Synthesis of High-Purity UCl_4 via a $BiCl_3$-Based Chlorination Route for Chloride Molten Salt Reactors

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1. Introduction

Molten Salt Reactors (MSRs) have attracted significant attention as next-generation nuclear systems owing to their high operating temperatures and favorable neutron economy. In particular, chloride-based nuclear fuels such as NaCl–KCl–UCl_3 are advantageous for achieving a fast neutron spectrum and offer flexibility in fuel cycle extension [1, 2]. However, high-temperature chloride environments are chemically aggressive, and the behavior of structural materials and fuel constituents is strongly influenced by the redox state of the molten salt [3-5]. Therefore, ensuring the chemical stability of the salt is a critical requirement for the practical realization of MSR technology.

During reactor operation, the redox environment of the molten salt may evolve over time due to impurity ingress, interactions with structural materials, and equilibrium with gaseous species. Under such conditions, a fraction of UCl_3 present in the fuel salt can be oxidized to UCl_4. At 650 ℃ in a chloride environment, the standard redox potentials are reported to be −2.29 V (vs. Cl_2/Cl^-) for the UCl_3/U couple and −0.98 V (vs. Cl_2/Cl^-) for the UCl_4/UCl_3 couple [5], indicating that UCl_4 is relatively more oxidizing. Accumulation of UCl_4 may promote chromium dissolution from structural alloys, thereby accelerating molten salt corrosion. Consequently, quantitative understanding of UCl_4 formation and behavior is essential.

The investigation of UCl_4 behavior requires the availability of high-purity UCl_4. However, in high-temperature chloride systems, UCl_4 is thermodynamically coupled with higher uranium chlorides such as UCl_5 and UCl_6, exhibiting complex phase behavior depending on temperature and chlorine chemical potential [1, 6]. Conventional synthesis routes employing Cl_2, HCl, or CCl_4 suffer from limitations including co-formation of higher chlorides, by-product management issues, and reduced purity. In particular, at temperatures above 600–700 ℃, disproportionation reactions and volatilization of higher chlorides further complicate compositional control.

To overcome these limitations, this study proposes a chlorination pathway using $BiCl_3$ for metallic uranium. In this approach, metallic bismuth formed as a reaction by-product can act as a reducing agent for higher uranium chlorides, thereby providing a self-regulating mechanism. Thermodynamic calculations and repeated reaction experiments were performed to evaluate the feasibility of obtaining high-purity UCl_4. The results provide fundamental data for understanding UCl_4 behavior and for developing salt purity control strategies in MSR systems.

2. Thermodynamic Assessment

Various chlorine-based oxidants, including Cl_2, HCl, and CCl_4, were initially evaluated as potential routes for UCl_4 synthesis. Oxidation of metallic uranium by Cl_2 gas is thermodynamically favorable and is expected to provide a relatively high conversion to UCl_4. However, under conditions of high chlorine chemical potential, higher uranium chlorides such as UCl_5 and UCl_6 are simultaneously formed [1]. In the temperature range above 600–700 ℃, these higher chlorides may partially exist in the vapor phase, making phase composition control difficult and limiting the production of high-purity UCl_4.

For HCl gas, thermodynamic simulations using HSC software predicted significant coexistence of UCl_3 at temperatures above 200 ℃. This indicates that HCl possesses insufficient oxidizing strength to shift the U^{3+}/U^{4+} equilibrium fully toward UCl_4. Moreover, the formation of hydrogen gas (H_2) during the reaction may introduce a reducing environment, further hindering stable UCl_4 formation.

In the case of CCl_4, UCl_4 formation is thermodynamically feasible; however, carbon is generated as a solid by-product. The presence of residual carbon complicates downstream processing and phase identification. Additionally, thermal decomposition and secondary reactions of CCl_4 at elevated temperatures introduce further uncertainties in compositional control. Overall, conventional chlorine-based oxidants share common limitations, including higher chloride co-formation, by-product handling challenges, and difficulty in maintaining compositional stability.

In contrast, this study proposes the chlorination of metallic uranium using $BiCl_3$ according to the reaction:

$$U+BiCl_3 \rightarrow UCl_3+Bi,\ \Delta G = -480.95\ kJ/mol$$

$U+4/3BiCl_3 \rightarrow UCl_4+4/3Bi$, $\Delta G = -509.91$ kJ/mol
$U+5/3BiCl_3 \rightarrow UCl_5+5/3Bi$, $\Delta G = -404.72$ kJ/mol
$U+2BiCl_3 \rightarrow UCl_6+2Bi$, $\Delta G = -306.81$ kJ/mol
* The reported ΔG values were calculated at 25 ℃.

