Effects of the U(III) and U(IV) Oxidation States on MSR Fuel Properties: A CALPHAD Model-Based Investigation

Chaerin Kim[a], Woei Jer Ng[a], Ho Jin Ryu[a,b*]
[a]*Department of Nuclear and Quantum Engineering, KAIST, Daejeon, Yuseong-gu 34141, Republic of Korea*
[b]*Department of Material Science and Engineering, KAIST, Daejeon, Yuseong-gu 34141, Republic of Korea*
[*]*Corresponding author: hojin.ryu@kaist.ac.kr*

1. Introduction

The Molten Salt Reactor (MSR) has gained attention as an emerging Generation-IV reactor concept due to its remarkable safety features. In this context, MSRs operate at atmospheric pressure and employ a homogeneous liquid fuel, which plays a vital role in minimizing the risk of catastrophic outcomes such as core meltdown, hydrogen explosion, and rapid fission product release in the event of severe loss of coolant accidents. As a result, one can argue that the safety features of MSRs are heavily contingent on their fuel properties.

Base salts and actinide salts are the two main constituents of MSR fuels. In fast reactors, chloride salts are the preferred option due to their higher Z number compared to fluorides. This makes them ideal for maintaining a fast neutron spectrum, which is crucial for efficient nuclear waste management. Additionally, chloride has higher actinide solubility, eliminating the need for highly enriched uranium (HEU) and improving the proliferation resistance of MSR fuels.

Actinides exist in multiple oxidation states in MSR fuels. In the case of uranium, the +3 and +4 oxidation states are the most ubiquitous. While U(III) is preferred in chloride fuels, the formation of U(IV) in irradiated nuclear fuel is unavoidable due to redox reactions with free chlorides, fission products, and structural material. Although U(IV) formation offers the benefits of lower fuel melting temperatures and increased actinide solubility, it is a strong oxidizing agent that may potentially accelerate the corrosion of structural materials. For that reason, controlling the formation of U(IV) is instrumental towards mitigating its adverse effects.

In this study, we propose a CALPHAD methodology to derive the optimum U(III)/U(IV) ratio in MSR fuels based on the effects of the U(III)/U(IV) ratio on the oxygen redox potential, fuel melting temperature, and actinide solubility.

2. Methods (Thermodynamic Modeling)

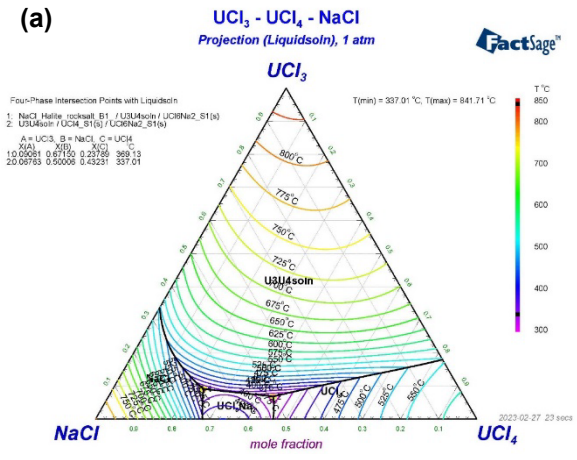
FactSage is a thermochemical software package used for thermodynamic modeling and the calculation of phase diagrams (CALPHAD) [1]. It is capable of performing thermochemical calculations and generating visual aids such as tables, graphs, and figures. FactSage 8.2 and the complementary Calphad Optimizer v1.0.0 module were used for all CALPHAD computations in this study.

Thermodynamic modeling was performed to simulate the phase behavior of several representative UCl4-containing ternary fuel systems. This was accomplished via the thermodynamic optimization (Calphad Optimizer v1.0.0) of their respective binary subsystems based on the two-lattice modified quasichemical model (MQM) [2] and the derivation of multicomponent fuel mixing behavior based on the Toop–Kohler interpolation scheme [3].

Henceforth, a comprehensive UCl_3–UCl_4–Base Salt thermodynamic database was developed. Based on this database, the effects of the U(III)/U(IV) ratio on the equilibrium eutectic temperature and actinide solubility of some representative MSR fuel compositions were derived by performing equilibrium thermodynamic calculations.

3. Results and Discussion

Figure 1 shows the projected ternary liquidus surfaces of three UCl_3–UCl_4–Base Salt systems. The projected ternary phase diagrams demonstrate remarkable consistency with those reported in [4,5] and, therefore, substantiate the precision of thermochemical values obtained via thermodynamic optimization in this study.



