A STUDY OF PRODUCTION PROCESS OF URANIUM METAL BY MOLTEN SALT ELECTROLYSIS USING ZINC CATHODE

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ABSTRACT

A molten salt electrolysis of uranium tetrachloride was investigated applying KCl - LiCl - NaCl - UCl₄ molten eutectic salts. This process is aimed at the production of high purity uranium metal for the ²³⁵U isotopic enrichment process by Atomic Vapor Laser Isotope Separation (AVLIS). High current efficiency has been confirmed in the salt electrowinning process by applying a liquid zinc cathode. A series of purification processes have also been demonstrated to produce high purity uranium metal by filtration, distillation and final vacuum refining treatments of Zn - U cathode products. Optimal operating conditions are discussed in terms of each unit process.

INTRODUCTION

The AVLIS isotopic separation technology for the enrichment of ²³⁵U has been studied intensively in Japan, the USA and European countries. The magnesium thermite method had been widely adopted to produce the uranium metal which is the starting material for AVLIS process. However, this resulted in a large amount of magnesium fluoride slag solid waste containing trace amounts of uranium. Hence the treatment and disposal of this radioactive waste should be required.

The molten salt electrolysis method has been developed for uranium metal production in Japan to avoid the waste problem. [1]-[3] We have been studying the electrolysis of UCl₄ (m. p. 590°C) using molten zinc as cathode. In the present paper, the experimental results on the effects of fundamental process parameters, i.e. anode geometry, current density, operating temperature, electrolyte salt composition, and the construction materials of electrolytic cells will be reported. The separation characteristics of uranium from zinc in
the cathode products are also reported. [4]-[8] Figure 1 illustrates the overall flowsheet of the present process.

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**EXPERIMENT**

**Molten Salt Electrolysis**

Prior to electrolysis experiments, uranium tetrachloride UCl₄ green powder was produced by a single reaction of UO₂ reduction with Cl₂ gas in the presence of carbon as a reductant. This operation was conducted efficiently by a vertical fixed bed reactor loaded with 1 kg/batch under the flow rate of 0.8 l/min Cl₂ at 900 °C.

\[
\text{UO}_2 + 2 \text{Cl}_2 + C \rightarrow \text{UCl}_4 + \text{CO}_2
\]  

[1]

Liquid zinc was selected not only to maximize the solubility of uranium in the cathode but also to facilitate the discharge of the product. Approximately 10 kg of fused zinc was charged as the cathode.

The geometry of the electrolytic cell and the two types of anodes, i.e. multi-hole and double-cylindrical ones, used in the present study is shown in Figs. 2 and 3. The cell and anode were covered by alumina or quartz cylinder to avoid the direct contact of molten salt and liquid cathode with graphite crucible. Multi-hole and double-cylindrical types of anode geometry were attempted: both types of anode geometry were aimed at facilitating the removal of electrolytic Cl₂ gas evolved during operations. The anode was set 5 cm above the surface of liquid cathode. Two component KCl - NaCl (m.p. 658 °C) and three component KCl - LiCl - NaCl (m.p. 346 °C) eutectic systems have been selected as the supporting molten salts for electrolysis. High purity guaranteed-grade salts were used in all experiments.

The operating temperatures were fixed to 800 °C with alumina insulator and 700 °C with quartz insulater respectively for the KCl - NaCl and KCl - LiCl - NaCl eutectic salts. All the experiments were carried out to maintain the concentration of uranium at constant by adding UCl₄ regularly during electrolysis.
The electrowinning of uranium was carried out at a constant current mode by monitoring the potential difference between the electrodes and that of the cathode with reference to an Ag/AgCl electrode:

\[
\begin{align*}
\text{UCl}_4 & \rightarrow \text{U}^{4+} + 4 \text{Cl}^- \\
\text{U}^{4+} + 4 \text{e}^- & \rightarrow \text{U} (s) \\
4 \text{Cl}^- & \rightarrow 2 \text{Cl}_2 (g) \uparrow + 4 \text{e}^-
\end{align*}
\]

As shown in Table 1, all the electrolytic reduction experiments were performed to confirm the effects of anode geometry, operating temperature, the concentration of uranium in the molten salt system, and the behavior of insulating crucible between the electrodes. The experiments were performed in a mode of constant electrical current to maintain the anodic current density at either 1.14 A/cm\(^2\) or 2.41 A/cm\(^2\); the total electrical current of either 45 A or 70 A was selected.

