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

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Introduction

- The **Molten Salt Reactor(MSR)** is one of the emerging Gen-IV reactor concept due to its remarkable safety features.
- The formation of U(IV) in irradiated nuclear fuel is unavoidable. Although U(IV) formation offers the benefits, it's a strong oxidizing agent that **accelerate the corrosion**. For that reason, **controlling the formation of U(IV) is instrumental in mitigating its adverse effects**.
- In this study, 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**.

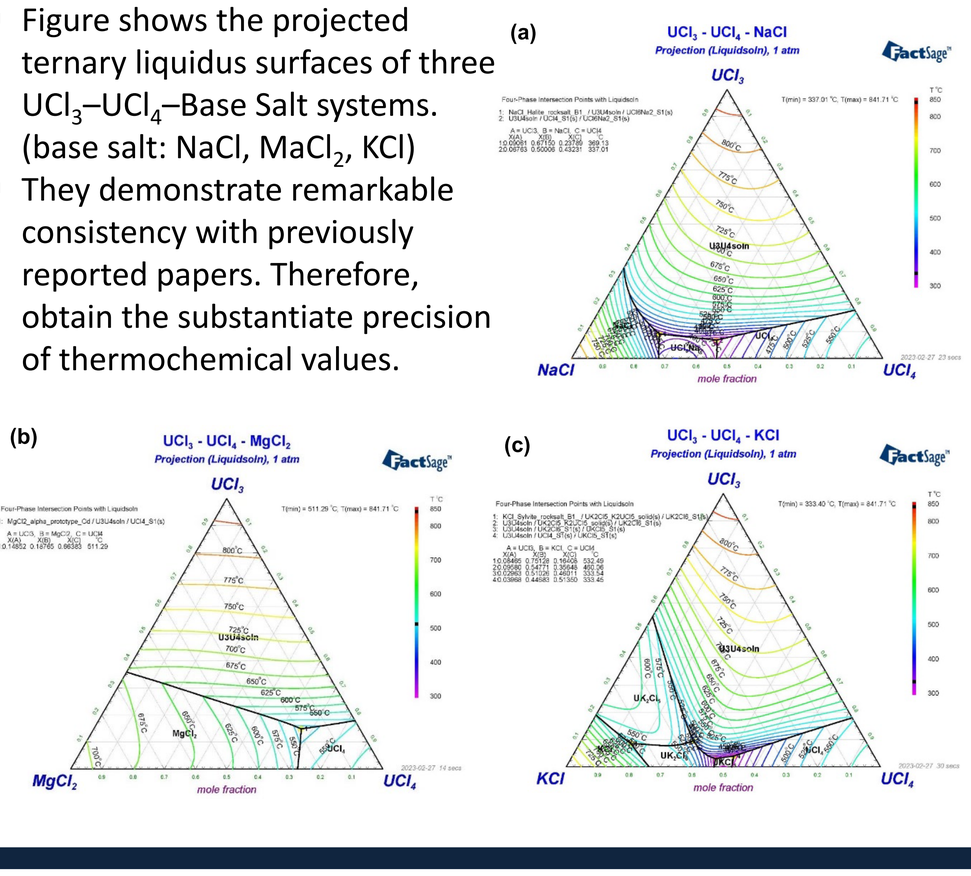
Experimental

- **FactSage 8.2** and the complementary **Calphad Optimizer v1.0.0** module were used for all CALPHAD computations in this study.
- Developed **UCl_3–UCl_4–Base Salt thermodynamic database**. Based on this database, the effects of the U(III)/U(IV) ratio on the equilibrium eutectic temperature and actinide solubility were derived by performing equilibrium thermodynamic calculations.
- Simulate the phase behavior of UCl_4-containing ternary fuel systems via the thermodynamic optimization of their respective binary subsystems based on the **two-lattice modified quasichemical model** (MQM).

