LiCl-KCl–UCl_3 Phase Diagram Studies

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International Pyroprocessing Research Conference

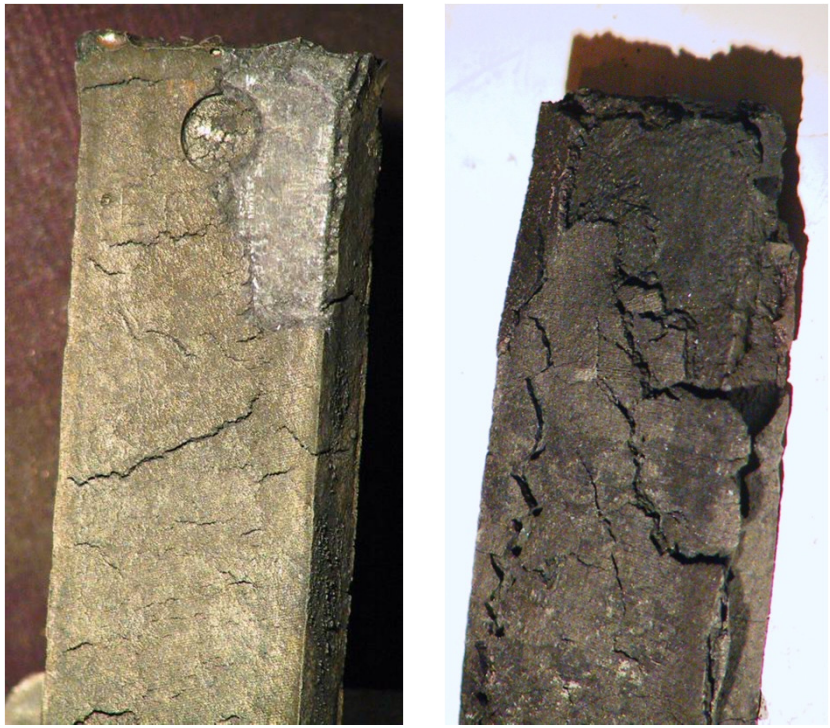
August 29, 2012

Outline

- Introduction
- Background
- Thermal analysis system
- Pseudo-binary systems
- Anneal and quench studies
- Summary

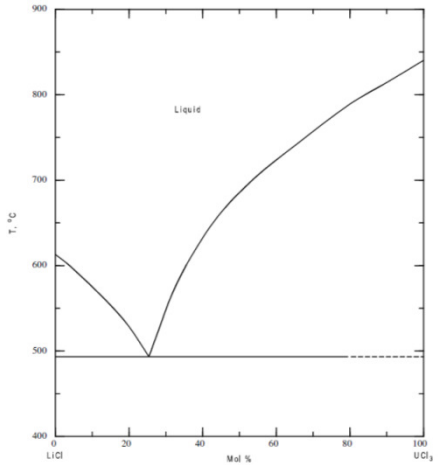
Introduction

- Goal is to elucidate phase behavior influencing and/or controlling processing in three actinide chloride concentration zones during electrorefining
  - Anode – salt interface
  - Bulk electrolyte
  - Cathode – salt interface
- Limited reliable and consistent published data available to characterize specific interactions
- Determining phase behavior of molten salts requires experimentation coupled with computational assessment techniques

