TRIALS OF PLUTONIUM ELECTROREFINING IN CALCIUM CHLORIDE

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ABSTRACT

Electrorefining of plutonium, containing gallium and other impurities, was conducted in a CaCl₂ melt at 850°C. Eight operations gave an average yield of 90%. Previously, NaCl-KCl at 750°C has been used for this process. Yields in NaCl-KCl are reported as 73-75%. The greater yield in CaCl₂ relative to NaCl-KCl is attributed to the increased operating temperature and consequent later onset of solid plutonium/gallium phases within the anode. A further three electrorefining runs gave rise to poorly coalesced metal. In these operations, the feed metal contained a greater quantity of dross material, such as oxide.

INTRODUCTION

The electrorefining process is an established method for the purification of plutonium (1). It is used to remove gallium, americium, neptunium and other impurities. A potential is applied between an impure liquid plutonium anode and an inert metal cathode. Plutonium is oxidised and transported through the salt and reduced at the cathode, where pure plutonium is collected.

Those impurities which are less electropositive than plutonium, such as gallium or uranium, remain in the anode. Impurities which are more electropositive than plutonium, such as americium or cerium, remain in the electrolyte (2).

Electrorefining of plutonium may be conducted in NaCl-KCl. However, such electrorefined plutonium contains volatile species such as Na, K, NaCl or KCl within it. Removing such volatile species requires further processing of the plutonium.

To eliminate the necessity of an additional volatile removal step, calcium chloride was proposed as a substitute electrolyte for NaCl-KCl. As CaCl₂ has a very low vapour pressure relative to NaCl-KCl it would not be necessary to remove entrained electrolyte prior to casting.

The electrorefining process using either CaCl₂ or NaCl-KCl as the electrolyte have previously been investigated (3). The average yield in 19 successful runs using CaCl₂ was 74% compared with 73% when using NaCl-KCl.
EXPERIMENTAL

Materials

Calcium chloride di-hydrate (Fisons Analytical Reagent with a stated assay of 101.1% and all recorded impurities present at < 100 ppm) was dried in a vacuum oven for 5 days at up to 210°C. This typically produces a salt containing < 0.1 wt% water.

Anhydrous magnesium chloride, 98%, from Lancaster Synthesis was used as received.

Salt blocks for use in electrorefining were made by melting the calcium chloride in a ceramic crucible with about 1.9 wt % magnesium chloride. For each run the total amount of salt was made up of a salt block and 200-300 g of CaCl₂ powder. The overall salt composition was 1765 g CaCl₂ plus 35 g MgCl₂. Chemical analysis of the salt blocks showed they contained about 0.6 wt % magnesium which was the target composition and a water content of < 0.04 wt %. No impurities in the blocks above 100 ppm were detected by ICP-MS.

Plutonium metal was cast into shape to occupy the inner cup of the crucible. This material was from a variety of legacy sources, varying in age and composition. The quality of the material also varied in its oxide composition.

Cell Design and Process Parameters

The process is carried out in an alumina ceramic crucible equipped with a concentric inner cup (Figure 1). The impure metal and salt are stirred by an alumina stirrer. An alumina sheathed tungsten rod contacts the plutonium anode. A tungsten cylinder acts as the cathode. Reduced plutonium drains from the cathode and collects in the outer portions of the crucible.

The cell was assembled and heated to 850°C in a resistance furnace under an argon atmosphere. Prior to the electrorefining process, an anodic current of 15 A at a potential of ca. 2 V was applied to the 'cathode' for 5 minutes with stirring. This reversed polarity mode was used to clean the cathode surface and strip impurities from the salt.

During electrorefining, polarity was returned to convention and a current of 25 amps was passed for 40 hours at a potential of 1.5 to 4 V, with stirring. During this time the applied potential was interrupted every 2 hours and the open circuit potential (Back emf or Bemf) of the cell measured and recorded. When the Bemf exceeded a predetermined value, the process was terminated. Once cold, the crucible was recovered from the furnace, broken and the salt removed to reveal metal product.
Process control Parameters

The Bemf is used during the electrorefining process to monitor the concentration of impurities at the anode (or concentration of plutonium at its surface), and to terminate the operation prior to an empirically determined point. This point may be prior to the oxidation of significant quantities of impurity from the feed metal. During Bemf measurement, the applied potential is removed and the potential between the anode and cathode determined. The potential is measured at a defined period after the interruption to the applied potential. The frequency of this measurement increases as the electrorefining operation approaches completion.

