A PARAMETRIC STUDY ON REDUCTION
OF URANIUM OXIDE BY FLUORIDE
MOLTEN SALT ELECTROLYSIS FOR SCALE-UP

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ABSTRACT

Uranium metal production from uranium oxide by molten salt electrolysis has been examined to get basic characteristics of electrolysis and design data for scale-up. Current efficiency obtained was around 50%, which was higher value than reported in early experiments. Lower concentration of UF₄, higher current density, adequate agitation, and lower temperature improved current efficiency. UO₂, U₃O₈ and UO₃ were all available as feed material, and adequate feed condition enabled the UF₄ salt not to decompose and to control its product nature.

INTRODUCTION

In the nuclear fuel cycle processes such as uranium enrichment, fuel fabrication, nuclear reactor, spent fuel management and waste management, bringing down the cost of each process to be acceptable to the public as well as safe is a never-ending theme. And there are many activities in all fields in order to improve its cost performance and safety. The uranium enrichment area is no exception. In this uranium enrichment, commercial production processes now in operation in the world are the gaseous diffusion process or the centrifugal process of uranium hexa-fluoride. And these cost performances are well achieved by operating deduced plants. However, it is considered to be more expensive if these plants will be dismantled and rebuilt applying the same process concepts. On the
other hand, atomic vapor laser isotope separation (AVLIS) will be a promising uranium enrichment technology for the next generation because of its high cost performance and high enrichment efficiency. In this AVLIS enrichment process, uranium metal or uranium metal alloy will be used as feed material. Today, commercial production of uranium metal in the world is done by thermite reduction of uranium tetra-fluoride with magnesium[1]. In this thermite process, magnesium fluoride is produced as a byproduct. This byproduct needs to be treated to reduce its uranium contamination for disposing of it or selling it on the market. Considering cost performance, minimization of waste production and continuous process concept, an electrolytic process for producing uranium metal directly from uranium oxide will offer potential advantages over the existing commercial process[2].

Metal Mining Agency of Japan has carried out a feasibility study on metallic uranium production systems for AVLIS feed materials since fiscal 1989[3]. In this study, parametric experiments were carried out to get basic characteristics of electrolysis and design data for a scale-up of electrolytic apparatus.

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EXPERIMENT

Materials

Barium fluoride, lithium fluoride and uranium fluoride salts mixture was used as electrolyte. Its composition was 74wt%BaF2-11wt%LiF-15wt%UF4. Uranium tetra-fluoride acts as solvent for uranium oxide in this electrolysis. LiF and BaF2 will act to lower the melting point of electrolyte and reduce vaporization of LiF respectively. And these salts were regent grade chemicals. Uranium tetra-fluoride was produced by the reaction of UO2 with HF at about 400°C. These fluorides were mixed and premelted before experiment. In most cases, uranium tri-oxide produced by fluidized bed denitration was used as starting material. UO3 was also treated in a vacuum furnace to remove remaining acidic moisture at 450°C. U3O8 was prepared by calcination of UO3 in the N2 atmosphere at 650 °C. UO2 was prepared by reduction of UO3 with hydrogen at 600 °C. Uranium dioxide was used as standard material, and other uranium oxides were used in a parametric examination.

Apparatus

The schematic feature of the apparatus and the outline of the electrolysis apparatus are described in the former presentation. The electrolytic cell made of graphite has a size of 200mm inner diameter and 350mm height. The anode is made of graphite which has a cylindrical shape with slits as a standard case. The cathode rod is made of tungsten. It is considered to act as uranium electrode under electrolysis because the tungsten surface is covered with liquid uranium. A graphite uranium metal receiver covered with boron nitride
has a capacity for 3 kg uranium metal and is set just below the cathode. The electrolytic cell is enclosed in a quartz tube with steel flanges so that a gas tight enclosure was achieved. High purity argon is used as purge gas in the cell. Off gas is introduced to gas mass spectrometer, for the measurement of gas composition such as CO, CO\textsubscript{2} and CF\textsubscript{4} with electrolysis. Direct current for electrolysis has a capacity of 0~20V and 0~500A. Induction heating which has a maximum heating capacity of 1400°C is used to bring the cell to the experiment temperature of about 1200°C and maintain it during the experiment.

