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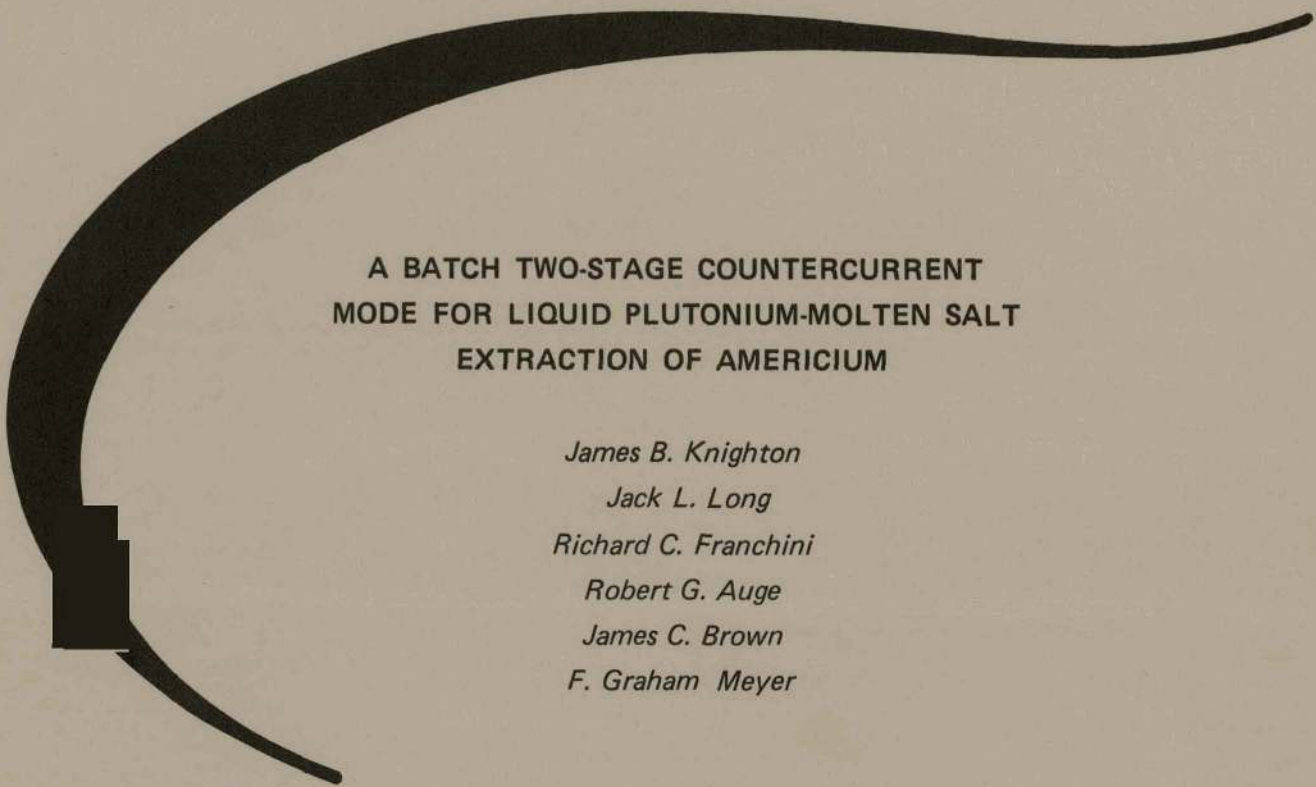
A BATCH TWO-STAGE COUNTERCURRENT
MODE FOR LIQUID PLUTONIUM-MOLTEN SALT
EXTRACTION OF AMERICIUM

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SUBJECT DESCRIPTORS

Americium
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MASTER

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Abstract. The production molten salt extraction process for the removal of americium from plutonium metal has been modified from crosscurrent to countercurrent flow of salt and metal. The $MgCl_2$ content of the KCl-$NaCl$-$MgCl_2$ salt was increased from 6 wt% to 8 wt%. These changes have resulted in a reduction in the amount of salt generated per kilogram of plutonium processed by a factor of approximately two without any significant sacrifice in americium removal efficiency.