Microscopy and Hardness Measurements

Micro sections of product plutonium were viewed on a Reichert Polyvar microscope. The micro-hardness measurements were taken with a Vickers Micro Hardness Indenter at 100 g load.

RESULTS AND DISCUSSION

High Current Efficiency Operations

Eight electrorefining runs have been successfully completed in CaCl₂ with an average yield of 90.5%. This value compares favourably with previous studies in CaCl₂ and with studies in NaCl-KCl. (Table I).

Table I: Yields and Current Efficiency of Electrorefining Runs Resulting in High Density Product

| Run No. | Yield (%) | Anode efficiency (%) | Cathode efficiency (%) |
|---------|-----------|-----------------------|------------------------|
| 1       | 89.6      | 93.2                  | 87.5                   |
| 2       | 90.9      | 98.6                  | 89.6                   |
| 3       | 90.4      | 98.6                  | 89.6                   |
| 4       | 88.9      | 102                   | 90.9                   |
| 5       | 89.9      | 97.6                  | 93.6                   |
| 6       | 88.8      | 95.6                  | 87.5                   |
| 7       | 94.6      | 91.9                  | 85.5                   |
| 8       | 85.1      | 85.4                  | 77.2                   |
| NaCl-KCl (Mean) | 75.0 | 86.8                  | 71.7                   |

Figure 2 shows an example of well consolidated plutonium product. Figure 3 shows the associated current/voltage/Bemf trace for the process. The Bemf is low throughout most of the run before rising very rapidly as the run nears completion. There is a steady increase in the applied potential as the distance between the anode and cathode increases as metal is removed from the anode.
The increased yield in these CaCl₂ electrorefining operations runs may be owing to a number of factors:

1. In NaCl-KCl, sodium metal can be formed at the cathode. This can then react with Pu³⁺ in the salt, generating a suspension of Pu metal in the salt.

2. There is complete coalescence of the metal collected in the cathode ring. In NaCl-KCl plutonium fines of are observed.

3. Because of the higher process temperature a greater proportion of the plutonium can be removed from the anode.

The amount of plutonium which can be removed from the anode during electrorefining is limited by the onset of solid plutonium – gallium phases (4). The electrorefining process in NaCl-KCl operates at a process temperature of ca. 750°C. At this temperature the anode will solidify when the gallium concentration reaches 25 atom % (8.85 wt %). CaCl₂ has a higher melting point (~800°C) necessitating a process temperature of about 850 °C. At this temperature the anode will solidify when the gallium concentration reaches about 34 atom % (13.07 wt %). The higher process temperature required by the use of CaCl₂ results in a small increase in the amount of plutonium which can be removed from the anode before it solidifies. For a feed anode containing 1wt% gallium it is calculated that by increasing the temperature from 750 to 850°C the amount of plutonium which can be removed is increased from 89.6 to 93.3%.

Yield and efficiencies in the electrorefining process are defined as:

\[ \text{Yield} = \frac{\text{product gross weight}}{\text{feed gross weight}} \]  

\[ \text{Anode Efficiency} = \frac{\text{feed gross weight} - \text{spent anode gross weight}}{\text{current passed}} \]  

\[ \text{Cathode Efficiency} = \frac{\text{product gross weight}}{\text{current passed}} \]

The current efficiency of electrorefining in CaCl₂ is significantly greater then in NaCl-KCl (Table 1). This result suggests that during electrorefining there is less salt electrolysis in CaCl₂ than in NaCl-KCl.