Thermodynamic calculations indicate that this reaction possesses a negative Gibbs free energy at ambient temperature and is therefore spontaneous. A key advantage of this route is that metallic bismuth produced as a by-product can reduce higher uranium chlorides (UCl_5, UCl_6) back to UCl_4 or UCl_3. Equilibrium calculations for systems containing 1 mol of UCl_5 or UCl_6 with 1 mol of metallic Bi predict complete conversion to lower chlorides below 1000 ℃.

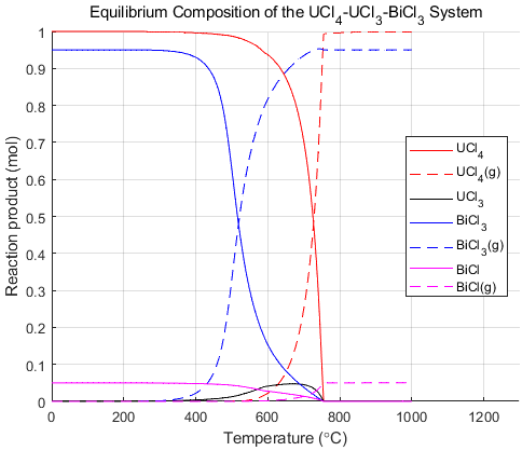

Fig. 1. Temperature-dependent equilibrium composition of UCl_3 and UCl_4 in the presence of $BiCl_3$ (HSC calculation)

This behavior implies that the $BiCl_3$-based process is not merely an oxidation pathway but incorporates an internal redox buffering mechanism, providing a self-regulating system. Even if higher chlorides are transiently formed, they can be reduced by metallic Bi, suppressing their accumulation. Therefore, compared with conventional chlorine-based oxidants, the $BiCl_3$ route offers superior compositional stability and controllability for UCl_4 synthesis.

3. Experimental Methods and Results

3.1 General Experimental Conditions

All experiments were conducted in an argon-filled glovebox maintained below 4 ppm O_2 and 1 ppm H_2O. High-temperature reactions were carried out using an electric furnace installed inside the glovebox. Quartz and Al_2O_3 reactors were employed, and each reactor was covered with a loosely fitted quartz cap to allow observation of volatilization and recondensation behavior at elevated temperatures. After reaction, products were retrieved inside the glovebox and analyzed by X-ray diffraction (XRD) for phase identification.

3.2 Volatilization and Recovery of $BiCl_3$

To evaluate the high-temperature volatilization behavior of $BiCl_3$, 0.5 g of $BiCl_3$ was loaded into a quartz reactor and maintained at 300, 400, and 500 ℃ for 24 h. After heating, no $BiCl_3$ residue was observed at the bottom of the reactor, indicating substantial volatilization. Solidified deposits were observed in the cooler upper region of the reactor. XRD analysis confirmed that the recovered material was pure $BiCl_3$.

These results demonstrate that $BiCl_3$ exhibits significant volatility in this temperature range and can re-condense along a temperature gradient [7]. Thus, residual $BiCl_3$ can be removed after reaction, although excessive volatilization may result in material loss when large excesses are used.

3.3 Removal of Metallic Bi via Bi–$BiCl_3$ Reaction

To verify the removal of metallic Bi generated as a by-product in the U–$BiCl_3$ reaction, Bi–$BiCl_3$ reaction experiments were performed. Metallic Bi (0.110 g, 5.26×10^{-4} mol) and $BiCl_3$ (0.835 g, 2.65×10^{-3} mol) were reacted at 330 ℃ for 24 h.

After reaction, the residual metallic Bi mass decreased to 0.025 g, corresponding to approximately 77.3% removal. Residual salt was not detected. This indicates that metallic Bi can react with $BiCl_3$ to form chloride species, preventing accumulation of metallic Bi in the $BiCl_3$-based process.

3.4 Synthesis of UCl_4 via U–$BiCl_3$ Reaction

Metallic uranium (2 g, 8.40×10^{-3} mol) and $BiCl_3$ (8 g, 2.54×10^{-2} mol) were reacted at 330 ℃ for 72 h. Same amount of $BiCl_3$ was added in excess to compensate for volatilization and to facilitate removal of metallic Bi.