**Experimental Procedure**

Mixture of LiF, BaF\textsubscript{2} and UF\textsubscript{4} was pretreated in a vacuum at 400°C and in Ar at 800°C for 30 minutes in order to evacuate volatile species and moisture, then heated up to about 1200°C, which is well over the melting point of LiF-BaF\textsubscript{2}-UF\textsubscript{4} electrolyte and the melting point of uranium metal(1130°C). The cathode and anode electrodes assembly, and uranium receiver were immersed slowly into the electrolyte to the desired depth and a brief pre-electrolysis was conducted to evacuate still remaining volatile impurities. Pre-electrolysis time was decided by measuring the off-gas composition such as CO, CO\textsubscript{2}, CF\textsubscript{4}. After pre-electrolysis, polarization curves before and after uranium oxides feed were measured in the range of 0 to 2.4 A/cm\textsuperscript{2} at anode. All of the experiments were carried out by constant current mode. During the experiments, uranium oxides were fed periodically into the cell and off-gas composition was analyzed continuously with electrolysis. Direct current, impressed voltage, temperature, and induction heating power were also recorded continuously. After electrolysis, cathode and anode electrodes assembly, and uranium metal receiver were removed upward in order to minimize back-reaction of the metal with the electrolyte. After cooling, uranium metal was removed from the receiver and was weighed. Current efficiencies were calculated by off gas volume of C0, CO\textsubscript{2} and CF\textsubscript{4}, and by weight of uranium metal produced.

**RESULTS AND DISCUSSION**

**UF\textsubscript{4} Concentration of The Salt**

The effect of uranium tetra-fluoride concentration of the LiF-BaF\textsubscript{2}-UF\textsubscript{4} salt was examined in the range of 10~20 wt % without changing its LiF to BaF\textsubscript{2} molar ratio. A summary result of calculated current efficiency was shown in Figure 1. Current efficiency had a tendency to increase with decrease of UF\textsubscript{4} concentration. This is a similar to the behavior which was reported by Piper[4] using a different type of electrolytic cell called the Hall process. The lower current efficiency at higher UF\textsubscript{4} concentration results from the formation of UF\textsubscript{3} by the reaction of uranium at the cathode with UF\textsubscript{4} in the salt( U + 3UF\textsubscript{4} \rightarrow 4UF\textsubscript{3} )[5]. Current efficiency is one of the important factors for electrolysis performance. However, decrease of UF\textsubscript{4} in the salt will result in decreasing the solubility of uranium oxide in the salt. Considering a scale up of the electrolytic cell, optimization of
current efficiency and uranium oxide solubility should be achieved. At present, 15 wt % of UF₄ is selected as a standard operational condition and a range of 10 to 20 wt % of UF₄ is treated as an operational deviation of UF₄ concentration of the salt.

**Oxidation States of Uranium Oxides**

Uranium oxides such as UO₂, U₃O₈ and UO₃ are typical products of the nuclear fuel cycle. And in the uranium metal production plant for AVLIS we are now considering, these uranium oxides are intermediate or final material for metal conversion. Thus availabilities of these oxides may enable its simplification of the plant pretreatment process such as calcination and reduction of uranium tri-oxide. The experimental results showed a possibility that any of the uranium oxides was available without any operational trouble. Figure 2 shows the results of obtained current efficiency. It shows that the higher the oxidation state of uranium oxide was fed, the higher the current efficiency calculated by off gas analysis was. In this calculation, UO₂, U₃O₈ and UO₃ were considered to be dissolved in their oxidation states and reduced electrolytically. On the other hand, off gas analysis results indicated that higher CO₂ concentration was obtained by feed of higher oxides, and that the CO₂ gas peak appeared immediately after the feed of oxide. Thus a part of excess oxygen in the oxides may be reduced chemically with carbon mono-oxide or carbon in the cell. Details of this evaluation will be discussed in another presentation at this meeting.

**Current Density**

Increase of current density can lead to the increase of electrolysis capacity or the contribute to cell compactness. However increase of current density on anode may cause the undesired anode effect. In this present work, more than 50 experimental runs have been conducted in the range of 0.242 ~ 1.74 A/cm² on anode. Electrolysis was successfully carried out without any decomposition of uranium tetra fluoride. And there were not any features of anode effect such as overvoltage during these experiments. As for cathode, Figure 3 shows a relation between cathode current density and current efficiency. Current efficiency had a slight tendency to increase with the increase of cathode current density. This is the similar to the behavior which was reported by Piper[4], too. From this result, one of the considerations for large scale apparatus is to keep the ratio of anode area to cathode area as high as possible.