Table II summarises the composition of the electrorefining operations which resulted in high current efficiencies.
Table II: Analysis of High Current Efficiency Electrefining Products

| Run No | Pu (wt %) | Ga (ppm) | Am (ppm) | Fe (ppm) | Ca (ppm) | U (ppm) | Np (ppm) | Al (ppm) |
|--------|-----------|----------|----------|----------|----------|---------|----------|----------|
| 1      | 99.97     | <10      | 42       | 30       | 65       | <30     | <20      | 120      |
| 2      | 99.96     | <14      | 85       | <20      | <12      | 32      | <30      | 48       |
| 3      | 99.95     | 3        | 38       | <30      | 22       | 28      | 75       | 45       |
| 4      | 99.88     | <8       | 20       | 22       | 5        | <20     | 65       | 54       |
| 5      | 99.96     | 8        | 22       | 28       | 70       | <20     | 160      | 80       |
| 6      | 100.01    | 10       | 28       | <30      | 20       | <20     | 100      | 55       |

Previous studies examined the relative efficiencies of impurity extraction of CaCl$_2$ and NaCl:KCl. Americium removals of 93 % are reported in CaCl$_2$ (3). Neptunium extraction in prior studies indicate 55 % removal (3). This compares to 70% americium and 87% neptunium extraction in NaCl:KCl. As americium chlorides are more stable than PuCl$_3$ the americium will concentrate in the salt, but as NpCl$_3$ is less stable than PuCl$_3$ the neptunium will remain in the spent anode, Table III.

Table III: Thermodynamic Data for Selected Actinide Chlorides at 1000K.(5,6)

|         | $\Delta G$ kJ/mol Cl$^-$ |
|---------|--------------------------|
| AmCl$_3$| 280                      |
| PuCl$_3$| 246                      |
| NpCl$_3$| 227                      |
| UC$_3$  | 215                      |

The difference in impurity extraction properties of each electrolyte may be attributed to the relative positions of the impurities' reduction potentials to one another. These reduction potentials are a function of temperature, concentration and the complexation of the impurity.

There is considerable evidence for the complexation of plutonium in halide melts. Phase diagram studies of Pu $^{3+}$ systems suggest the formation of complex compounds of the type A$^+_2$Pu$^{6+}$, A$^+_1$PuCl$_6$ and A$^+_2$PuCl$_3$ in alkali chlorides and A$^+_3$PuCl$_9$ in alkaline earth chloride (7,8,9). No such complex was found in NaCl-PuCl$_3$ (10,11). Benz et al demonstrated the formation of at least two compounds, including K$_3$PuCl$_6$ and perhaps K$_2$PuCl$_5$, in their studies of PuCl$_3$ in KCl (12).

Spectroscopic evidence suggests the lanthanide and actinide chlorides exist as networks of distorted LnCl$_6$$^{3-}$ or AnCl$_6$$^{3-}$ octahedra bound by their edges in alkali halide melts (13,14). The attractive coulombic Ln$^{3+}$ - X$^-$ and repulsive X$^-$ - X$^-$ interactions influence the degree of distortion of these octahedra. Fujii et al observed a change in the co-ordination status of NdCl$_3$ in LiCl-KCl as a function of both temperature and Ca$^{2+}$ addition to the melt (15). As the ionic radius decreases and the cationic charge increases on substituting potassium by calcium (group I to group II), the charge-to-size ratio of the cations in the electrolyte increase. A high charge-to-size ratio is associated with a strongly polarizing cation. Ca$^{2+}$ is therefore likely to change the co-ordination status of
chloride ion onto the central actinide metal cation in the melt. The higher temperature may also play a role in the changing complexation.

The reduction of Na\(^+\) in a NaCl-KCl melt containing Pu\(^{3+}\) has been reported as being coincident with the Pu\(^{3+}\) reduction (16). This represents a significant anodic shift in Na\(^+\) reduction potential and may be attributed to complexation with the Pu\(^{3+}\).

The increase in the extraction of the americium by CaCl\(_2\) relative to NaCl-KCl may be attributed to the differing stabilities of the of the Pu\(^{3+}\) complexes in each case. In NaCl-KCl the chloro-plutonium anions, such as PuCl\(_6^{3-}\), are stabilised by the K\(^+\) cation. This has the effect of reducing the activity coefficient of Pu\(^{3+}\) in NaCl-KCl compared with in CaCl\(_2\) where the plutonium Pu\(^{3+}\) cation is not complexed. This pushes the actual (as opposed to thermodynamic) reduction potentials of Pu\(^{3+}\) and Am\(^{3+}\) further apart in CaCl\(_2\) than in NaCl-KCl. Therefore, in CaCl\(_2\) americium is more readily oxidised than plutonium into the salt phase and less readily reduced into the product metal phase leading to a lower concentration of Am in the product metal in CaCl\(_2\) than in NaCl-KCl.