XRD analysis after the initial reaction indicated that UCl_3 was the predominant product (Fig. 2), while UCl_4 peaks were not observed. The recovered solid was obtained as a dark greenish-brown powder, consistent with the formation of UCl_3 (Fig. 3). This suggests that UCl_3 formation is thermodynamically favored in the early stage, and that a surface chloride layer formed on uranium may hinder further oxidation. Metallic Bi produced during the reaction exists in liquid form at 330 ℃ (melting point 271.3 ℃) and may influence reaction kinetics at the uranium surface.

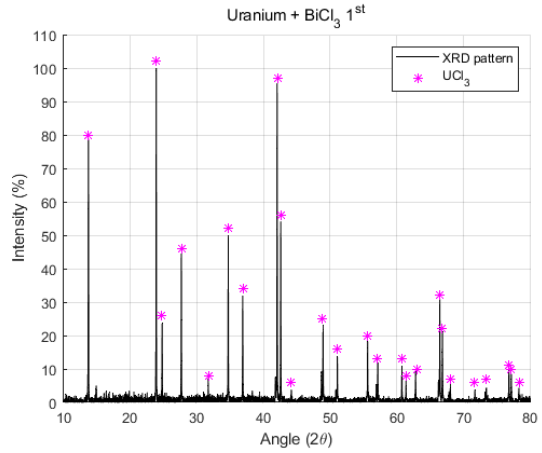

Fig. 2. XRD pattern of the reaction products after the first U–$BiCl_3$ reaction cycle

Fig. 3. Reaction products obtained from the $BiCl_3$-based chlorination of uranium: UCl_3 (left) and UCl_4 (right)

$BiCl_3$ was subsequently replenished, and the reaction was repeated under identical conditions. After five repeated cycles involving intermediate removal of surface chlorides, XRD analysis revealed that UCl_4 became the dominant phase (Fig. 4), with no detectable metallic uranium or higher chlorides (UCl5, UCl6). The final product was recovered as an olive-green powder, characteristic of UCl_4 (Fig. 3).

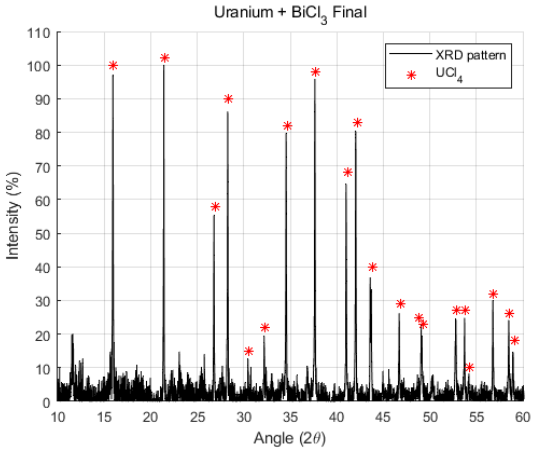

Fig. 4. XRD pattern of the reaction products after the fifth U–$BiCl_3$ reaction cycle.

These results demonstrate that the U–$BiCl_3$ reaction proceeds stepwise via UCl_3 as an intermediate, ultimately yielding high-purity UCl_4 through repeated processing. However, the high consumption of $BiCl_3$ and the requirement for multiple reaction cycles indicate that process efficiency improvement remains necessary.

4. Conclusions

This study evaluated the thermodynamic feasibility and limitations of conventional chlorine-based oxidants (Cl_2, HCl, CCl_4) for UCl_4 synthesis and proposed an alternative chlorination route using $BiCl_3$. Unlike conventional routes that suffer from higher chloride co-formation, by-product management issues, and compositional instability, the $BiCl_3$-based reaction provides a redox-buffering effect through metallic Bi formation, thermodynamically suppressing the accumulation of higher uranium chlorides.

Experimentally, the U–$BiCl_3$ reaction at 330 ℃ initially produced UCl_3 as an intermediate, followed by conversion to UCl_4 through repeated reaction cycles. The volatilization–recondensation behavior of $BiCl_3$ and the removal of metallic Bi via Bi–$BiCl_3$ reactions were also verified. These findings demonstrate the feasibility of obtaining high-purity UCl_4 through the $BiCl_3$ route and provide a foundation for future studies on UCl_4 behavior and salt purity control in MSR systems.

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