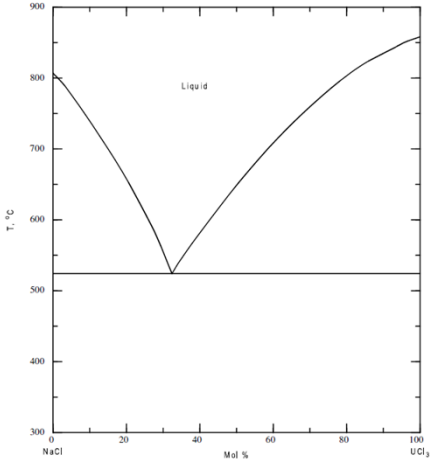


Salt layer observed on anode during uranium electrorefining

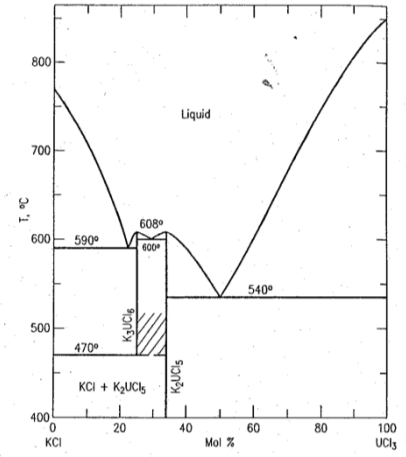
Alkali Chloride - UCl_3 Phase Diagrams



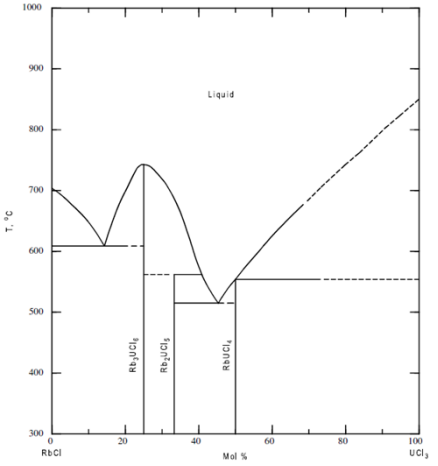
$LiCl\text{-}UCl_3$



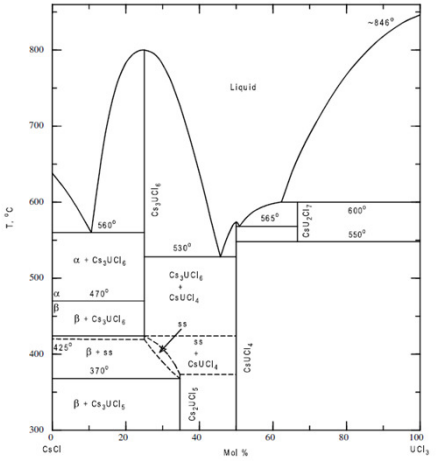
$NaCl\text{-}UCl_3$



$KCl\text{-}UCl_3$



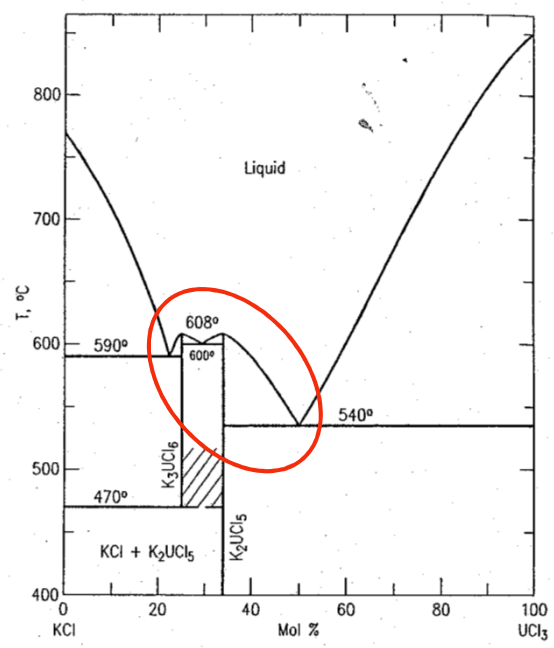
$RbCl\text{-}UCl_3$



$CsCl\text{-}UCl_3$

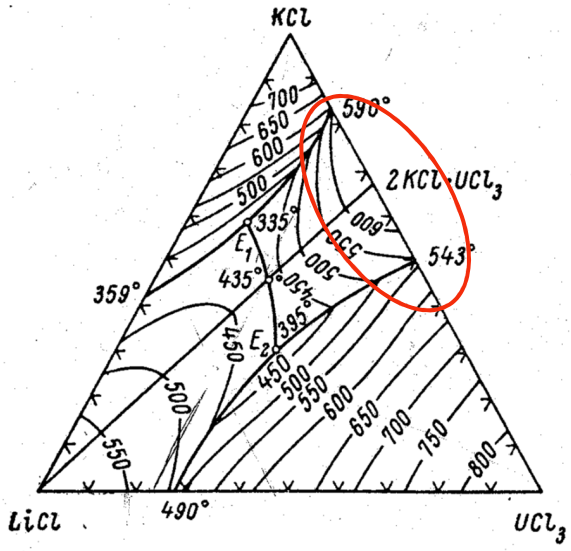
With increasing alkali metal cation size, the stability of the ternary phase increases producing a higher melting intermediate compound