**Temperature**

Electrolysis temperature was controlled by induction heating power. And a temperature range from 1150 to 1300 °C was examined. Uranium metal melting point is 1130°C so that produced uranium metal could be treated in liquid condition and recovered in receiver. A summary result of current efficiency is shown in Figure 4. Current efficiency had a tendency to decrease with the increase of temperature. This is also the same behavior
which was reported by Piper. However, higher temperature reduced the impressed voltage of the electrode so that energy consumption was less at higher temperature. Besides these results, the solubility of $\text{UO}_2$ in the electrolyte and the limiting anode current density generally increase with temperature[4]. And carbon contamination and corrosion of the cell materials increase with temperature. Thus in a design of large scale apparatus, consideration of these relations with temperature becomes important.

**Agitation**

Uniform distribution of dissolved uranium oxide in the salt may be desired for stable electrolysis. Uniformity of dissolved uranium oxide may cause the decomposition of uranium tetra-fluoride or the overvoltage of electrodes. Argon bubbling and/or superposition of alternating current were examined for their agitation effects. As for argon bubbling, argon gas tube was introduced under the uranium metal receiver, and flow rates of 0, 0.05 and 1 Nl/min were tested. At any condition, degradation of uranium tetra-fluoride was not observed, and current efficiencies calculated by off gas showed almost same values. However at 1 Nl/min flow rate, uranium metal produced seemed to be mechanically dispersed out of the receiver so that current efficiency calculated by uranium metal showed less value. Generally higher agitation will result in better electrolysis. However, in this experimental system with uranium metal receiver, adequate gas flow agitation seems to exist. On the other hand, the effect of alternating current addition to direct current on electrolysis was examined by changing its ripple factor from 1 ~ 44 % which is defined as:

$$\text{Ripple value} = \frac{\Delta V_{\text{peak-peak}}}{V_{\text{mean}}} \sqrt{\frac{2}{\pi}} \times 100 \ (\%)$$

The result of current efficiency is shown in Figure 5. In this range, current efficiency didn't seem to be affected by superposition of alternating current component. Figure 6 shows its electrolysis energy for production of 1 kg uranium metal(energy cost kWh/kg-U). The result indicates that superposition of alternating current seems to improve its energy cost. Chemla et al[6] reported the reduction of the formation of a passivating layer of CFx on the carbon anode by superposition of pulsed current in their HF-KF molten salt electrolysis. Thus in this present work, a similar effect may occur to reduce the overvoltage on the anode.

**Graphite Anode Shapes**

Graphite anode is consumed with electrolysis to produce CO and CO$_2$ so that its design and cost have to be as simple and cheap as possible. In the standard experiments, cylindrical type anode with vertical slits was used, which will be expensive if it is used for
a large scale apparatus. Thus rod and plate type anode were examined which seem to be more realistic shapes. A result of current efficiencies obtained by different anode shapes is shown in Figure 7. The current efficiencies obtained showed there were no difference between these anodes types. Thus rod and plate types are promising anode shapes for large scale apparatus.

CONCLUSION

Uranium metal production from uranium oxides by molten salt electrolysis was examined to get basic characteristic effects on UF$_4$ concentration, oxidation states of uranium oxides, current density and temperature. Higher current efficiency could be achieved by:

- Lower UF$_4$ concentration
- Higher cathode current density
- Lower electrolysis temperature

And any of the uranium oxides is available as a feed material for electrolysis. Agitation effect by argon is not so clear but it could support stable electrolysis and reduce the decomposition of UF$_4$. Agitation by alternating currency did not seem to effect current efficiency but seemed slightly effective in lowering the energy cost. Anode shapes such as rod or plate seem to be promising for large scale apparatus.

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Fig 1 Current Efficiency vs. UF$_4$ Concentration in the Salt.

Fig 2 Current Efficiency vs. Oxidation State of Uranium Oxides.

Fig 3 Current Efficiency vs. Cathode Current Density.

Fig 4 Current Efficiency vs. Temperature.
Fig 5  Current Efficiency vs. Ripple Factor.

Fig 6  Electrolysis Energy vs. Ripple Factor.

Fig 7  Current Efficiency vs. Anode Shapes.