Results

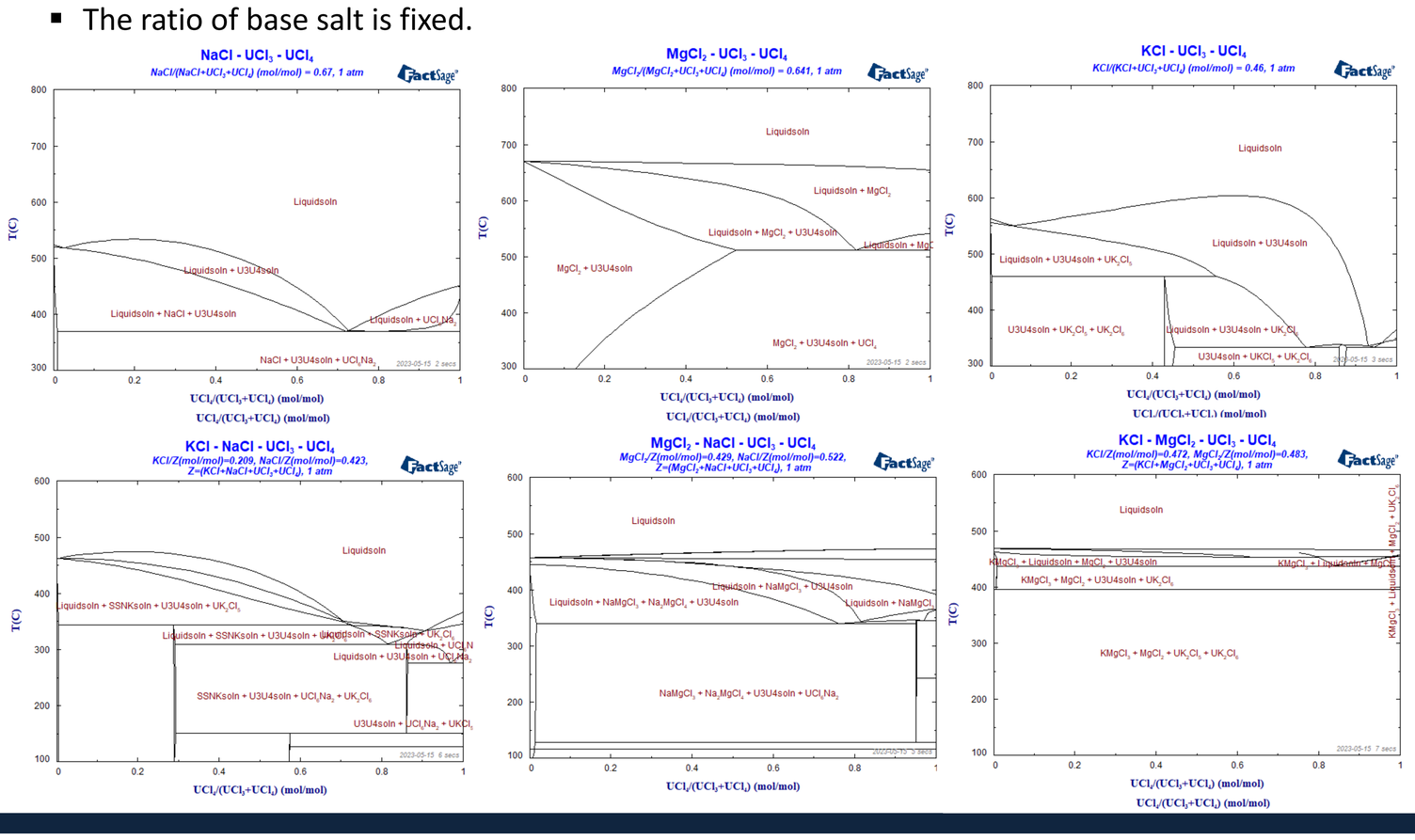
UCl_3–UCl_4–Base Salt database

- Figure shows the projected ternary liquidus surfaces of three UCl_3–UCl_4–Base Salt systems. (base salt: NaCl, $MaCl_2$, KCl)
- They demonstrate remarkable consistency with previously reported papers. Therefore, obtain the substantiate precision of thermochemical values.