Literature Data for Phase Diagrams Relevant to Electrorefining



Suglobova, I. G.; Chirkst, D. E. Koorinatsionnaya Khimiya **1981**, 7, 97-102.

- Limited published data on ternary LiCl-KCl-UCl_3 salt system
- LiCl-KCl and LiCl-UCl_3 well characterized
- Discrepancies among published data on KCl-UCl_3 binary system.

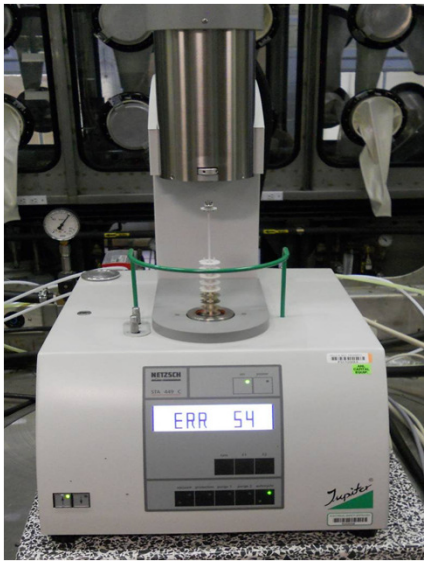


Desyatnik, V. N.; Dubinin, B. V. Journal of Applied Chemistry of the USSR **1975**, 48, 923-925

Objective: Re-evaluate KCl-UCl_3 binary phase diagram to refine ternary LiCl-KCl-UCl_3 phase diagram

Current Thermal Analysis Experimental Approach

- Argon glovebox
  - <6ppm oxygen, <3ppm moisture
- UCl_3 synthesized from U dendrites
- Calibrated STA 449 F1 Jupiter
- Homogenized sample
  - mixed w/ mortar and pestle
  - pressed with pellet press
- Open, nickel DTA crucible
- Various rates of heating/cooling
- Netzsch Proteus Thermal Analysis software