The experimental equipment was installed in a glove-box of argon atmosphere (>99.999 %) in order to avoid the effects of atmospheric moisture and oxygen, since they have deleterious effects in fused salt experiments.

**Zinc Separation**

To separate U/Zn alloys from metallic zinc and other impurities, three steps were performed: (1) the filtration of U-Zn cathode products to separate solid U/Zn alloys from zinc, (2) the distillation of filtered cake alloys to obtain sponge uranium, and finally (3) the vacuum refining of uranium. The outline of the distillation equipment is shown schematically in Fig. 4.

After the electrolysis process, solid intermetallic alloy compounds, i.e. UZn\(_{12}\) and U\(_2\)Zn\(_{17}\), were formed in the cathode melt by decreasing the temperature, and these solid alloys were sedimented by the difference of specific gravities from the metallic zinc which contains a very low amount of uranium. Thus, these intermetallic alloys were separated
mechanically by either graphite or alumina ceramic filter elements at about 500 °C in argon atmosphere.

In the distillation step, the filtered cakes were then heated up to 900 °C to 950 °C in argon atmosphere to remove residual zinc and other impurities from the filtered cake. In this treatment calcia, magnesia and yttria were examined as the construction material for the crucibles.

The final finishing vacuum purification step was performed at 1250 °C, and the reactivity of the yttria, high-purity magnesia, and yttria-coated graphite crucibles with uranium were also studied.

RESULTS AND DISCUSSION

Molten Salt Electrolysis

The experimental results are summarized in Table 1. Maximum current efficiency of 87 % was attained in Run E1. The uranium content in the bath was maintained constant by adding UCl₄ regularly. This was attained by monitoring the potential between the electrodes during electrolysis as shown in Fig. 5. Current efficiency of 77 % was obtained in Run E2 when the content of UCl₄ was 20 wt % in the electrolytes. The current efficiency tends to decrease with the increase of UCl₄ contents in the molten salts. This might be explained by the increase of the counteracting effects of the reverse reactions. After electrolysis, the salts attached to the cathode products were removed easily, because the surface of the alloy was flat. Besides, it was confirmed that the deposited uranium was distributed homogeneously in the cathode (Fig. 6).

Although it was confirmed from the phase diagram that operation under high temperature will favor the solubility of uranium into the cathode, the operation should be made at 700 °C rather than 800 °C to mitigate the corrosion of construction materials. The selection of the material for the crucible should be important. In the operations at 800 °C, alumina was adopted instead of quartz, since the quartz crucible was attacked by the deposited metal uranium and it caused to promote the side-reactions to decrease the current efficiency. Hence, it is confirmed that the selection of crucible materials is important.
Stable electrolysis was attained with maximum total current of 70 A by applying double-cylindrical anode in Run E3, while it was reduced to 45 A with multi-hole anode. It has been confirmed that the effective removal of Cl₂ gas is also an important factor for electrolysis. This was confirmed by visual observation that the double-cylindrical geometry is superior to the multi-hole geometry for gas removal.

**Zinc Separation**

The experimental results are summarised in Tables 2 to 4. The uranium concentrations of 7 wt % to 8 wt % in the cathode zinc were further increased up to 14 wt % to 18 wt % by the filtration step. The filtration was conducted easily by 140 μm and 400 μm of pore sizes. The separation performance is dependent on the distribution of uranium in the cathode: both the operational temperature and pore size of the filter had no significant effects. The residual uranium concentrations in the zinc filtrate were limited to less than 0.12 wt %.

The filtered cake was then distilled to remove zinc from uranium at 900 °C to 950 °C in argon atmosphere. It has been confirmed that pure uranium sponge can be produced free from carbon by applying either calsia, yttria, or magnesia crucible, and caution should be paid to the handling of the uranium, because of its ignition behavior even at room temperature.

The uranium sponge was further refined under 10⁻³ Torr vacuum at 1250 °C to produce about 850 g of purified uranium. Magnesia crucible can be applied for this vacuum refining, because magnesium can easily be removed in the vacuum refining step. As can be seen from Table 5, the final concentrations of various impurities, such as Zn, Mg, Na and K, were reduced to trace levels of several 10 ppm. This level of contamination is compatible to the preliminary specifications for the starting material in the AVLIS process. On the other hand, the metallic zinc recovered by these steps can be returned to the electrolysis process as the cathode.

