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# CALPHAD Studies on KCl as a Candidate Base Salt for U/Pu Fast Breeding Molten Salt Reactor Cycles

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## 1. Introduction

Molten salt reactors (MSRs) are a subset of Generation IV reactor designs that aim to address the shortcomings of conventional nuclear reactors. The key advantages of MSRs include (1) high thermal efficiency due to high operating temperatures; (2) inherent safety due to its strong negative temperature coefficient; (3) operation at atmospheric pressure, which greatly cuts down costs associated with reactor pressurization and eliminates the pressure gradient that drives the dispersion of radionuclides during accident scenarios; (4) low volume of radioactive waste generation due to the ability of the hard neutron spectrum to transmute long-lived fission products into less radiotoxic isotopes. [1,2].

Inevitably, the most unique and integral characteristic of MSRs is the molten salt mixture, which comprises two distinct components: (1) the actinide salts and (2) the base salts (or solvent) [3]. Ultimately, the choice of molten salt is dependent on the reactor design and function. For example, fluoride-based fuels are typically coupled with graphite or hydrogen moderators to give softer neutron spectrums that facilitate the operation of burner reactors, while chloride-based fuels can more efficiently harness the harder neutron spectrum that allows the simultaneous occurrence of both breeding and burning [4]. On the other hand, the base salt is chosen based on numerous factors, such as eutectic temperature, solubility of minor actinides, generation of radioactive by-products, and thermophysical properties [5]. With a desirable molten salt composition, neutronics analysis is performed to balance the fissile and fertile inventory of molten salt fuels and assess the feasibility of the design specifications [6].

From the descriptions above, it is evident that base salts play a key role in regulating the behavior and performance of MSR fuels. Moreover, the use of non-unary base salts is projected to increase the solubility of actinides and further lower the liquidus temperature of molten salt mixtures. Such is in the case of the Thorium Molten Salt Reactor (TMSR), which employs $^7\mathrm{LiF}$–$\mathrm{BeF_2}$ binary base salts coupled with the Th/U fast breeding cycle [7]. While the use of binary base salts is common for Th/U breeding cycles, research efforts on the U/Pu breeding cycles have historically employed $\mathrm{NaCl}$ as the sole base salt [8]. Additionally, we have noticed a paucity of literature that elucidates the effect of non-unary base salts on the performance of U/Pu breeding cycles.

In this study, we propose the usage of $\mathrm{KCl}$ as a base salt additive in MSR fuels with U/Pu breeding cycles. Using the Calculation of Phase Diagrams (CALPHAD) method, we demonstrate how the addition of $\mathrm{KCl}$ into $\mathrm{NaCl}$–$\mathrm{UCl_3}$–$\mathrm{PuCl_3}$ fuel systems lower their liquidus temperature. Subsequently, we investigate the effects of the $\mathrm{KCl}$ on modifying the response of the fuel liquidus temperature to transient changes in the fuel composition.

## 2. Methodology

FactSage 8.1 was used for all CALPHAD computations in this study.

### *2.1 Thermodynamic Modeling*

The $\mathrm{NaCl{-}KCl{-}UCl_3{-}PuCl_3(-RbCl)}$ fuel system was modeled by first evaluating and reconstructing the phase diagrams of all its binary subsystems. Thermochemical data—namely, the standard enthalpy of formation, standard entropy, and specific heat capacity—of end-members and intermediate compounds were obtained from the following sources [9–11]. In the case of unreported thermochemical data for intermediate compounds, the specific heat capacity was estimated using the Neumann–Kopp rule [12], while the standard enthalpy of formation and standard entropy were independently assessed to give the best reproduction of the phase diagrams. The two-lattice modified quasichemical model (MQM) [13] was used to evaluate the non-ideal mixing behavior of ionic liquid solutions, whereas the one-lattice polynomial solution (QKTO) model was used to assess the excess mixing energies of binary solid solution formation. All parameters used in the simulations above were either independently assessed or obtained from the available literature [9,10,14,15].