INTRODUCTION

Americium-241 grows in plutonium by beta decay of plutonium-241, the rate being dependent upon the concentration of the plutonium-241 isotope. At the Rocky Flats Division, Dow Chemical U.S.A., americium is removed from plutonium to reduce the impurity content and to reduce the possibility of personnel exposure to gamma radiation from the americium in subsequent operations. The americium obtained is ultimately converted to the oxide form and distributed by the U.S. Atomic Energy Commission to private industries and universities for peaceful applications.

Workers at the Los Alamos Scientific Laboratory reported the distribution of americium between molten KCl-49 mole% NaCl-2 mole% $PuCl_3$ and molten plutonium metal which was observed in electrorefining.[1] Workers at the Argonne National Laboratory found that americium and plutonium could be separated by equilibrating molten chloride salt systems with alloy systems such as Mg-Zn.[2,3] At Rocky Flats the distribution of americium between molten salt mixtures containing $MgCl_2$ and molten plutonium metal was investigated and a process was developed.[4] Multi-kilogram quantities of plutonium metal are processed by this method.[5] Initially, the production process made use of a KCl-49.1

mole% NaCl-1.8 mole% $MgCl_2$ (2.5 wt% $MgCl_2$) salt mixture. Each batch of metal was contacted consecutively with two salt charges, each being of the same weight as the batch of metal. The effect of increasing the $MgCl_2$ content to 6 wt% and decreasing the salt-to-metal ratio was investigated. This innovation was put into production operation, thereby reducing the salt generation rate by a factor of 1.8 while maintaining a 90% americium extraction efficiency, or approximately 70% extraction per contact. The amount of plutonium metal sent to the molten salt extraction process increased with time to the point where the waste salt recovery facility could not stay current with the amount of salt residue generated, and therefore a backlog developed. Action was required to further reduce the salt generation rate. The requisite process changes were increasing the magnesium chloride content and changing from batch two-stage crosscurrent to batch two-stage countercurrent flow of salt and metal.

SUMMARY

Process changes have been developed and put into production practice which reduce the salt generation rate in the molten salt extraction process by a factor of approximately two.

THEORY

Americium is separated from plutonium by liquid-liquid extraction using molten salts and metals as the immiscible liquid phases. In this extraction americium is oxidized by $MgCl_2$ and $PuCl_3$ by the following reactions:

$$Am^\circ + \tfrac{3}{2} MgCl_2 \rightarrow AmCl_3 + \tfrac{3}{2} Mg^\circ \quad (1)$$

$$Am^\circ + PuCl_3 \rightarrow AmCl_3 + Pu^\circ \quad (2)$$
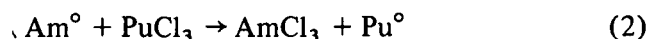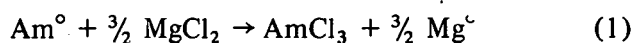
To lower the americium content in the plutonium to acceptable levels, about 90% removal of americium is required. The mode of extraction was changed from batch two-stage crosscurrent to batch two-stage countercurrent extraction.

The crosscurrent mode (previous mode) of extraction is shown as follows:

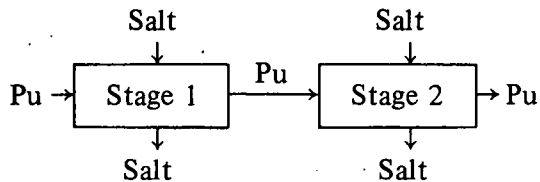In the production operation of this process, about 2.2 kg of plutonium metal is contacted sequentially with two separate batches of salt each weighing about 1.4 kg.

In crosscurrent extraction the fraction of a solute partitioning to each of the immiscible liquid phases is expressed as follows:[6]

$$f_m = \frac{1}{(a + 1)^n} \qquad (3)$$

$$f_s = 1 - f_m = \frac{(a + 1)^n - 1}{(a + 1)^n} \qquad (4)$$

where:

f_m = fraction of americium remaining in metal

f_s = fraction of americium extracted to salt

n = number of extraction stages

a = extraction factor = (K_d) (s/m) (F) (5)

K_d = distribution coefficient =

$$\frac{\text{Am conc. in salt (wt\%)}}{\text{Am conc. in metal (wt\%)}} \qquad (6)$$

s/m = salt-to-metal weight ratio

F = fraction of equilibrium

To obtain 90% removal of americium with 2 stages of cross current extraction, the extraction factor of $a = 2.16$ is required. With this value of the extraction factor, a separation of 68.4% is obtained in each stage.

