from the residue) and selective extraction of the product Pu from the liquid alloy by solvent electrorefining.
- Removal of americium as a waste.
- Concentration of the nontrans-uranic tramp elements in a zinc waste.
- Removal of oxygen and recovery of calcium by electrolysis of CaO.

Two variations of this flowsheet are also under investigation: (1) the reduction may be conducted in two steps, with the bulk of the tramp elements reduced ahead of the Pu so that they will not be present during the solvent electrorefining; and (2) chemical salt-extraction and metal-extraction steps may be substituted for solvent electrorefining. This latter alternative would enhance kinetics but increase the solvent and reactant recycling requirements. Another variation, which is in an earlier stage of development, involves direct electrowinning liquid Pu from a salt suspension/solution of the residue to decrease further the reagent recycling requirements.

A material balance flowsheet is presented in Fig. 3 for an ash-heel feed. It is on a molar basis and follows the reference process in Fig. 2. The feed and exit streams for this flowsheet are summarized in Table 2 on both a molar and mass basis. For 8.7 kg of residue, the total mass of solid waste is 5.4 kg, most of which is metallic. This waste contains zinc, which is added to the system as ZnCl_2 (1) to

oxidize excess calcium following the reduction step, and (2) to scrub the waste alloy prior to disposal. Calcium, magnesium, americium, and oxygen, which also are present in the residues, are not removed in the waste alloy. Some salt must be discarded to remove calcium, as CaCl_2 , from the system. CaF_2 , which is discarded with the CaCl_2 , must be replaced in the feed. It is expected that the magnesium will collect with Pu in the electrorefining step; this magnesium will be distilled from the Pu and collected for disposal. Americium will be reduced from electrorefiner salt periodically with calcium. The oxygen from the residue forms CO (and CO_2) at a consumable carbon electrode in the recycle electrolysis step. This stream can be decontaminated and disposed of easily.

Although calcium reductant for the residue reduction is generated as a zinc-calcium alloy in the electrochemical reagent-recycle step, a small amount of fresh calcium is proposed for reduction of the americium-rich material. If the americium were reduced with a zinc-calcium alloy, slightly less zinc would be discarded in the metallic waste, slightly less salt would be discarded, and no metallic calcium would be added. A disadvantage would be that the americium concentrate would contain zinc.

Development efforts at ANL have been directed at several aspects of the flowsheet. Preliminary emphasis has been on the reduction step to assure that the "intractable" residues are completely digested by the pyrochemical systems. Chemical extraction of the reduced Pu has been tested, and solvent-electrorefining tests are desirable. The electrochemical step for calcium and salt recycle is important to avoid excessive waste volumes. Equipment is being readied to resume development of that step, which was investigated briefly as part of an earlier program at ANL.⁴ Retorting operations were a routine part of the engineering studies of pyrochemical processing of fast reactor fuels,⁵ which were performed in the 1960s, and are believed to require testing but at a later stage in the process development sequence.

Figure 2. PuRR process.

Figure 3. Material-balance flowsheet.

Table 2. PuRR process feed and exit streams.

Basis: 100 mol Residue Feed (992 g Pu)					
Feed Streams			Exit Streams		
	mol	gram		mol	gram
Residue			Zinc Retort Heel		
PuO ₂	4.15	1125	Zn	7.29	477
Ag ₂ O	0.13	30	Ag	0.26	28
Al ₂ O ₃	14.30	1459	Al	28.60	772
Am ₂ O ₃	0.02	11	Cr	4.36	227
CaO	7.17	402	Cu	0.98	62
Cr ₂ O ₃	2.18	331	Fe	18.86	1052
Cu ₂ O	0.49	70	Ni	2.42	142
Fe ₂ O ₃	9.43	1506	Pb	0.32	66
MgO	2.00	81	Si	56.56	1590
NiO	2.42	181	Sn	0.20	24
PbO	0.32	71	Ti	0.63	30
SiO ₂	56.56	3400		120.48	4470
SnO ₂	0.20	30			
TiO ₂	0.63	50			
	100.00	8747	Salt Waste		
			CaCl ₂	7.29	809
			CaF ₂	1.43	112
				8.72	921
Salt					
CaF ₂	1.43	112			
ZnCl ₂	7.29	994			
	8.72	1106	Gaseous Effluent		
			CO	213.40	5975
Metal					
Ca	0.12	5	Magnesium Retort		
			Mg	2.00	49
Carbon					
C	213.40	2561	Americium Reduction		
			Pu	0.04	10
			Am	0.04	10
				0.08	20
			Plutonium Product		
			Pu	4.11	982

B. Experimental Studies

Materials and Ultrasonic Agitation

The work reported here is either a continuation of experiments or follow-on activities to conceptual work reported previously.