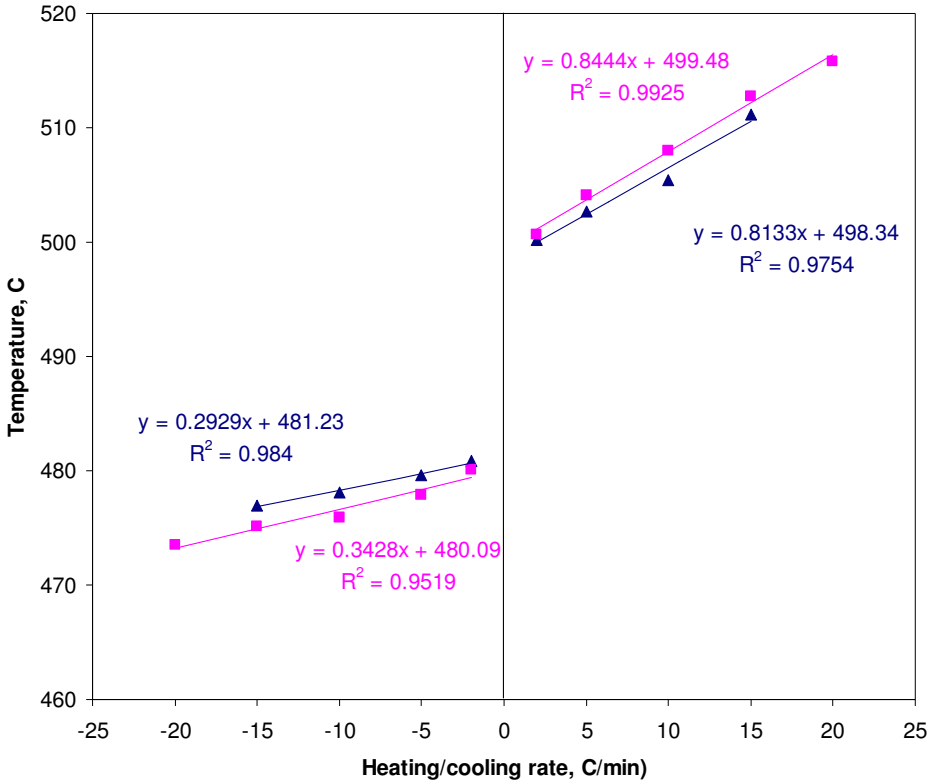


Netzsch STA 449C

Pellet Press with die set and torque wrench

Transition Temperature Varies with Heating/Cooling Rates

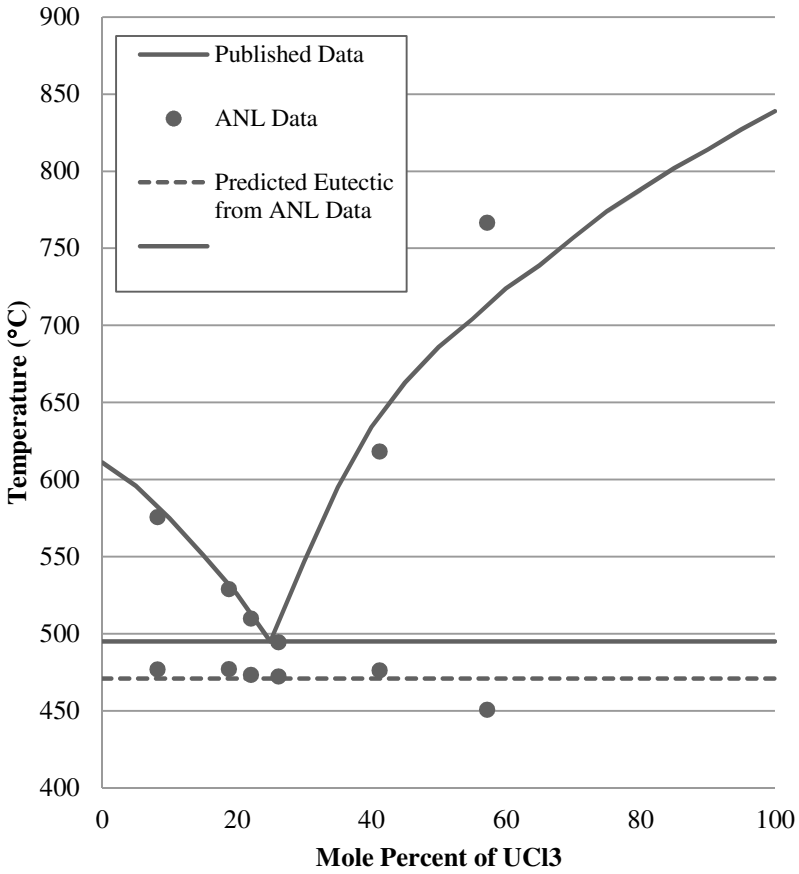
- Data indicates linear variation of transition temperature with heating and cooling rates
- Both heating and cooling produce reproducible transitions
- Difference between heating and cooling can be minimized by extrapolating to zero heating rate
- Solidus temperatures (not shown) are very consistent and do not vary with rate
  - Heating: 354.6°C +/- 0.35
  - Cooling: 349.7°C +/- 1.19



Liquidus transition temperatures as a function of heating and cooling rate for 46.6 mol % LiCl in KCl (duplicate experiments)

Results: LiCl-KCl and LiCl-UCl_3 Binary Systems

- LiCl-KCl results consistent with published values
  - Demonstrates that the calibration and techniques used for preparing and testing samples are consistent and reliable
- LiCl-UCl_3 data reveals eutectic temperature is 471 °C
  - Less than the published value of 495°C
- LiCl-UCl_3 eutectic composition is between 22.1 mol% and 29.4 mol% UCl_3
  - Fits with the published value of 25 mol% UCl_3, 75mol% LiCl



Interpolated zero-rate transitions overlaid on Barton, Wilkerson, and Grimes diagram (Ref 2).