In countercurrent extraction (new mode), the salt and metal solvents move countercurrent to each other through the extraction stages as shown below:
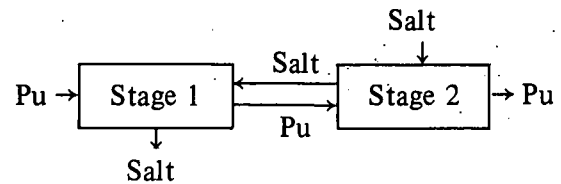
The fraction of a solute partitioning to each phase in countercurrent extraction is expressed as follows:[7]

$$f_m = \frac{a - 1}{a^{n+1} - 1} \qquad (7)$$

$$f_s = 1 - f_m \qquad (8)$$

To obtain 90% removal of americium in two stages of countercurrent extraction, the required value of the extraction factor is $a = 2.54$. If the value of the extraction factor of 2.16 (from crosscurrent extraction) is used in countercurrent extraction, the extraction of americium drops from 90 to 87.2%. Therefore, to obtain a given separation (90%) the value of the extraction factor must be larger for countercurrent extraction than for crosscurrent extraction.

Countercurrent extraction is favored over crosscurrent extraction for the extraction of americium from plutonium because:

1. Less salt is required to obtain the same separation (even with the larger value of the extraction factor).

2. The plutonium loss to the salt is lower.

3. Less magnesium metal by-product is generated.

4. The salt feed to the waste chloride salt recovery line is cut in half.

To obtain larger values of the extraction factor, the value of at least one term in the extraction factor relationship must increase.

$$a = (K_d) \text{ (s/m) (F)} \qquad (5)$$

The distribution coefficient (K_d) is dependent upon $MgCl_2$ concentration in the salt, americium

concentration in the feed plutonium metal, and temperature. The salt-to-metal ratio (s/m) is determined by the weights of the salt and metal feed. The fraction of equilibrium (F) is dependent upon the time and degree of mixing. It is obvious that an infinite number of combinations of values of K_d, s/m, and F exist, the product of which yields the required value of the extraction factor ($a = 2.54$) for 90% removal of americium in two-stage countercurrent extraction.

It was arbitrarily decided to hold the value of the salt-to-metal ratio (s/m) constant at

$$\frac{1.4 \text{ kg salt}}{2.2 \text{ kg metal}} = 0.636$$

Therefore, to obtain the increased value of the extraction factor (2.16 to 2.54) the value of the distribution coefficient (K_d) must be increased from $K_d = 3.40$ for crosscurrent extraction to a value of 3.99 for countercurrent extraction. In this analysis the value of F (fraction of equilibrium) is assumed to be one. The increase in the value of the distribution coefficient was obtained by increasing the $MgCl_2$ content in the salt from 6 to 8 wt%.

If the salt composition was not changed, the value of the salt-to-metal ratio (s/m) would have been increased from 0.636 to 0.747 to obtain the desired value of the extraction factor ($a = 2.54$). This increase of the salt-to-metal ratio would be obtained by increasing the weight of the 6 wt% $MgCl_2$ salt from 1.4 to 1.64 kg and with the feed-metal weight remaining at 2.2 kg plutonium.

In the above analysis of crosscurrent and countercurrent extraction the assumption is made that the extraction factor and distribution coefficient are the same for both stages of crosscurrent extraction and likewise the same for both stages of countercurrent extraction. Factors which may cause deviations in the value of the extraction factor (a) and the distribution coefficient (K_d) from stage 1 to stage 2 are listed below:

1. Plutonium oxide has been shown to extract americium from plutonium metal.[8] Plutonium oxide associated with the plutonium metal feed

is present in multigram quantities in stage 1 with only small amounts present in stage 2. The side reaction between PuO_2 and americium is therefore appreciable only in stage 1. This side reaction results in larger values of the extraction factor and the apparent distribution coefficient in stage 1 rather than in stage 2.