As the mixing behavior of chlorides consisting of three or more end-members are rarely reported, computational methods that predict the behavior of high-order mixtures are necessary. One of these predictive methods is the Toop-Kohler interpolation scheme which makes use of the interactions between individual binary mixtures to extrapolate the mixing reaction of high-order mixtures [16]. In our calculations, the symmetric Kohler interpolation scheme was used to assess ternary mixtures for ion pairs with cations from the same periodic group, e.g. NaCl–KCl–RbCl. In all other cases, the asymmetric Kohler interpolation scheme was used, with the "odd" end-member being designated as the asymmetric component. For example, NaCl is chosen as the asymmetric component in the $\mathrm{NaCl-UCl_3-PuCl_3}$ ternary, while $\mathrm{UCl_3}$ is chosen as the asymmetric component in the $\mathrm{NaCl-KCl-UCl_3}$ ternary. This method is justified due to the behavior of the end-members in ionic melts, whereby NaCl, KCl, and RbCl behave as ionic liquids, whereas $\mathrm{UCl_3}$ and $\mathrm{PuCl_3}$ tend to behave more as molecular liquids [10]. With the interpolation of all ten ternary combinations, the behavior of high-order mixtures is derived.

### *2.2 Compositional Shifts during MSR Operation*

In our simulated fuel system, we designated NaCl–KCl as the base salt, $\mathrm{UCl_3}$–$\mathrm{PuCl_3}$ as the fissionable component, and RbCl as the sole fission product. A simple model was used to simulate the transient compositional changes that occur in the reactor lifetime:

$$(UCl_3)_{1-x}(PuCl_3)_x \rightarrow \alpha\, RbCl + (UCl_3)_{1-x-\alpha}(PuCl_3)_x \,. \qquad \text{(Eq. 1)}$$

The reaction can be understood as follows. The base salts are not involved in any reaction; their composition remains unchanged. On the other hand, both $\mathrm{UCl_3}$ and $\mathrm{PuCl_3}$ undergo fission, which results in the formation of $\alpha$ mol% of fission products that accumulate in the fuel. Meanwhile, the breeding of fissile $^{239}$Pu proceeds as a result of neutron capture reactions by fertile $^{238}$U isotopes, resulting in the concentration of $\mathrm{PuCl_3}$ being restored to near its initial concentration [17]. Consequently, this leads to the net reaction whereby the formation of all fission products seemingly originates from $\mathrm{UCl_3}$ only.

## 3. Results and Discussion

The concentration of fissionable actinides in the fuel varies by reactor design. At 10mol% intervals of $\mathrm{UCl_3}$ and $\mathrm{PuCl_3}$, respectively, we derived the optimum base salt composition of NaCl – KCl for which the liquidus temperature is minimized. The minimum liquidus temperature was then compared to that of when NaCl is set as the sole base salt. All results are given in **Table 1** and **Table 2**.

**Table 1. Calculated minimum liquidus temperatures and their corresponding base salt compositions at 10mol% intervals of $\mathrm{UCl_3}$.**

| $\chi_{UCl_3}$ (mol%) | $NaCl$ only | | $(NaCl)_x(KCl)_{1-x}$ | |
|---|---|---|---|---|
| | $NaCl$ $fraction,$ $x$ | Liquidus Temp. ($°C$) | $NaCl$ $fraction,$ $x$ | Liquidus Temp. ($°C$) |
| 0 | 1.00 | 800.64 | 0.514 | 657.48 |
| 10 | 1.00 | 746.05 | 0.409 | 580.10 |
| 20 | 1.00 | 650.87 | 0.484 | 521.89 |
| 30 | 1.00 | 546.64 | 0.621 | 491.84 |
| 40 | 1.00 | 586.63 | 0.537 | 487.37 |
| 50 | 1.00 | 653.96 | 0.194 | 533.26 |
| 60 | 1.00 | 707.31 | 0.000 | 624.80 |
| 70 | 1.00 | 751.76 | 0.000 | 711.60 |
| 80 | 1.00 | 788.38 | 0.000 | 772.32 |
| 90 | 1.00 | 818.02 | 0.000 | 814.31 |
| 100 | 1.00 | 841.71 | 0.000 | 841.71 |

