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LIQUID-LIQUID EXTRACTION OF AMERICIUM
FROM MOLTEN PLUTONIUM METAL

J. D. Moseley
J. B. Knighton

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I. INTRODUCTION

Dow Chemical U.S.A. operates the Rocky Flats facility for the United States Atomic Energy Commission. A principal product of the Chemical Operations section is highly pure plutonium metal. One of the principal impurities of plutonium that requires periodic removal is americium, which grows into the metal during long-term storage by the beta decay of the 241 isotope of plutonium. There are metallurgical reasons *deletes* necessitating the removal of the americium, but our primary motivation is to reduce the radiation exposure to personnel working with the materials after they leave the chemical purification area. The radiation exposure problem is due to americium-241 emitting penetrating gamma ray radiation that is difficult to shield against. Yet another motivation for the separation and purification of americium is that it serves as a target material in the nuclear reactor synthesis of plutonium-238, which is used for a variety of scientific, space exploration and medical purposes.

II. PROCESS DESCRIPTION

The process is quite simple. Molten plutonium metal is equilibrated with a molten salt and the americium is preferentially extracted into the salt. This is accomplished

within a conventional glovebox held at a slight vacuum due to the toxicity of the actinide metals. The plutonium metal is placed inside a tantalum crucible, a salt cake is placed in the crucible, and the crucible is placed in a pot furnace. The furnace is closed, evacuated, and filled with argon at a slight overpressure. This slight argon overpressure is maintained during the course of the run to inhibit oxidation of the plutonium and the tantalum. The furnace contents are heated to about 750°C (approximately 100°C above the melting point of the contents) and stirred to achieve rapid equilibration. The stirrer is lifted from the melt and the furnace allowed to cool. The americium-depleted plutonium metal and the salt containing americium and some plutonium are then separated. The salt solvent commonly used is the NaCl-50 mole % KCl eutectic composition. To this one may add plutonium trichloride, one of the plutonium fluorides, or magnesium chloride to act as an oxidant in the reaction shown on Slide 1. We choose to use magnesium chloride due to relative ease of material handling.

III. THERMODYNAMIC BASIS FOR EXTRACTION

The standard free energies of formation reported for several elements of interest are shown on Slide 2.

SLIDE 1

SLIDE 2

STANDARD FREE ENERGIES OF FORMATION OF SELECTED CHLORIDES IN ORDER OF INCREASING STABILITY AT 1000°K*

Compound	$-\Delta G^\circ$ kcal/g atom Cl
MgCl ₂	58
PuCl ₃	59
CeCl ₃	66
AmCl ₃	67
NaCl	76
KCl	82

*Glassner, A., USAEC Report
ANL-5750.

From the relationship $-\Delta G = RT \ln K$ and with the assumption that all activity coefficients are unity, it is seen that the ratio shown on Slide 3 should equal about 10^5 . In fact, the ratio obtained in an extended series of equilibrations is about 10^3 less than this, or about $3 (\pm 0.5) \times 10^2$. It is generally believed that the reported ΔG value for AmCl_3 is in error by about 5 kcal/g atom Cl. Observations of the analogous ratio for cerium are in agreement with the theoretical values. Efforts are being made to more precisely determine the correct thermodynamic values.

IV. EXTRACTION COEFFICIENTS

In countercurrent extraction processes, our present mode of operation, the salt and metal solvents move countercurrent to each other through the extraction stages as shown in Slide 4.

The fraction of a solute partitioning to each phase may be expressed using the extraction factors as shown on Slide 4. We have found it convenient to operate a two-stage process and to operate with an f_s overall of 0.9. Our extraction factor must therefore be 2.5 or greater for our particular operating conditions.

The extraction factor is defined on Slide 5.

SLIDE 3

$$K = \frac{\text{ppm Am}^* \text{ in salt}}{\text{ppm Am}^* \text{ in metal}} \approx 10^5$$

*parts of americium per million
parts of plutonium.

SLIDE 4

$$f_m = \frac{\alpha - 1}{\alpha^{n+1} - 1}$$

$$f_E = 1 - f_m$$

n = number of stages

α = extraction factor

SLIDE 5

$$\alpha_{Am} = (K_{d_{Am}}) \times (s/m) \times (F)$$

α_{Am} = americium extraction factor

$K_{d_{Am}}$ = equilibrium distribution coefficient

$$= \frac{\text{Am in salt (wt \%)}}{\text{Am in metal (wt \%)}}$$

s/m = salt to metal weight ratio

= solvent 2/solvent 1

F = fraction of equilibrium

Assuming the achievement of equilibrium, it is seen that we have two variables--(K_d Am), a function of $MgCl_2$ content-- and (s/m) a matter of choice and/or equipment design (within limits).

Johnson at the Argonne National Laboratory has reported a relationship for these types of systems, shown on Slide 6, and has shown its utility for a number of fission product rare earths and for some actinides.

Using data points from 0 to 30 mole % $MgCl_2$ and extrapolating beyond using Johnson's relationship, we have obtained the distribution coefficient plot as a function of $MgCl_2$ content in the solvent salt (NaCl-KCl equimolar) shown on Slide 7.

From this plot, and based on equipment configurations, we operate with a s/m of 0.65, and a $MgCl_2$ content of 6 mole %.

The molten salt extraction of americium from plutonium metal ^{is} ~~has been~~ a production process at the Rocky Flats facility, ~~for about 2 1/2 years. It replaced an aqueous process for separating plutonium and americium, and resulted in a considerable cost savings. We now feel that we understand the chemistry reasonably well, and our future efforts will be concentrated on equipment improvements and on developing methods for recycle of the waste salt.~~

SLIDE 6

$$K_d = c (\text{MgCl}_2)^{3/2}$$

K_d = equilibrium distribution coefficient

c = constant for a solvent system

(MgCl_2) = mole fraction of MgCl_2

Distribution of Americium between NaCl-KCl-MgCl₂
Salt (Solvent 2) and Plutonium (Solvent 1)