Graphitic vs Vitreous Carbon

We performed two experiments on graphitic carbon (gc) to see how it compared with vitreous carbon (vc) as a possible consumable anode material at which oxygen is evolved.

The vc results were reported last quarter.³ It was reported that vc performed well and did not flake from either electrolysis or intense ultrasonic agitation. From the weight loss, it was inferred that some of the discharged oxygen did not produce CO_2 . It was also observed that the vc, during electrolysis, gave the electrolyte a pale yellow color, and one of the rods seems to have had nearly invisible pre-existing cracks. Ultrasonics had a minimal effect on electrode performance.

With gc, two experiments were performed. The first was with electrolysis only, using the same duration (30 min), current density (0.1 A/cm^2), electrolyte (1.9 M NaOH), anode size (3-mm o.d. x 150-mm rods), cathode material (304 SS), and temperature (30°C) as before. The gc was Union Carbide's electrolytic ECV grade, which means the ash content usually is about 50 ppm but can go as high as 100 ppm. It had many pores. Some were as large as 0.3 mm and open porosity was present.

The electrolyte did not change color, so we infer the presence of a trace impurity in vc. The nominal weight loss of the gc was 0.0348 g, which again suggests, based on Faraday's Law, some O_2 evolution rather than just CO_2 . There was NaOH or Na_2CO_3 dried on some of the internal pore surfaces, so the

actual weight loss was a bit higher. Most importantly, flaking was observed during electrolysis (no ultrasonics). We estimate 1 mm^3 of various size particulates were formed during the 30-min run. When ultrasonics with a probe* was used alone, the gc was remarkably rugged. Following a 30-min exposure to intense agitation, only about 0.1 mm^3 was dislodged. There was a weight gain of 0.0009 g, probably due to NaOH dried in internal pores.

Depending on the follow-on process steps, gc may or may not be an acceptable material for use as a consumable anode. If it fails as an anode, it might find some other application, such as a crucible material.

Other investigations have shown that aqueous NaOH will chemically corrode gc when the gc is used as a cathode. Such results, however, have been evident only after exposure to the electrolyte for more than 1000 hrs. The results reported here must be due to undercutting and dislodging of some grains by oxidation to form CO_2 of other more active grains.

Alternative Ultrasonic Stirring

We evaluated ultrasonic sound (for agitation) produced and delivered to the electrolyte in a different manner from that reported in the previous quarter.

The ultrasonics used in the work reported here were provided by a magnetostrictive transducer bonded to the bottom of a stainless steel tank. The energy intensity was substantially lower than in the previous experiments that used a piezoelectric-driven probe. In question was the ability of the lower-intensity (but more uniform) ultrasonic agitation to knock out gc grains, detach oxygen or carbon dioxide bubbles, and stir the electrolyte.

*Bronwill Biosonic, Powertron model B10-II, 150 W operated at 50% full power.

Bubble detachment (depolarization) was shown previously to be of little concern or utility in this aqueous solution. The magnetostrictive source was not a particularly effective bubble remover, although bubble evolution was copious and uniform. The current density was about 0.5 A/cm². The stainless steel tank functioned as the cathode.

Erosion of the gc by magnetostrictive ultrasonics seemed to be slightly less than with the probe, which could be expected on the basis of energy density. The gc electrode was the rod used in the first gc experiment reported previously.

Stirring occurred, but a rather unexpected phenomenon was observed. Some bubbles and a couple of particulates seemed to become trapped in "energy wells" in the electrolyte on the stainless steel tank surfaces. When the ultrasonic power was shut off, the bubbles would rise to the liquid surface and the particulates would move more freely in the solution. Such behavior was not observed in the bulk of the solution. We do know that with this type of transducer, standing waves of ultrasound exist in the tank. The "energy wells" may correspond to the nodes of these waves.

From these observations, we are unable to say with certainty that ultrasonic agitation provided in this fashion is either superior or inferior to that provided by a piezoelectric-driven probe. One benefit is that no extra hardware is in the electrolyte. However, bonding the transducer to a high-temperature electrolysis cell may be very difficult.

Pyrolytic Boron Nitride

In our first chemical compatibility test of pyrolytic boron nitride (PBN), before loading, two small crucibles were cleaned and thermally cycled to 925°C in an Ar atmosphere glovebox. Then, in the glovebox, they were loaded with equal volumes of Ca, dried CaCl₂, and Zn, and heated to 900°C for 8 hrs in argon.