**CONCLUSIONS**

The molten salt electrowinning of uranium tetrachloride applying liquid zinc as the cathode was investigated experimentally, and sufficient current efficiency has been attained. Moreover, high purity uranium has been obtained by separating uranium in the
U/Zn alloys from zinc and other impurities by filtration, distillation and vacuum refining steps. The process developed in the present study has demonstrated that the product uranium metal is applicable to the AVLIS isotopic enrichment process as the starting material. Further studies on the production process are under way. This study was conducted by Sumitomo Metal Mining Co., Ltd. under contract with the Metal Mining Agency of Japan.

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Table 1  Summary of Molten Salt Electrolysis Operations

| Test No. | Run E1 | Run E2 | Run E3 |
|----------|--------|--------|--------|
| Support electrolyte | KCl - NaCl - LiCl | KCl - NaCl - LiCl | KCl - NaCl |
| Charged salt kg | 1.66 | 1.66 | 1.68 |
| Charged Zn kg | 9.86 | 10.0 | 9.86 |
| UCl₄ content wt % | 10 | 20 | 10 |
| Temperature °C | 700 | 700 | 800 |
| Total current A | 45 | 45 | 70 |
| Current density A/cm² | 1.14 | 1.14 | 2.41 |
| Current density A/cm² | 0.28 | 0.28 | 0.45 |
| Anode type | Multi-hole | Multi-hole | Double-cylindrical |
| Voltage V | 4.5 - 5.1 | 3.7 - 4.8 | 4.7 - 6.6 |
| Deposited U g | 896 | 791 | 827 |
| Current efficiency % | 87 | 77 | 83 |

Electrode distance is fixed at 5 cm, 1) anode, 2) cathode.

Table 2  Summary of Cathode Filtration Operations

| Test No. | Run F1 | Run F2 | Run F3 |
|----------|--------|--------|--------|
| Temperature °C | 550 | 500 | 500 |
| Filter material | Graphite | Graphite | Alumina |
| Pore size μm | 10 | 120 | 400 |
| Charged ingot kg | 10.22 | 9.83 | 8.86 |
| Filtercake kg | 5.18 | 5.43 | 4.72 |
| U content wt % | 18.6 | 13.8 | 15.3 |
| Filtrate zinc kg | 4.87 | 4.31 | 4.14 |
| U content wt % | - | 0.06 | 0.12 |
Table 3 Summary of Distillation Operations

| Test No. | Run D1 | Run D2 | Run D3 |
|----------|--------|--------|--------|
| Crucible material | - | Calcia | Ytoria | Magnesia |
| Charged cake kg | 7.36 | 8.04 | 6.99 |
| Recovered U g | 471 | 857 | 796 |

Temperature was fixed at 920 °C.

Table 4 Summary of Vacuum Refining Operations

| Test No. | Run R1 | Run R2 | Run R3 |
|----------|--------|--------|--------|
| Crucible material | - | Ytoria | High purity Magnesia | Graphite coated with Ytoria |
| Charged U g | 852 | 791 | 828 |
| Purified U g | 852 | 791 | 827 |

Temperature and vacuum were fixed at 1250 °C and ~ 10⁻³ Torr, respectively.

Table 5 Analytical Results of Impurities in Uranium Products

|        | A1      | C       | K       | Mg      | Na      | Si      | Y       | Zn      |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| Filtercake | 480-880 | 220-680 | <100    | <2      | <160    | <50     | <10     | -       |
| Distilled U | 510-950 | 120-600 | <55     | <12     | <110    | 30-300  | 6-600   | 46-202  |
| Purified U  | 460-700 | 160-600 | <10     | <3      | <40     | 40-200  | <1-200  | <22-43  |

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Fig. 1 Flowsheet for high purity uranium metal production.

Fig. 2 Schematics of Electrolytic Cell
Fig. 3 Anode Geometry

Fig. 4 Distillation Furnace

Thermocouple
Ceramic Crucible
Heater
Thermocouple
Graphite Crucible
Filtercake
Vacuum
Ar Gas
Ar Gas
Zn

Quartz Cover
Alumina Cover
Cl Removal Outlet
Multi-Hole Type
Double-Cylindrical Type
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Fig. 5 Potential difference between the electrodes vs. Time

Fig. 6 Uranium Concentration in the Electrolytic Cathode