Neptunium chloride is less stable than PuCl\(_3\). This is reflected in its reported reduction potential (17). Therefore, plutonium is more readily oxidised than neptunium, which remains in the anode. The low activity coefficient of Pu\(^{3+}\) in NaCl-KCl results in a greater separation of the reduction potentials of Pu\(^{3+}\) and Np\(^{3+}\) than expected from the thermodynamic data. As Pu\(^{3+}\) behaves more ideally in CaCl\(_2\) then the actual reduction potentials are closer together than in NaCl-KCl and more neptunium will be oxidised at the anode and transferred to the product metal.

Because PuCl\(_3\) is significantly more stable than UCl\(_3\) there is no observed change in the purification of plutonium from uranium in these two salt systems.

The difference is operating temperature may directly impact upon the extraction behaviour of the salts. The influence of temperature and concentration on standard reduction potentials are described by the Nernst relationship:

\[
E = E^\circ + \frac{RT}{nF} \ln[M^{n+}] \tag{4}
\]

The amount of plutonium in the feed material is hugely greater than either americium or neptunium. Given that the activity of Pu\(^{3+}\) must therefore be significantly greater than either Am\(^{3+}\) or Np\(^{3+}\) in the melt, the influence of temperature would also be greater. Consequently, the 100°C increase of substituting NaCl-KCl by CaCl\(_2\) would also cause a narrowing of the difference in potentials of Pu\(^{3+}\) and Np\(^{3+}\) with an increase in the difference of potentials between Pu\(^{3+}\) and Am\(^{3+}\).

Silin et al found the Pu\(^{3+}\) reduction potential's temperature dependence to be a function of the electrolyte composition (18). The presence of K\(^+\) mitigated the effect of temperature indicating a stabilisation of the chloro-plutonium complex.

Overall, the trend of reduction potentials follow:

Am (II/ III) < Pu (III) (K\(^+\)/ 750°C) < Pu (III) (Ca\(^{2+}\)/ 850°C) < Np (III) < U (III) \tag{5}
Lower Current Efficiency Operations

Three of the eleven operations in CaCl\textsubscript{2} gave rise to significantly lower yields than in other cases. These lower yields were accompanied with lower current efficiencies during electrorefining and are summarised in Table IV.

Table IV: Yields and Current Efficiency of Electrorefining Runs Exhibiting Low Current Efficiencies

| Run No. | Yield (%) | Anode efficiency (%) | Cathode efficiency (%) |
|---------|-----------|-----------------------|------------------------|
| 9       | 67.3      | 77.8                  | 62.0                   |
| 10      | 66.9      | 82.5                  | 68.0                   |
| 11      | 87.0      | 90.2                  | 78.5                   |

In contrast to the homogenous high current efficiency product, distinct sections were visible in this metal (Figure 4). This was despite the product being well above the melting point of plutonium. The structure might suggest that plutonium formed on the inner and outer surfaces of the cylindrical cathode did not coalesce successfully.

Figure 5 illustrates the Bemf trace for a typical example of an electrorefining operation demonstrating high current efficiency. The value of the Bemf is considerably higher than observed in high current efficiency operations throughout run (Figure 3).

In the less successful runs in CaCl\textsubscript{2}, it is believed that calcium metal is produced at the cathode and this results in poor coalescence of the plutonium. A similar mechanism may operate during NaCl-KCl electrorefining where sodium metal may hinder the coalescence of plutonium.

The low current efficiency product was re-cast. This formed a solid with distinct upper and lower sections. Chemical analysis was conducted on each section (Table V).