Duplicates were run to check reproducibility. After cooling, the crucibles were intact. Metal buttons from the Zn and Ca had formed, and they were stuck to the wall and were removed with HCl and gentle mechanical action. Their before and after weights were:

	<u>Crucible I</u>	<u>Crucible II</u>
Before loading		
and heating	2.4878 g	2.5062 g
After final		
cleaning	2.4219 g	2.4469 g
Loss	0.0659 g	0.0593 g

Mechanically, the crucibles were in excellent shape, but the weight loss was more than expected. A Union Carbide Corp. representative had assured us that CaCl₂ would be successfully contained. He was not asked about the liquid metals, however. When the weight loss was observed, it was logical to suspect that Ca was attacking the PBN.

Because we plan to electrowin Ca from a CaCl₂/CaO melt, in the second run we eliminated the Zn. In addition, one of the crucibles was run as a control rather than loading them both to check repeatability. The loaded crucible contained 0.80 g CaCl₂ and 0.50 g Ca.

The physical behavior of the charge was the same as before, i.e., it stuck to the PBN after cool-down and did not crack the crucible. The CaCl₂, however, did not appear to have completely melted. Cleaning of both crucibles with HCl (and some mechanical scraping) removed the sample. The crucible weights were as follows:

	<u>Loaded</u>	<u>Control</u>
Initial	2.4219 g	2.4469 g
Final	2.2088 g	2.4320 g
Loss	0.2131 g	0.0149 g

In the absence of Zn to lower the Ca activity, it aggressively attacked the crucible, so PBN must be judged unsuitable for containing high-temperature molten Ca. Remarkably, the control lost much more weight than expected. It could have sublimed or reacted with trace gases in the glovebox's argon atmosphere, or else it could have reacted with the HCl during the cleaning step. This was addressed in the third and final experiment.

The last run again used the same crucibles, but one was charged only with CaCl_2 and the other was a control. The control was to be weighed after the thermal cycle but before the HCl cleaning. No attack by the CaCl_2 was expected, and the molten halides are of interest even without Ca metal presence.

The loaded crucible contained 1.6005 g of CaCl_2 . The thermal cycle was to 900°C for 24 hrs. The masses recorded were:

	<u>Loaded</u>	<u>Control</u>
Initial	2.4320 g	2.2088 g
Loaded	4.0325 g	2.2088 g
After heating	3.9341 g	2.2055 g
Heating loss	0.0984 g	0.0033 g
After HCl cleaning	2.4263 g	2.2033 g
Total loss	0.0057 g	0.0055 g

The loss during heating of the loaded crucible exceeds its total loss, probably due to some CaCO_3 decomposition because CaO is a known impurity of the CaCl_2 . We note that the control crucible showed small losses in mass during both the heating and the HCl cleaning operations. Its total loss was only a third that observed in the previous experiment, and nearly identical to the one filled with CaCl_2 . Based on the weight losses, it seems the molten salt did not attack the PBN.

Regardless of the reasons for the unexplained weight loss on the control crucible, it is our judgment that PBN is not an attractive crucible material for these materials under the conditions imposed in these experiments. PBN is not totally inert, and it is relatively expensive. Although it is not an attractive material, it may be the best available in some of our applications not involving molten Ca.

Experiments with Zinc-Calcium System

As reported in the October-December 1988 quarterly report,² the focus of the PuRR project was directed to the zinc system. Calcium is being investigated as an alternative to magnesium as the reductant because (1) its greater thermodynamic driving force may

permit smaller excess reductant, and (2) the CaO reaction product is more easily converted back to metal for recycle than is MgO. The reference flowsheet guiding the present experiments is as presented in Figs. 2 and 3.

Results of Reduction Experiments with Zinc-Calcium

Two runs to reduce ash heel with zinc-calcium are presented in Table 3. The runs differ in the concentration of calcium: Run SRP-33 was designed to have 10 wt% calcium in zinc after the reduction, and Run SRP-36 was to have 6 wt% calcium after the reduction. These concentrations were selected after runs with a final calcium concentration of 2 wt% had Pu recoveries of only 92-95%, as reported last quarter. The MgO crucibles cracked during each of the recent runs; however, gamma-spectrometric analyses of the salt phase from these runs show that 99.5% and 97.2%, respectively, of the Pu had been extracted.

The experimental results exhibit a marked improvement as the concentration of calcium was increased from 2 to 10 wt%; however, the expected thermodynamic equilibrium was with over 99.9% of the Pu in the metal phase for all the calcium concentrations studied. Excess calcium results in increased reagent and waste recovery as can be seen from the calcium extraction step in Fig. 3. An effort will be made to determine why so much excess calcium was required and whether the excess can be minimized.