2. The effect of the americium concentration in the feed metal may change the value of the distribution coefficient. The americium concentration, in the plutonium product and feed, ranges between about 200 to 2000 ppm.

3. Insufficient mixing results in nonequilibrium conditions.

4. The salt and metal phases change weights as americium and plutonium in the metal exchange with magnesium from the salt. These weight changes are slight, but will result in a small change in the value of the salt-to-metal ratio.

OPERATING PROCEDURE

Approximately 2.2 kg of plutonium metal is placed in a tantalum crucible. A 1.4-kg salt cake of initial composition KCl-47.1 mole% NaCl-5.8 mole% $MgCl_2$ *, which has been previously contacted with molten plutonium partially depleted in americium, is placed on top of the plutonium. The crucible and contents are then placed in a cylindrical (5-inch i.d. by 12-inch deep) furnace.

The furnace is evacuated and back-filled to about 2 pounds overpressure with argon gas. The argon protects the tantalum and plutonium from oxidation.

The furnace temperature is raised to the operating temperature (750°C) in about 2 hours, at which time a flat-bladed tantalum stirrer is lowered into the melt. The molten metal and salt are equilibrated with stirring for 1 hour, then the stirrer is lifted

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*KCL-NaCl equimolar, with approximately 8 wt% $MgCl_2$ added.

from the melt and the furnace and contents are cooled.

The salt, which has had two contacts with plutonium metal, is then sent to the waste chloride salt recovery glovebox for aqueous dissolution and recovery of the plutonium and americium values. The metal, now partially depleted in americium, is then contacted with fresh salt.

RESULTS AND DISCUSSION

Table 1 gives the data from 18 production molten salt extraction runs. The weight of the individual salt cakes was not recorded, but the average weight was approximately 1.4 kg. The americium removed from the plutonium metal during the first and second stages was calculated according to the following relationship:

% Am removed =

$$\frac{(\text{g Pu feed}) \times (\text{ppm Am}_f) - (\text{g Pu product}) \times (\text{ppm Am}_p)}{[(\text{g Pu feed}) \times \text{ppm Am}_f]} \times 100 \quad (9)$$

(ppm Am_f and ppm Am_p are americium content in feed and product, respectively.)

The overall or total extraction was calculated with the same relationship using feed data from stage 1 and product data from stage 2. To correct for sample losses, the weight of the plutonium metal sample (taken between the first and second stages) was added to the weight of the product metal from stage 2.
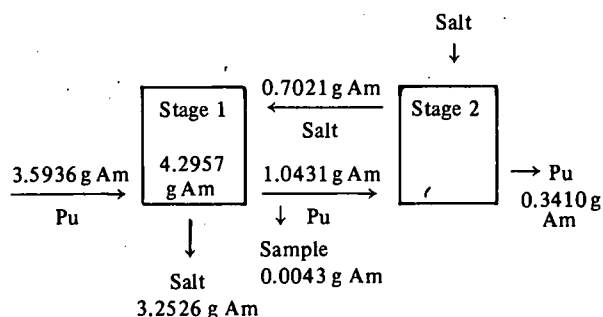
To provide data for determining the actual extraction performance (overall and for each stage), an americium material balance was made around each stage and the overall process. The data input to this material balance was the average weight of the salt and metal feed and products, and the average americium content of the metal feed and products. The output from this material balance was the total americium present in stage 1 and the americium contained in the salt products from each stage. This material balance is summarized below, with the weight of americium in each stream being expressed in grams.

Table 1. Americium Extraction Data.

