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

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ABSTRACT

The production process of uranium tetrachloride powder by a single reaction of uranium oxide reduction and chlorination with chlorine gas in the presence of carbon as a reductant was investigated. 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). Direct production of uranium tetrachloride became possible by using a vertical type chamber. A high reaction temperature and low chlorine potential are necessary for uranium tetrachloride production. UO2, U3O8 and UO3 had no significant difference as starting uranium oxides.

INTRODUCTION

The AVLIS (Atomic Vapor Laser Isotope Separation) technology for the enrichment of 235U has been studied intensively in Japan, USA and France. The magnesium thermit method has been widely adopted to produce the uranium metal which is the starting material for the AVLIS process. However, a large amount of magnesium fluoride slag is produced as solid waste containing trace amounts of uranium. The molten salt electrolysis method has been developed for uranium metal production in Japan to avoid this problem1-3. The authors have been studying the uranium metal production process by molten salt electrolysis of UC14 using a molten zinc cathode. Fig.1 illustrates the overall flow sheet of the process. The present report is concerned with the authors studies of UC14 direct production by Cl2 gas with carbon as a reductant.
Experiments were carried out by the following three scales;

1. **30g-U scale**: study on the influence of reaction temperature, amount of reductant and chlorine gas volume
2. **300g-U scale**: study on the influence of chamber type, reaction temperature, starting oxide, carrier gas and contamination of impurities
3. **1kg-U scale**: study on factors in larger-scale experiments

**EXPERIMENTAL**

**30g-U scale experiment (horizontal type chamber)**
A schema of the reaction chamber is illustrated in Fig. 2. The starting material was a mixture of uranium dioxide powder and graphite powder as a reductant. Uranium chloride was produced by chlorine gas, then vaporized uranium chloride was condensed in the cooling part in a quartz cell. Experimental conditions are listed in Table 1. Chlorine and uranium in the chloride were analyzed by titration and ICP respectively.

**300g-U scale experiment (vertical type chamber)**
A schema of the reaction chamber is illustrated in Fig. 3. The starting material was a pelletized mixture of uranium oxide and graphite powder. Ar or N2 was used as carrier gas. The other experimental procedures were basically the same as the 30g-U scale experiment. Experimental conditions are listed in Table 2.

**1Kg-U scale experiment**
The size of the experimental apparatus was twice the diameter of the 300g-U scale. Experimental procedures were the same as the 300g-U scale. Experimental conditions are listed on Table 4.

**RESULTS AND DISCUSSION**

**30g-U scale experiment (horizontal type chamber)**
The results are listed in Table 1. All of the uranium dioxide was chlorinated under all the experimental conditions except 1hr chlorination. Cl/U molar ratios were around 6. This means that the produced uranium chlorides were UCl6.

[1], [2], [3] are the equations of Cl4, Cl5, Cl6 formation from UO2, respectively.

\[
\text{UO}_2 + C + 2\text{Cl}_2 = \text{UCl}_4 + \text{CO}_2 \quad [1]
\]

\[
\text{UO}_2 + C + 2/5\text{Cl}_2 = \text{UCl}_5 + \text{CO}_2 \quad [2]
\]
If UCl₆ was produced directly from UO₂, the reaction proceeded according to eq.[3]. However, from a thermodynamic point of view, it is hardly considered that direct UCl₆ formation proceeded under these conditions. Fig. 4 shows the potential diagram of the U-O-Cl ternary system at 1173K. Considering that carbon was saturated and the inlet gas was only Cl₂, it is reasonable to assume that log pO₂ is -15--20(atm) and log pCl₂ is 0. Given these potentials, the governing equation has to be [2]. On the other hand, as shown in eq.[4], ΔG° is negative under 800K. This means that UCl₅ is possibly chlorinated to UCl₆ at lower temperature whenever Cl₂ pressure is high enough. That is to say, it is speculated that UCl₅ was produced in the furnace then chlorinated to UCl₆ by excess Cl₂ gas at a lower temperature zone.

\[
2\text{UCl}_5 + \text{Cl}_2 = 2\text{UCl}_6 \quad \Delta G^\circ (J) = -138,000 + 172.4T \quad [4]
\]

For producing UCl₄, from this speculation, it is necessary not only to raise the reaction temperature but also to reduce excess Cl₂ gas.

### 300g-U scale experiment (vertical type chamber)

Vertical type chamber has a structure which allows Cl₂ gas to pass through the pellet zone. That structure is suited to reduce excess Cl₂.

The efficiency of Cl₂ and Cl/U molar ratios are listed in Table 2. The efficiency was much higher than the horizontal chamber and Cl/U ratios of all products were almost 4. This means that the reaction proceeded according to eq.[1] and direct production of UCl₄ from UO₂ became possible by using the vertical type chamber.

Another controlling factor was carrier gas. Chlorine potential was decreased (log pCl₂ < -0.3) by introducing Ar gas. Considering that the chlorine potential between UCl₄ and UCl₅ is -0.45 in Fig. 4, the numerical value of -0.3 is low enough for tetrachloride production.

**Temperature:** The yield of uranium chloride(calculated value into weight of uranium in chloride) at 1073K was much less than that of 1173K. Operation at 1173K was preferable to 1073K.

**Carrier gas:** Ar and N₂ had no significant difference on the chloride products. Production cost will be reduced by using N₂ gas instead of Ar gas.

**Starting oxide:** UO₂, U₃O₈ and UO₃ had no significant difference on the
treatment efficiency. From a thermodynamic point of view, this result is reasonable as far as $O_2$ and $Cl_2$ potentials are low enough. Production cost will be possible to be reduced by using $U_3O_8$ or $UO_3$ instead of $UO_2$.