Results of Salt-Extraction Experiments with ZnCl_2

Although, as indicated in Fig. 2, the reference flowsheet employs solvent electrorefining to recover Pu from the reduction alloy, at this time, salt extraction with ZnCl_2 is being used to demonstrate the availability of the Pu. Solvent electrorefining experiments are in the planning stage. Runs SRP-34 and -37 (see Table 3) are extraction runs for the ingots from

Table 3. Material balances for calcium-alloy runs (total quantities in grams).

Run	SRP-33 Reduction	SRP-34 Extraction	SRP-35 Scrub	SRP-36 Reduction	SRP-37 Extraction	SRP-38 Scrub
Metal Charge:		SRP-33 ingot 493			SRP-38 ingot 343	SRP-38 ingot 131
Zinc	450		450	450		450
Calcium	64		50.4	43		28.0
Plutonium	0	1.80 ^b	0	0	1.05 ^b	0.40
Salt Charge:			SRP-33 salt 119.0			SRP-38 salt 173
CaCl ₂	136.1			138.1		
CaF ₂	23.9			23.9		
LiCl		29.9			30.6	
ZnCl ₂		258			128.0	
Plutonium	0	0	0.0033 ^c	0	0	0.043
Ash Heel Charge:						
Plutonium	13.88 ^a			13.35		
	1.88 ^a			1.55		
Posttest						
Salt Plutonium Content:						
Filt. Sample	<0.02			<0.02	0.58	
Ingot	0.0033 ^d (outside salt 0.0058)	1.18	0.0007	0.044 ^d	0.53	0.0097
Metal Plutonium Content:						
Filt. Sample	0.21	<0.05	0.002	0.28	0.021	0.48
Ingot	1.67 ^b	<0.04	ND	1.51 ^b	0.012	ND

^a Corrected for ash containing 0.10 g of plutonium stuck on baffles above melt following initial melting.

^b Calculated value, assuming all plutonium not accounted for in the salt is in the alloy.

^c Plus plutonium on the baffles following SRP-34.

^d Crucible cracked during run and some salt recovered from outside crucible. The two salts could not be separated for Run SRP-36 and were combined for the analysis.

Runs SRP-33 and -36. Analysis of the metal ingots following each extraction showed virtually all of the Pu was removed; however, the Pu accounted for in the salt analyses does not complete the material balance for either pair of runs. This discrepancy is disturbing and must be resolved in future runs.

Results of Calcium-Zinc Scrubbing of the Reduction Salt

The reduction salts from Runs SRP-33 and -36 were each scrubbed with zinc-calcium to further decrease the Pu content (see Table 3). For Run SRP-35 with the SRP-33 salt, a zinc-10 wt% calcium alloy was used. The SRP-36 salt could not be completely separated from the metal phase because the metal and salt ingots, both of which are brittle, broke up during break-out from the crucible, and many small pieces of each phase were present. All of the metal pieces that could be recovered cleanly were charged to the extraction Run SRP-37; the balance of the metal was charged along with the salt to the salt scrub Run SRP-38. Additional zinc-5 wt% calcium also was charged.

About 80% of the Pu was scrubbed from the reduction salt in scrub Runs SRP-35 and -38. This is much less than would be expected from a simple chloride equilibrium, which should give >99% removal. The possibility of scrubbing the salt to the desired <100 nCi/g will be investigated further, but the salt from the single scrub in SRP-35 is already <400 nCi/g.

Discussion

In most runs, two distinct regions of salt are defined by their color. The top region is light colored and the lower region is grey or black. The darkness is caused by the entrainment of a small amount of the metal or other insoluble phase. When the metal and salt ingots are separated after the SRP runs, a thin layer of the dark salt remains on much of the metal ingot. This layer can generally be removed by striking it with a hammer, but the

recovered fines, which may contain some metal, have not been analyzed. It was assumed that the adhering salt had the same composition as the balance of the dark salt. When the adhering salt was not removed from the metal ingot before the ingot was moved to an air box, the layer picked up water and became slime. This was washed off and discarded before a sample was cut from the ingot.

In view of the poor material balances, which have been encountered in a number of the calcium runs, the failure to analyze the material adhering to the ingots was a mistake. This layer may have contained missing Pu. The ingots are somewhat reactive with water, but washing them with water is probably the best approach for recovering the adhering layer.