	(Stage 1[a])				(Stage 2[a])				% Am Extracted 1st Stage	% Am Extracted 2nd Stage	% Am Extracted Total
	Feed		Product		Feed		Product				
Run No.	Wt, g	ppm, Am	Wt, g	ppm, Am	Wt, g	ppm, Am	Wt, g	ppm, Am			
1	1799	1680	1752	354	1741	354	1710	73	79.5	79.8	95.9
2	2307	1336	2271	385	2264	385	2241	127	71.6	67.4	90.7
3	2213	1597	2177	527	2170	527	2153	188	67.5	64.6	88.4
4	2355	1277	2296	472	2287	472	2232	131	64.0	72.9	90.3
5	1947	1737	1923	570	1918	570	1852	122	67.6	79.3	93.2
6	2302	1510	2304	430	2296	430	2251	119	71.5	72.8	92.3
7	2254	1954	2224	466	2218	466	2194	139	76.5	70.5	93.1
8	2282	1610	2130	267	2123	267	2048	150	84.5	45.8	91.6
9	2279	1636	2270	445	2265	445	2219	140	72.9	69.2	91.7
10	2259	1589	2248	427	2242	427	2204	118	73.3	72.8	92.8
11	1992	1114	1981	311	1960	311	1935	93	72.2	70.5	91.8
12	2187	1577	2162	480	2151	480	2137	168	69.9	65.2	89.5
13	2189	1608	2155	542	2142	542	2133	190	66.8	65.3	88.5
14	2284	1752	2262	491	2251	491	2231	160	72.2	67.7	91.0
15	2218	1886	2188	592	2178	592	2160	237	69.0	60.3	87.7
16	2290	1749	2275	732	2265	732	2244	295	58.4	60.1	83.4
17	2286	1722	2264	591	2257	591	2231	199	66.0	66.7	88.7
18	2273	1981	2226	599	2215	599	2191	225	70.4	62.8	89.0
Average	2206	1629	2173	483	2164	482	2131	160	70.7[b]	67.2[b]	90.5[b]

[a] Refers to the metal phase.
[b] Weighted average.

Salt ↓

| Stage 1 | 0.7021 g Am ← Salt | Stage 2 |
| 4.2957 g Am | 1.0431 g Am → Pu | → Pu 0.3410 g Am |

3.5936 g Am → Pu

↓ Salt 3.2526 g Am

↓ Pu Sample 0.0043 g Am

From this material balance, the fractions of americium partitioning to the salt (f_s) and metal (f_m) were obtained for each stage and for the overall extraction. The fraction of americium partitioning to the metal (f_m) was used to determine the values of the extraction factors (a) obtained in each stage and in the overall extraction. The values were calculated using Equations 3 and 7, respectively.

The value of the salt-to-metal ratio (s/m) at the end of the equilibration was estimated to be 0.67. This value was obtained by factoring in the weight changes caused by americium and plutonium transfer to the salt and the reverse transfer of magnesium from the salt to the metal.

From the above values of the extraction factor (a) and the salt-to-metal ratio (s/m), the values of the apparent americium distribution coefficient (K_d') for each stage and for the overall extraction were calculated by Equation 5. Table 2 gives: the fraction of americium partitioning to the salt and metal phases, the extraction factor, and the distribution coefficient for the individual stages and for the overall extraction.

Table 2. Extraction Performance.

Extraction	f_s	f_m	a	K_d'
Stage 1	0.756	0.244	3.10	4.63
Stage 2	0.673	0.327	2.06	3.07
Overall	0.905	0.095	2.63	3.93

In an ideal system, the values of the distribution coefficient for each stage and for the overall extraction are the same. However, the values of the distribution coefficient are 3.07 and 4.63 for stage 2 and stage 1, respectively, and 3.93 for the overall extraction. Because of this variance, the values of the distribution coefficient (K_d) are expressed as an apparent distribution coefficient (K_d'). The apparent distribution coefficient (K_d') is defined in this study as the product of three terms: (1) the true distribution coefficient (K_d), (2) the fraction of equilibrium obtained during the extraction (F), and (3) a term (β) to account for side reactions.

$$K_d' = (K_d) \times (F) \times (\beta) \qquad (10)$$

The side reaction term (β) is introduced into this study to quantitize the side reaction effect caused by the presence of PuO_2, etc., in the stage 1 extraction. At equilibrium (when F = 1) and in the absence of side reactions (when $\beta = 1$), the value of K_d' is equal to K_d.