Table V: Analysis of a Low Current Efficiency Electrorefining Product

| Pu (wt %) | Ga (wt%) | Am (ppm) | Fe (ppm) | Ca (ppm) | U (ppm) | Np (ppm) | Cl (ppm) | Al (ppm) |
|-----------|----------|----------|----------|----------|---------|----------|----------|----------|
| Upper     | 99.42    | 0.0040   | 110      | 17       | 2800    | <20      | <20      | 550      | 220      |
| Lower     | 99.95    | 0.0034   | <15      | 70       | 9       | <20      | -        | 160      |

Both upper and lower section of this materials was found to have higher americium content than was typical for high current efficiency CaCl\textsubscript{2} electrorefining.

Chemical analysis of the upper section of this plutonium indicates it to be particularly enriched in calcium and chloride. As the stoichiometry is not ideal (Ca:Cl should be 1:2) this might suggest that both calcium and calcium chloride are entrained...
within the electrorefining product. Analysis of each element was carried out on different portions of the sample.

Optical microscopy with simultaneous hardness measurement was conducted on the upper section of the poorly formed metal product (Figure 6). The bulk of the metal was α plutonium (Fig.6, A) with some voidage (Fig.6, B). A CaCl₂ matrix is observed at the surface (Fig 6, C) which contains beads of metal (Fig.6, D). Hardness values of 233, 215, 241 and 291 H Vickers were obtained for these smaller, more reflective, structures. Unalloyed plutonium gives hardness values of about 250 to 280 H Vickers and δ stabilised plutonium about 45 to 50 H Vickers. This result suggests that the smaller structures are α plutonium.

The larger globules had hardness values of 73, 75, 75, 71, 47, 96 and 103 H Vickers. As they are reflective it is unlikely that they are ionic compounds. Covalent compounds would typically have a greater hardness. Elemental calcium has a hardness of 17 H Vickers. These structures are therefore probably a δ plutonium alloy or may be a calcium alloy. The lower specific heat capacity of CaCl₂ may also allow for more rapid cooling of the melt, favouring formation of the δ phase via poorer homogenisation of the product.

It is proposed that during these less successful operations, dross material accumulates at the surface at the anode. This depletes the availability of plutonium for electrorefining. Consequently, electrolysis of the salt takes place. This process contributes towards the diminished current efficiencies observed and the poor coalescence of the plutonium. Chemical analysis indicates that calcium is subsequently found within the product metal.

Given that calcium is reduced at the cathode, the electrolyte must be depleted in Pu³⁺. Under these circumstances, the reduction potentials of Pu³⁺ would approach that of Am³⁺ and this may also lead to poorer americium extraction prior to the onset of calcium deposition (Equation 4).

CONCLUSION

CaCl₂ has proven to be a suitable replacement for NaCl-KCl for plutonium electrorefining. A yield of 90 % was achieved giving high purity metal.

It is reported that CaCl₂ demonstrates enhanced americium separation relative to NaCl-KCl and poorer neptunium separation. This is attributed to the temperature and differing activity of Pu³⁺ in the melt.

Those operations which resulted in low current efficiency product contained higher quantities of dross material in the feedstock. Analysis of these cases suggested calcium and calcium chloride were entrained within the plutonium metal.
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Electrochemical Society Proceedings Volume 2004-24 757
A. Alumina Crucible with Alumina Inner Cup  
B. Electrolyte  
C. Electorefinined Plutonium  
D. Impure Plutonium  
E. Tungsten Anode  
F. Alumina Stirrer  
G. Tungsten Cathode. The cathode is shown as a rod for ease of illustration, but is a cylinder surrounding the anode cup.

Figure 1: The Electorefining Cell

Figure 2: Well Consolidated Plutonium Product
Figure 3: Current, Voltage and Bemf Trace for an Electrorefining Operation Leading to High Current Efficiency

Figure 4: Low Current Efficiency and Poorly Consolidated Plutonium Product (Boundary of the Poorly Coalesced Material is Marked)
Figure 5: Current, Voltage and Bemf Trace for an Electrefinign Operation Leading to Low current Efficiency

Figure 6: Optical Micrograph and Hardness Measurement Assignments for a Section of Low Current Efficiency Electrefinign Plutonium.

A. \(\alpha\) Plutonium

B. Void

C. Calcium Chloride (dark areas)

D. Calcium Alloy or \(\delta\) Plutonium Alloy (light globules)