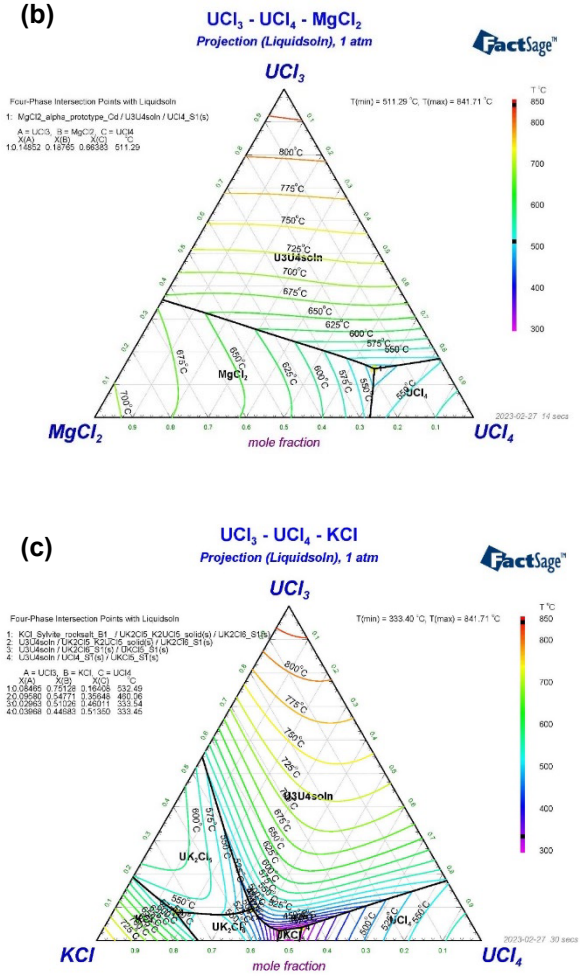


Figure 1. Projected ternary liquidus surfaces of UCl_3–UCl_4–Base Salt systems (Base Salt: NaCl, $MgCl_2$, KCl).

Based on this thermodynamic database, the effect of UCl_4 on the eutectic temperature and actinide solubility of UCl_3–Base Salt systems can be derived. Table 1 depicts the calculated changes in fuel eutectic temperatures and actinide solubilities as a function of the *U(III)/U(IV)* ratio at the primary eutectic composition of various Base Salt–UCl_3 systems. Here, the primary eutectic composition is defined as the eutectic composition with the highest UCl_3 solubility.

Table 1. Calculated changes in fuel eutectic temperatures and actinide solubilities as a function of the *U(III)/U(IV)* ratio for different Base Salt–UCl_3 systems.

i) KCl–UCl_3 *(46.0 mol% KCl–54.0 mol% UCl_3)*

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	554.77	0.549
99:1	553.38	0.548
95:1	549.23	0.541
90:10	545.08	0.533
80:20	535.38	0.518

ii) NaCl–UCl_3 *(67.0 mol% NaCl–33.0 mol% UCl_3)*

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	518.77	0.336
99:1	518.77	0.332
95:1	514.62	0.324
90:10	510.46	0.317
80:20	500.77	0.307

iii) $MgCl_2$–UCl_3
(64.1 mol% $MgCl_2$–35.9 mol% UCl_3)

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	669.69	0.358
99:1	669.69	0.359
95:1	666.92	0.370
90:10	664.15	0.384
80:20	657.23	0.417

iv) NaCl–KCl–UCl_3
(42.3 mol% NaCl–20.9 mol% KCl–36.8 mol% UCl_3)

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	462.05	0.368
99:1	461.34	0.367
95:1	458.43	0.359
90:10	454.57	0.352
80:20	445.55	0.343

v) NaCl–$MgCl_2$–UCl_3
(52.2 mol% NaCl–42.9 mol% $MgCl_2$–4.91 mol% UCl_3)

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	443.78	0.118
99:1	443.54	0.118
95:1	442.46	0.118
90:10	440.83	0.119
80:20	436.42	0.125

vi) KCl–$MgCl_2$–UCl_3
(47.2 mol% KCl–48.3 mol% $MgCl_2$–4.50 mol% UCl_3)

U(III)/U(IV) ratio	Eutectic temperature [°C]	Actinide Solubility
100:0	467.98	0.0450
99:1	467.88	0.0457
95:1	467.46	0.0485
90:10	466.89	0.0523
80:20	465.53	0.0609

Our results indicate that an increase in the proportion of U(IV) generally constitutes a decrease in the fuel eutectic temperature and an increase in the actinide solubility of the fuel system. Even when the eutectic actinide solubility decreases with the increasing proportion of U(IV), the magnitude of change in actinide solubility is relatively minuscule and sufficiently

compensated by the significantly larger decrease in eutectic temperature.

In essence, this suggests that the formation of U(IV) due to the oxidation of U(III) during the normal operation of MSR fuels may enhance their thermophysical properties. However, as an excessively large proportion of U(IV) would inevitably accelerate the corrosion of structural materials in MSR settings, the redox behavior of MSR fuels with their surrounding materials needs to be further investigated to arrive at an optimum U(III)/U(IV) ratio.

4. Conclusions

In this study, we applied the CALPHAD methodology to investigate the impact of UCl_4 on the properties of UCl_3-based molten salt fuels. Our simulation results showed that the main benefit of UCl_4 is its ability to lower fuel melting temperatures and increase actinide solubilities. However, as UCl_4 increases the susceptibility of structural materials to corrosion, an ideal balance between U(III) and U(IV) needs to be reached to harness the merits whilst limiting the drawbacks of U(IV).

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