The assumption is made that metal insoluble impurities (PuO_2, etc.) are taken up by the salt in stage 1. Thus, these impurities are absent (or minimized) in stage 2. Side reaction effects caused by these impurities exchanging with americium will occur only in stage 1. The equilibration in stage 2 represents the ideal liquid-salt-metal system as the system is essentially free of salt and metal insoluble materials. Therefore, the value of β for stage 2 is assumed to be one since no side reactions are expected to be present. Likewise, the value of β for stage 1 is expected to be greater than one because of side reactions.

The value of F (fraction of equilibrium) is assumed to be the same for both stages. The same mode of mixing, mixing speed, and time of mixing was present in both stages. Other data suggest that the value of F is actually about 0.81 in both stages.

The value of the true distribution coefficient (K_d) is assumed to be the same in both stages. The effect of americium concentration (200 to 2000 ppm) in the metal upon the value of K_d is assumed to be negligible over the above concentration range.

From the above assumptions ($K_{d_1} = K_{d_2}$, $F_1 = F_2$, and $\beta_2 = 1$), the value of the side reaction term for stage 1 (β_1) is estimated by:

$$\frac{(stage\ 1)}{(stage\ 2)} = \frac{K_{d_1}'}{K_{d_2}'} = \frac{(K_{d_1}) \times (F_1) \times (\beta_1)}{(K_{d_2}) \times (F_2) \times (\beta_2)} \quad (11)$$

which reduces to:

$$\beta_1 = \frac{K_{d_1}'}{K_{d_2}'} = \frac{4.63}{3.07} = 1.51 \quad (12)$$

The plutonium weight loss (feed weight-product weight) for stage 2 (average of 32.6 g/melt) represents the weight of americium and plutonium taken into the salt as $AmCl_3$ and $PuCl_3$. Factors controlling this weight loss are: (1) the $MgCl_2$ content of the salt, (2) the total amount of salt, and (3) the fraction of equilibrium obtained in the equilibration. Subsequent equilibrations of this -salt with plutonium metal are not expected to result in appreciable weight changes of the plutonium metal phase by liquid salt-liquid metal equilibrium mechanisms.

The plutonium weight loss (feed weight-product weight) for stage 1 (average of 33.8 g/salt) is believed to represent the weight of metal insoluble compounds (PuO_2, etc.) associated with the plutonium metal feed. These metal insoluble compounds are taken up by the salt during equilibration. If this postulated mechanism is correct, the plutonium metal weight loss to the salt in stage 1 should vary as the quality of the plutonium metal feed varies. Likewise, the value of β_1 (Equation 12) should also vary in proportion to the plutonium weight loss observed in stage 1.

The value of K_{d_0}' (3.93) lies about midway between the values of K_{d_1}' (4.63) and K_{d_2}' (3.07) as would be expected. The calculation of K_{d_0}' by Equation 7 assumes that:

$$K_{d_1}' = K_{d_2}' = K_{d_0}'$$

which we observe from Table 2 to be false. However, values of K_{d_0}' are very useful in process design.

The overall performance (percent of americium removal) observed in this series of runs is in agreement with the expected performance of the counter-current mode of extraction described in the theory section of this report. The process change (to countercurrent extraction from crosscurrent extraction) resulted in a decrease in the rate of waste generation by a factor of two.

Anomalies observed in Table 2 are explained as follows:

1. The percent of americium removed in Run No. 1 is much higher than for the other runs. This higher removal is the result of: (1) the larger salt-to-metal ratio caused by the light metal feed weight and (2) in starting the counter-current mode of extraction, the first metal actually is treated by a cross-current mode of extraction. Higher removals are expected with cross-current extraction than with counter-current extraction.

2. In stage 2 of Run No. 8, the analysis of the metal product is believed to be low. A high apparent removal of americium in stage 1 and a low apparent removal of americium in stage 2 is expected if the mid sample is low. The overall removal of americium (91.6%) is near the average (90.5%).

3. The low removal of americium obtained in Run No. 16 (83.4%) was probably caused by insufficient mixing of the salt and metal phases: i.e., the fraction of equilibrium obtained was substantially less than one.

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