Electrochemical Experiments

Electrorefining is being considered for two applications in the PuRR process: (1) recovery of Pu from the reduction ingots, and (2) recycle of calcium from the reduction salt. The major reason for both applications is minimization of wastes. The Pu electrorefining is similar to the electrorefining step under development at ANL for the Integral Fast Reactor. A reference electrode is important to the control of proposed extraction reactions, whether performed electrochemically or by direct chemical reactions.

Reference Electrode

To continue the development of a reference electrode for use in a zinc-alloy/molten-salt system (see January-March 1989 report³), two experiments were performed to test a simple zinc electrode. The electrode comprises an alloy contained in a porous tube, which has pores that fill with salt but will not permit metal entry. A concentration cell is established between the reference alloy and an alloy being measured. The electrode is immersed into the cover salt over the alloy of interest. Because of the volatility of zinc, a small amount of cover salt is also charged to the reference electrode.

- **Zinc Electrode:**

The first experiment (Run DRY-18) was made to investigate the effect of the porosity of the MgO electrode tube on the performance of the electrode. Each of the 5-mm-i.d. x 10-mm-o.d. MgO tubes was initially filled with 1 g of zinc and 1 g of salt. The reference electrodes again showed a strong potential change with the calcium concentration of the alloy in which the electrode was immersed.

The test results indicate that the porosity of the tube has a strong effect on the stability of the electrode potential. An MgO tube with a medium porosity (medium density) showed only a slight decrease in potential from 1.31 V to 1.28 V after 30 mins in a Zn-7.2 wt% Ca melt. However, with a high-porosity (low-density) tube, the cell potential dropped from 1.26 V to 0.68 V in the same period. After about 16 hrs of immersion in the alloy, both electrodes approached a relatively stable potential of 0.4-0.5 V.

Reversing the polarity of the cell for a period by imposing a small current (50 to 100 μ A) had no effect on cell potential. This suggests that the deterioration in cell potential was not due to a reversible charge-transfer reaction in the electrode. Addition of 1 g of zinc to the medium-density MgO electrode resulted in recovery of the potential from 0.50 V to 1.20 V. This indicates that the potential change was a result of a change in the composition of the zinc in the reference electrode. Because calcium has a finite solubility in the salt phase, it is likely that calcium was diffusing between the two zinc alloys under a concentration gradient.

Tubes of higher density will be sought for future testing, and the area of the tube that is porous also may be decreased. These changes will reduce the rate of change of the electrode composition and the associated drift in potential. For the duration of a process development experiment, the potential of an electrode from the medium-density MgO should be sufficiently stable to follow the process of the chemical or electrochemical reaction of interest, and until less porous tubes are available, the medium-

density tubes will be used. In addition, the reference alloy will be selected with a significant calcium concentration to give an interpretable signal and one of greater stability. Figure 4, which presents calculated potentials as a function of the calcium concentration in the reference alloy, illustrates the extreme sensitivity of the electrode potential at low concentrations of calcium. From this figure, it also is apparent why the rate of change of the potential in our tests slowed markedly at around 0.4-0.5 V.

- **Electrode Response:**

The second experiment was made to investigate the potential change as calcium, magnesium, and aluminum are extracted sequentially from a zinc alloy by incremental additions of ZnCl_2 to the cover salt. Instead of pure zinc, Zn-3.8 wt% Ca alloy was used as the reference alloy. One gram of this alloy was charged to a medium-density MgO electrode tube. The alloy being studied initially was 575 g of approximately 3.6 wt% Ca, 0.3 wt% Mg, 0.9 wt% Al, and 95.2 wt% Zn; the Ca-Mg-Zn alloy from Run DRY-18, with added Al, was used. The magnesium content was a result of attack of the MgO crucible by calcium during DRY-18. The alloy was covered with CaCl_2 - CaF_2 and maintained at about 735°C for the test.

Before ZnCl_2 additions were made, the cell potential ranged randomly from 0.007 V to 0.03 V. A low potential was expected because of the nearly identical calcium content of the electrode and the melt. A 20-g addition of ZnCl_2 resulted in a potential change to -0.024 V. A second 20 g of ZnCl_2 dropped the potential to -0.058 V. A third addition of 20 g of ZnCl_2 dropped the potential to -1.17 V. In 45 mins, the cell potential drifted to -1.09 V. At this time, an additional 10 g of ZnCl_2 were added, and the potential dropped to -1.15 V. Over the next 5 hrs, the potential drifted to -0.20 V.

Expected potentials for the extraction are presented in Table 4. A comparison of these numbers with the experimental results indicates that the calcium content of the melt

Figure 4. Effect of zinc concentration in reference electrode on reading against 8 wt% Ca-Zn.

Table 4. Calculated potentials for extraction run.