**Impurities:** The impurities in uranium chloride are listed in Table 4 with Pre-AVLIS requirement data. Product had less impurity than Pre-AVLIS requirement. As for the uranium oxi-chloride, no evidence of its existence was observed in any of the experiments.

**1Kg-U scale experiment**

The results are listed in Table 3. $Cl/U$ molar ratio were almost 4. Recovery of uranium was high; (>96%). These results show that this method was able to be adopted to a larger size uranium tetrachloride production process.

**CONCLUSIONS**

1. The vertical type chamber is very suitable for the $UCl_4$ production process.
2. The influences of fundamental parameters were confirmed as follows;
   1. reaction temperature; 1173K was preferable to 1073K
   2. carrier gas; there are no differences between Ar and N2
   3. starting oxide; there are no differences among $UO_2$, $U_3O_8$ and $UO_3$
   4. impurities; the percentage of impurities in the product was low enough
3. This method is possible to be adopted to a larger size uranium tetrachloride production process.

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Fig. 1 Flowsheet of Uranium Metal Production Process

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Fig. 3 Schema of Vertical Type Chamber

Fig. 4 Potential Diagram of U-O-Cl Ternary System
Table 1  Experimental conditions and results of the 30g-U scale experiments

|                     | UO2 | UO2 | UO2 | UO2 | UO2 | UO2 | UO2 | UO2 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Starting Oxide      |     |     |     |     |     |     |     |     |
| Weight of Uranium Oxide (g) | 30  | 30  | 30  | 30  | 30  | 30  | 30  | 30  |
| Weight of Uranium in Oxide (g) | 26.3| 26.3| 26.3| 26.3| 26.3| 26.3| 26.3| 26.3|
| Weight of Carbon Reductant (g) | 1.99| 1.99| 1.99| 1.99| 1.99| 1.99| 1.33| 2.66|
| Equivalent Value of Carbon | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1   | 2   |
| Temperature (K)     | 973 | 973 | 973 | 1073| 1173| 1223| 1073| 1073|
| Rate of Chloride Gas Supply (l/min) | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Reaction Time (min) | 60  | 120 | 180 | 240 | 120 | 120 | 120 | 120 |
| Efficiency of Chloride Gas | 13% | 33% | 19% | 15% | 30% | 30% | 31% | 31% |
| Cl/U Molar Rate      | 6.2 | 6.5 | 5.6 | 6.0 | 5.9 | 5.9 | 6.0 | 6.0 |
| Yield of Uranium (g-U) | 6  | 26  | 26  | 26  | 26  | 26  | 26  | 26  |
| Recovery of Uranium  | 21% | 100%| 100%| 100%| 100%| 100%| 100%| 100%|
Table 2  Experimental conditions and Results of the 300g-U scale experiments

|                     | UO2 | UO2 | UO2 | UO2 | UO2 | UO3 | UO3 | UO3 | UO3 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Starting Oxide      |     |     |     |     |     |     |     |     |     |
| Carrier Gas         | Ar  | Ar  | Ar  | Ar  | N2  | N2  | N2  | N2  | N2  |
| Temperature (K)     | 1173| 1173| 1073| 1073| 1173| 1173| 1173| 1173| 1173|
| Rate of Chloride Gas Supply (l/min) | 0.1 | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 | 0.1 | 0.05| 0.2 |
| Rate of Chloride Gas Supply (l/min) | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Reaction Time (min) | 100 | 50  | 100 | 50  | 50  | 50  | 100 | 200 | 50  |
| Efficiency of Chloride Gas | 91% | 89% | 90% | 93% | 90% | 89% | 77% | 92% | 94% |
| Cl/U Molar Rate     | 3.9 | 4.0 | 4.1 | 3.8 | 4.1 | 3.8 | 4.0 | 4.1 | 3.9 |
| Yield of Uranium (g-U) | 29  | 27  | 8   | 8   | 21  | 16  | 16  | 26  | 23  |
Table 3  Experimental conditions and results of the 1kg-U scale experiment

|                       | Starting Oxide | Weight of Uranium Oxide (g) | Carrier Gas | Temperature (K) | Rate of Chloride Gas Supply (l/min) | Rate of Chloride Gas Supply (l/min) | Reaction Time (min) | Cl/U Molar Rate | Yield of Uranium Tetrachloride (g) | Recovery of Uranium (%) |
|-----------------------|---------------|-----------------------------|-------------|----------------|----------------------------------|----------------------------------|---------------------|----------------|----------------------------------|------------------------|
|                       | UO2           | 1134                        | Ar          | 1173            | 0.8                              | 0.8                              | 449                 | 4.1             | 1571                             | 98                     |
|                       | UO2           | 1134                        | Ar          | 1173            | 0.8                              | 0.8                              | 402                 | 4.2             | 1554                             | 96                     |
|                       | UO2           | 1134                        | Ar          | 1173            | 0.8                              | 0.8                              | 422                 | 4.1             | 1563                             | 97                     |

Table 4  The list of impurity in Uranium Tetrachloride

| Element | Al | B  | Ca | Cr | Cu | Fe | K  | Mg | Na | Ni | Si | Y  | Zn |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| PRE-AVLIS (ppm) | <50 | <50 | <50 | <200 | <200 | <50 | <50 | <50 | <200 | <100 | <50 | <50 |
| This Result (ppm) | <20 | <20 | <20 | <10 | <5 | <10 | <20 | <10 | <20 | 22 | <5 | <10 |