**Table 2 Calculated minimum liquidus temperatures and their corresponding base salt compositions at 10mol% intervals of $\mathrm{PuCl_3}$.**

| $\chi_{PuCl_3}$ (mol%) | $NaCl$ only | | $(NaCl)_x(KCl)_{1-x}$ | |
|---|---|---|---|---|
| | $NaCl$ $fraction,$ $x$ | Liquidus Temp. ($°C$) | $NaCl$ $fraction,$ $x$ | Liquidus Temp. ($°C$) |
| 0 | 1.00 | 800.64 | 0.514 | 657.48 |
| 10 | 1.00 | 774.06 | 0.371 | 598.13 |
| 20 | 1.00 | 712.28 | 0.418 | 543.85 |
| 30 | 1.00 | 575.58 | 0.625 | 461.36 |
| 40 | 1.00 | 504.99 | 0.625 | 425.20 |
| 50 | 1.00 | 589.51 | 0.374 | 455.53 |
| 60 | 1.00 | 643.08 | 0.000 | 511.31 |
| 70 | 1.00 | 684.57 | 0.000 | 616.01 |
| 80 | 1.00 | 717.68 | 0.000 | 689.60 |
| 90 | 1.00 | 743.83 | 0.000 | 737.32 |
| 100 | 1.00 | 764.40 | 0.000 | 764.40 |

From the results, we can observe that the addition of KCl significantly lowers the liquidus temperature of the fuel systems. This is expected as the incorporation of additional components increases the configurational entropy of the system, thereby lowering the liquidus transition temperature. This feature is important as it can help greatly improve the performance and safety of MSRs. For example, less thermal energy input is required for reactor startup if the fuel has lower liquidus temperatures. Moreover, in the case whereby the operating temperature of MSRs is constrained due to the compatibility of the surrounding materials, lowering the liquidus temperature allows for lower operating temperatures whilst maintaining similar temperature margins, herein mitigating the risk of potential corrosion [5].

We apply this idea to the REBUS-3700 reactor fuel concept, which employs the NaCl–$UCl_3$–$PuCl_3$ fuel system [18]. **Figure 1** depicts the NaCl–KCl pseudobinary phase diagram with the concentrations of $UCl_3$ and $PuCl_3$ fixed at 38 and 7 mol%, respectively. From our calculations, we infer that the liquidus temperature of this proposed system can be lowered from 617 to 498 °C by modifying the base salt composition from pure NaCl to $(NaCl)_{0.348}(KCl)_{0.652}$.

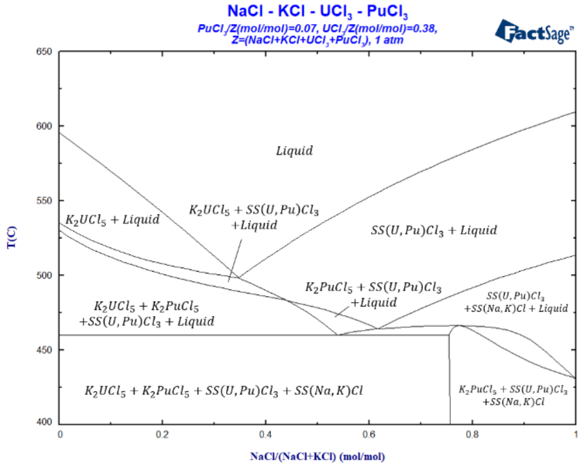

**Figure 1 NaCl–KCl pseudobinary phase diagram with concentrations of $UCl_3$ and $PuCl_3$ fixed at 38 and 7 mol%, respectively.**

Additionally, we model the response of the fuel liquidus temperatures to the evolution of RbCl (**Eq. 1)** at different base salt compositions. **Figure 2** illustrates the liquidus temperature change as a function of RbCl concentration at intervals of $\chi_{NaCl}/(\chi_{NaCl}+\chi_{KCl}) = 0.1$. Our calculations indicate that there are two distinct sets of responses to the evolution of RbCl, namely one that exhibits positive gradients and one that displays negative gradients with respect to RbCl concentration. Moreover, the transition between the positive and negative gradients seems to occur abruptly between the base salt compositions of $(NaCl)_{0.30}(KCl)_{0.70}$ and $(NaCl)_{0.40}(KCl)_{0.60}$. This range of compositions includes the minimum of the NaCl–KCl pseudobinary phase diagram in **Figure 1**.