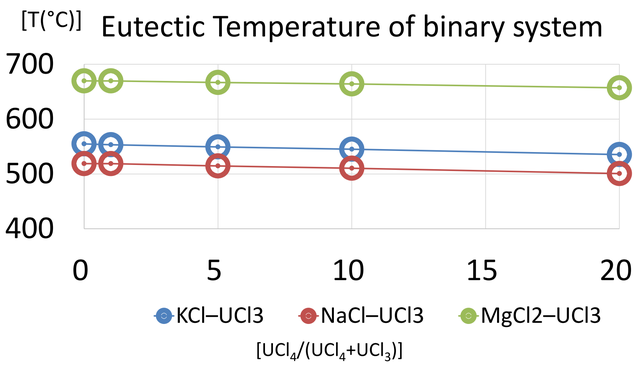
Pseudo Binary Phase Diagram of UCl_3–UCl_4–Base Salt system

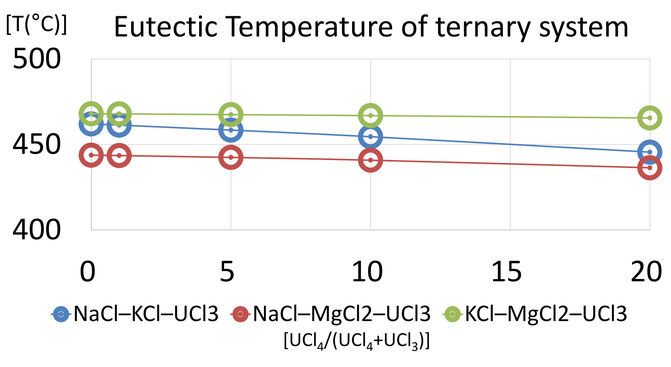
- The ratio of base salt is fixed.

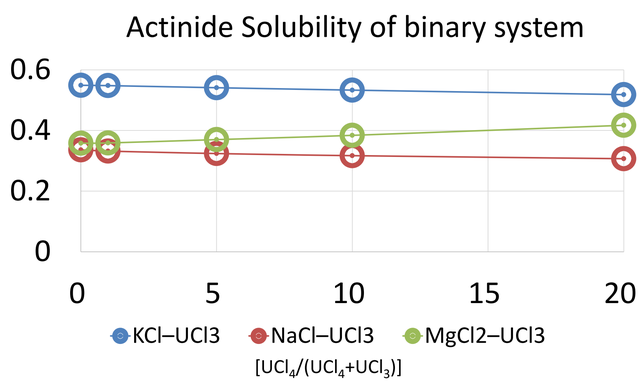


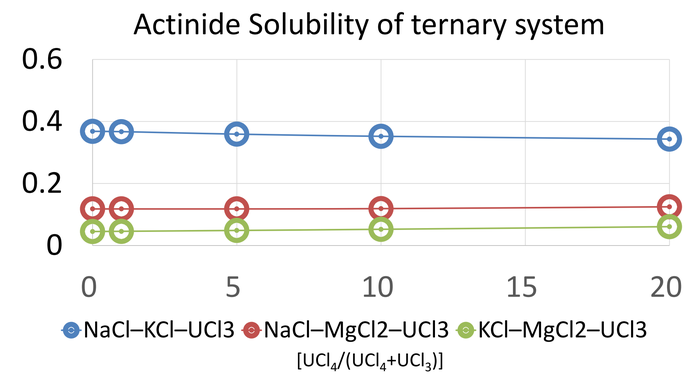
Fuel eutectic temperatures and actinide solubilities as a function of the U(III)/U(IV) ratio

- 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. (The primary eutectic composition is defined as the eutectic composition with the highest UCl_3 solubility.)









- 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 increase of U(IV), the change in actinide solubility is relatively minuscule and compensated by the larger decrease in eutectic temperature.
- 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 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.

Summary

- 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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