Charge:	(ZnCl ₂ Equivalent)		
	Zinc	550 g	
	Calcium	21 g	(72 g)
	Magnesium	1.7 g	(10 g)
	Aluminum	5 g	(25 g)

Calculated Potentials versus Zn-3.8 wt% Ca Reference Electrode:

Initial	-0.006 V
1/3 Calcium Removed	-0.039 V
2/3 Calcium Removed	-0.091 V
All Calcium Removed	-0.67 V
3/4 Magnesium Removed	-0.73 V
All Magnesium Removed	-1.12 V

was less than expected, and that the third ZnCl_2 addition was enough to react the balance of the calcium and all of the magnesium. With that assumption, the observed potentials agree well with predictions. The final potential was established by the aluminum in the melt, but as calcium was being extracted from the reference alloy, the signal drifted toward zero. This again illustrated the importance of an electrode with more resistance to diffusion through the salt bridge.

CaO Electrochemical Reduction

In the previous quarterly report, results were presented for experiments to determine the solubility of calcium in $\text{CaCl}_2\text{-CaF}_2$ in the presence of a zinc-calcium alloy. Because of the low activity of calcium in zinc solutions, a low solubility was expected. The high results obtained have now been shown to be in error and to be a result of reaction between calcium and the MgO crucible. The CaO thus produced was indistinguishable from calcium by the acid titration technique used for analysis. The run will be repeated when a better analytical technique (determination of hydrogen liberated from the titration) is ready.

C. Theoretical Studies

Distribution of Americium between Liquid Pu and Molten NaCl-KCl

The experimental data reported by Mullins, et al.,⁶ on the distribution of americium between liquid Pu and a molten equimolar mixture of NaCl and KCl have been analyzed to verify the conclusion of these authors that the americium exists in the divalent state in the molten salt mixture, and to use the data to estimate the activity coefficient of AmCl_2 in the molten salt mixture. This analysis is possible because these authors fully reported the experimental data, a practice often not followed in many current publications. It was found that these data support a divalent oxidation state for most of the americium in the molten salt mixture and that the activity coefficient of AmCl_2 is about 10 times that of PuCl_3 in the NaCl-KCl salt mixture.

In this system, the following equilibrium reactions are expected:

from which the following equilibrium constant relations may be derived:

$$\frac{a_{\text{Pu}} a_{\text{AmCl}_3}}{a_{\text{Am}} a_{\text{PuCl}_3}} = K_{3a}, \quad (3)$$

$$\frac{a_{\text{Pu}}^2 a_{\text{AmCl}_2}^3}{a_{\text{Am}}^3 a_{\text{PuCl}_3}^2} = K_{2a}, \quad (4)$$

in which the a 's are activities and the K 's are thermodynamic equilibrium constants. By substituting for the activities the product of atom (mol) fractions, X_i , and the activity coefficients, γ_i (i.e., $a_i = X_i \gamma_i$) and combining the activity coefficients with the equilibrium constants, two equations are obtained of the same form as Eqs. 3 and 4, but the a 's are replaced by X 's and the two equilibrium constants by the two new constants given by the relations:

$$K_3 = K_{3a} \frac{\gamma_{\text{Am}} \gamma_{\text{PuCl}_3}}{\gamma_{\text{Pu}} \gamma_{\text{AmCl}_3}}, \quad (5)$$

$$K_2 = K_{2a} \frac{\gamma_{\text{Am}}^3 \gamma_{\text{PuCl}_3}^2}{\gamma_{\text{Pu}}^2 \gamma_{\text{AmCl}_2}^3}. \quad (6)$$

From these equations, it is possible to deduce the following relation for the distribution coefficient for americium, $D_{Am} = X_{salt}/X_{metal}$

$$D_{Am} = K_3 D_{Pu} + K_2^{1/3} D_{Pu}^{2/3} \quad (7)$$

The two terms on the right hand side of Eq. 7 are proportional to the contribution of trivalent and divalent americium to the species present in the molten salt mixture. The values of D_{Am} were computed using Eq. 7 and compared with the experimental values. The two "constants," K_3 and $K_2^{1/3}$ were computed on the assumption that all activity coefficients in Eqs. 5 and 6 were equal to one (ideal solutions). The computed values were found to be larger than the experimental values by a factor that increased from about 1.4 to 1.6 as the concentration of $PuCl_3$ increased. Examination of the experimental data indicated that it could not be fit to an equation of the form suggested by Eq. 7 with reasonable values for the two constants. It was found that the data could be fit to an empirical relation whose parameters were close to what would be expected if only the second term on the right hand side of Eq. 7 was significant. The power of D_{Pu} was not exactly 2/3 but varied from about 0.63 to 0.69, and the value of the constant, K_2 , was smaller than the theoretically computed value, being about 70-90% of the expected value (if γ 's are unity).