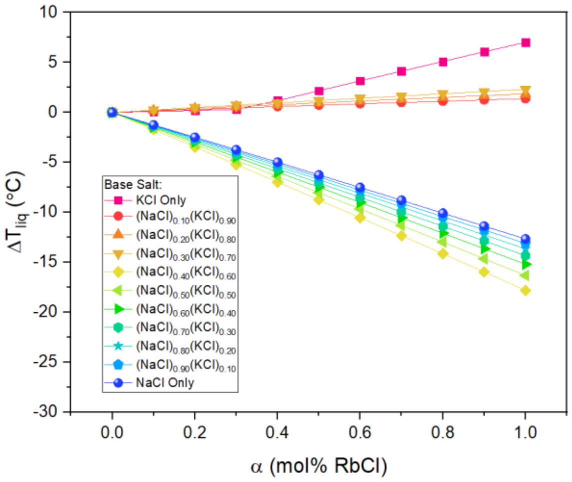

**Figure 2 Fuel liquidus temperature change as a function of RbCl concentration. Fissionable content fixed at 38mol% $UCl_3$ and 7mol% $PuCl_3$.**

One possible reason behind this result is the formation of $K_2UCl_5$ as RbCl gradually displaces $UCl_3$ from the fuel system. In this context, $K_2UCl_5$ is an intermediate compound with a relatively high congruent melting point of 628°C [14]. In the given fuel compositions, the KCl: $UCl_3$ molar ratio for all base salt compositions is less than the ideal stoichiometric ratio of 2:1 in $K_2UCl_5$. Hence, as RbCl supplants $UCl_3$ from the fuel system, the KCl: $UCl_3$ molar ratio increases commensurately towards that of $K_2UCl_5$, which implies the formation of more $K_2UCl_5$; raising the liquidus temperature of the fuel system. However, when the concentration of KCl in the base salt is sufficiently diluted, i.e., $\chi_{KCl}/(\chi_{NaCl}+\chi_{KCl}) < 0.652$, there is insufficient KCl to form intermediate compounds with $UCl_3$ at the rate that $K_2UCl_5$ is lost due to fission. Consequently, there is a net loss of $K_2UCl_5$ and the liquidus temperature decreases.

Another salient intermediate compound that can significantly raise the liquidus temperature of fuel systems is $K_3PuCl_6$, which is reported to have a congruent melting point of 685°C [19]. From **Figure 2**, we can infer that the liquidus temperatures of all base salt compositions exhibit continuous linear behavior with increasing concentration of RbCl, bar the fuel system with KCl as the unary base salt. This particular composition exhibits two adjoining linear lines with positive but discontinuous slopes. While the initial linear line with the smaller gradient is attributed to the formation of $K_2UCl_5$, the latter line with the larger gradient is assigned to the formation of $K_3PuCl_6$.

The mechanism of $K_3PuCl_6$ formation can be understood as follows. As the fission reaction in **(Eq. 1)** progresses, $U^{3+}$ ions that have large coordination numbers are supplanted by $Rb^+$ ions that have comparatively smaller coordination numbers. Consequently, $K^+$ ions originating from $K_2UCl_5$ now become "free ions" and favor SNN bond formation with $Pu^{3+}$ over $Rb^+$ due to the larger coordination number of $Pu^{3+}$ ions. Under these circumstances, $K_3PuCl_6$ becomes a dominant species and the fuel liquidus is raised. Nonetheless, similar to $K_2UCl_5$, the formation of $K_3PuCl_6$ becomes less pronounced as the concentration of KCl is diluted in the base salt due to the insufficiency of $K^+$ ions. At lower concentrations of KCl in the base salt, the formation of $K_3PuCl_6$ only occurs at larger concentrations of RbCl, implying that the increase in liquidus temperature only occurs when the fission has progressed for a prolonged period.

## 4. Conclusions

In this study, we used CALPHAD simulations to determine the ability of $KCl$ to lower the liquidus temperature of the $NaCl-UCl_3-PuCl_3$ fuel system and subsequently the behavioral trend of the liquidus temperature to compositional changes during normal operation. Our results demonstrate that $KCl$ is an excellent candidate base salt to lower the fuel liquidus temperature when the designated fuel composition is 55mol% Base Salt–38mol% $UCl_3$–7mol% $PuCl_3$. Moreover, we found that the response of the fuel system towards compositional changes varies according to the compositional fraction of $KCl$ in the base salt. In general, a greater rise in the liquidus temperature is projected when the fractional composition of KCl in the base salt is large due to the formation of $K_2UCl_5$ and $K_3PuCl_6$.

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