Two facts need explanation: first, why the first term on the right hand side of Eq. 7 does not appear to be significant; and second, why the empirical constants are different from the expected values. The computed values of the standard free energies of reactions 1 and 2 are about -7 and -25 kcal/mol, respectively. Since the values of the free energies of formation of $PuCl_3$, $AmCl_3$, and $AmCl_2$ all have large uncertainties, it is possible that the computed value of the standard free energy of reaction 1 is smaller; a combined error of 4-5 kcal/mol would not be unreasonable. While such an error (in the "right" direction) could make the contribution of the trivalent form of americium

insignificant, it would have a smaller effect on the predicted contribution of the divalent form of americium. This appears to be a situation in which high accuracy (uncertainties of ± 1 kcal/mol) in the thermodynamic data is required to make a definitive decision based on theoretical computations.

Considering the scatter of the experimental data (see Fig. 5), the deviation of the power of D_{Pu} from exactly 2/3 (a slope of 2/3 in Fig. 5 in which the logarithms of the two constants are plotted) is not unexpected. It is reasonable to assume that the 2/3 power is appropriate for the analysis of these data. Therefore, the values of $K_2^{1/3}$ were computed from the experimental data on the assumption that the 2/3 power dependence on D_{Pu} was correct. An example of the results obtained for the data at 1003K is shown in Fig. 6. Similar results were obtained for the other two temperatures; however, the scatter is even greater. It was found that the values of $K_2^{1/3}$ were smaller than the values computed on the assumption that all of the activity coefficients were equal to one and appeared to decrease as the mol fraction of $PuCl_3$ increased. In addition, it was found that the $K_2^{1/3}$ computed from the experimental data decreased in value as the temperature increased, whereas the values computed from the free energies of formation increased with increase in temperature. Since K_2 involves not only the thermodynamic equilibrium constant, K_{2a} , but also the product of four different activity coefficients, this difference in temperature dependence may be the result of different temperature dependences for the free energies of formation and the activity coefficients.

The ratio of the activity coefficients of americium and Pu in the metallic phase can probably be safely assumed to be close to unity. The value for γ_{Pu} must be close to one for these very dilute solutions of americium in Pu (the metallic phase is almost pure Pu). The values of γ_{Am} , while possibly not exactly one, would be expected to be constant (Henry's Law followed). Therefore, the difference between the observed and theoretical values of $K_2^{1/3}$

Figure 5. Distribution of Am between Pu and NaCl-KCl.

Figure 6. Equilibrium constant, $K_2^{1/3}$ Am extraction from Pu by PuCl_3 in NaCl-KCl.

are principally due to the two salt activity coefficients.

To study the possible effect of variations in the salt activity coefficients on the values of $K_2^{1/3}$, values of γ_{PuCl_3} were computed for each of the experimental data sets and used to compute the value of γ_{AmCl_2} on the assumption that reaction 2 applied (a slope of exactly 2/3 and the theoretical values of K_{2a} were used). It was found that the average values of γ_{AmCl_2} were 10.4 times the value of γ_{PuCl_3} . Thus, for values of γ_{PuCl_3} of about 0.001-0.002 estimated for the NaCl-KCl salt system (for the range of PuCl_3 concentrations and temperatures), values of γ_{AmCl_2} of about 10 times larger, i.e., 0.01-0.02, are found. When this result is substituted into Eq. 6, it is found that:

$$K_2^{1/3} = K_{2a}^{1/3} \frac{1}{10.4 \gamma_{\text{PuCl}_3}^{1/3}} \quad (8)$$

For values of γ_{PuCl_3} of 0.001 and 0.003 (the range found for the data at 730°C), $K_2^{1/3}$ is found to vary from 0.96 to 0.67 times $K_{2a}^{1/3}$. It should be noted that, if the activity coefficients of AmCl_2 and PuCl_3 were equal and equal to the values for PuCl_3 found for this system, the extraction of americium from Pu would be almost 10 times larger. The various "salt effects," which are noted when the effect of changing the composition of the "inert" salt used to dilute the PuCl_3 has been studied, are due to the differences in the effect of the salt composition on the activity coefficients of AmCl_2 and PuCl_3 .

If the extraction of americium from Pu involved the formation of the trivalent AmCl_3 in the molten salt, the extraction with PuCl_3 would be significantly smaller than observed. For example, for the present series of experiments, computed values of D_{Am} would be about 25% of the observed values. In addition, there would be a smaller dependence on the "inert" diluent salt used. This latter effect is predicted from the fact that the difference in the ionic radius of Pu^{3+} and Am^{3+} is very small, and deviations from ideal behavior are dependent

on the differences between the ionic radii and charge of the solute and solvent cations. On the other hand, both the ionic radii and charge are different for Pu^{3+} and Am^{2+} cations; hence the effect of diluent salts on their activity coefficients would be expected to be different, as was found in this study. In the experimental data analyzed, the concentration of both PuCl_3 and AmCl_2 in the molten salt was small; hence the salt effects are dominated by the properties of the NaCl-KCl solvent salt. When the PuCl_3 concentration is increased, as has been the case where the range from pure PuCl_3 to very dilute solutions in an "inert" diluent salt have been used, the effect of PuCl_3 as a "solvent" salt on the activity coefficient of AmCl_2 must be considered. As the salt approaches pure PuCl_3 , its activity coefficient will approach one, while the activity coefficient of AmCl_2 will approach its value as a dilute solute in molten PuCl_3 , which is likely to be less than one. This will lead to values of K_2 larger than K_{2a} , hence enhanced extraction of americium from Pu.

The details of the numerical computations are given here. Two sets of computations dependent on information not found in the paper by Mullins, et al.,⁶ are involved in this analysis. The first is the computation of the thermodynamic equilibrium constants, while the second is the computation of the activity coefficients of PuCl_3 in the molten NaCl-KCl salt mixture. By giving more details of these computations, some of the uncertainties in the thermodynamic data can be stated so that the conclusions of this analysis can be more realistically evaluated.

The numerical values for the two thermodynamic equilibria are given in Table 5. The free energy data for PuCl_3 was obtained from the data selected for the solid by the IAEA⁷ and the enthalpy of fusion estimated by Rand.⁸ The thermodynamic data for the two americium chlorides are from a recent assessment by this author. The free energy values given in Table 5 are for the liquid chlorides (super-cooled, if necessary), and the subscripts refer to the trivalent or divalent americium chloride.

Table 5. Thermodynamic equilibrium constants.

<u>T, K</u>	<u>971</u>	<u>1003</u>	<u>1048</u>
$\Delta G_f(\text{PuCl}_3)$, kcal/mol	-176.5	-175.1	-173.2
$\Delta G_f(\text{AmCl}_3)$, kcal/mol	-183.7	-182.6	-181.0
$\Delta G_f(\text{AmCl}_2)$, kcal/mol	-125.9	-125.2	-124.4
ΔG_3 , kcal/mol	-7.26	-7.48	-7.79
K_{3a}	43.1	42.5	42.2
ΔG_2 , kcal/mol	-24.6	-25.5	-25.8
K_{2a}	3.48×10^5	3.58×10^5	3.79×10^5
$K_{2a}^{1/3}$	70.4	71.0	72.4

The activity coefficients of PuCl_3 in the equimolar NaCl-KCl salt mixture were computed using the relations developed by Gohil, et al.,⁹ for the excess free energies of the three binary systems as a function of composition and temperature, and the Toop¹⁰ relation for estimating excess free energies in ternary solutions. The Toop relation is exact for regular systems, and has been found to be a good approximation for more complex systems.

The numerical details of the computations may be obtained from ANL upon request.

Conclusions - This analysis of the experimental data reported by Mullins, et al., confirms their conclusion that AmCl_2 is the main product formed by the extraction of americium from liquid Pu by PuCl_3 dissolved in a molten equimolar mixture of NaCl-KCl. It was also found that the observed dependence of the distribution of americium on the distribution coefficient of Pu indicates that the activity coefficient of AmCl_2 in this salt mixture is about 10 times that of PuCl_3 . The method of analysis developed for these experiments should be useful in understanding the "salt effect" observed when different diluent salts are used.

III. Other Recent Activities

Actinide Separations Conference

A few members of the PuRR project staff from both ANL and LLNL attended the Thirteenth Actinide Separations Conference held at Idaho Falls, ID May 16-18. Most of the presentations concerned Pu process operations, and many had direct relevance to the PuRR project. Some of the concepts developed at LLNL were already in use at other DOE facilities.

LLNL Management Review

As mentioned in the previous quarterly report, a decision on the future direction and sponsorship within LLNL was expected. The PuRR project as an independent entity ceased June 30, 1989. Beginning October 1, very similar activities will be performed under the auspices of LLNL's Isotope Separation and Material Processing Program. It is expected that ANL will continue to have a role in the research.

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