Results: KCl-UCl_3 Binary System

There are significant differences between ANL data and published Suglobova and Chirkst diagram (Ref 3).

- Inconsistencies exist between the limited literature on the KCl-UCl_3 system and ANL data.
  - current work shows that quartz reacts with UCl_3, bringing published data into question

- Determine validity of UCl_3-KCl ternary phases by running anneal and quench experiments to identify ternary phases present in system

Possible Quartz-UCl_3 Reaction

- Possible reaction is:

$$2UCl_3\,(s) + SiO_2\,(s) = 2UOCl\,(s) + SiCl_4\,(g)$$

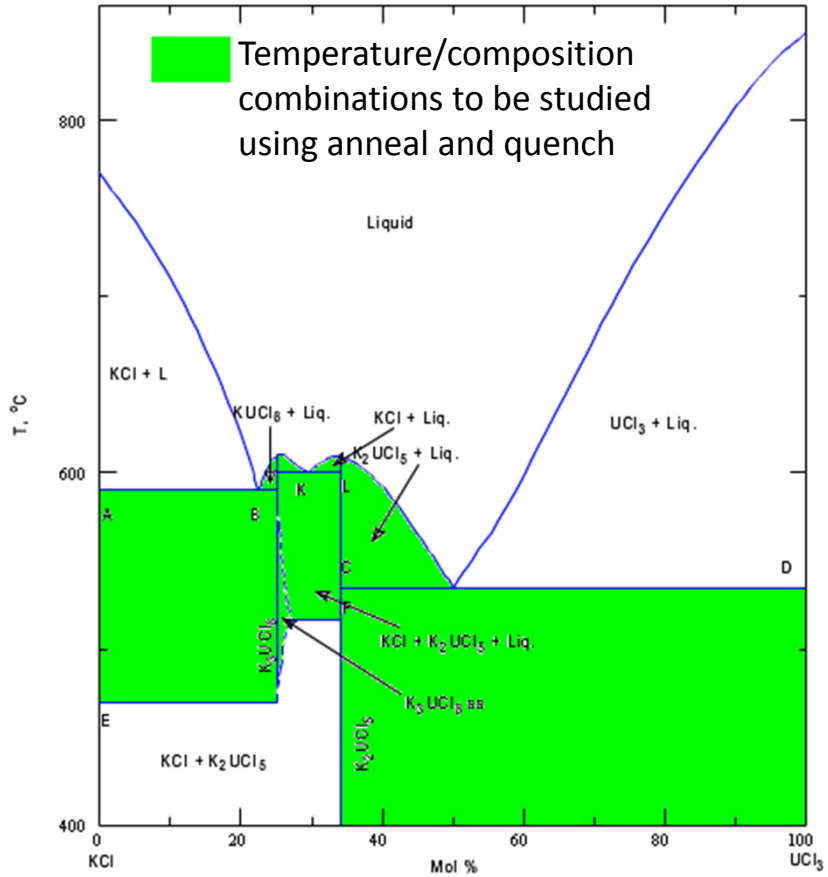
- Quartz was added to UCl_3-KCl and UCl_3-LiCl systems
  - Data exhibited shifts in transition temperature on repeated cycles
  - No such systematic shifts were observed on repeated cycling in the absence of quartz

- X-ray diffraction (XRD) was employed to verify the presence of UOCl, the reaction product of the SiO_2-UCl_3 reaction.
  - Thermal cycled sample loaded onto slide in inert atmosphere glovebox

- XRD Samples analyzed possessed unidentifiable peaks
  - Peak intensities were low, inconsistent in repeated runs, and did not exhibit exact matches in 2θ values for the largest peaks of any of the possible substances present
  - Most intense observable peaks for SiO_2, UOCl, and UCl_3 are at very close 2θ values
  - Larger sample sizes would improve the quality of the X-ray data

In Progress: Anneal and Quench of $KCl\text{-}UCl_3$ Compositions

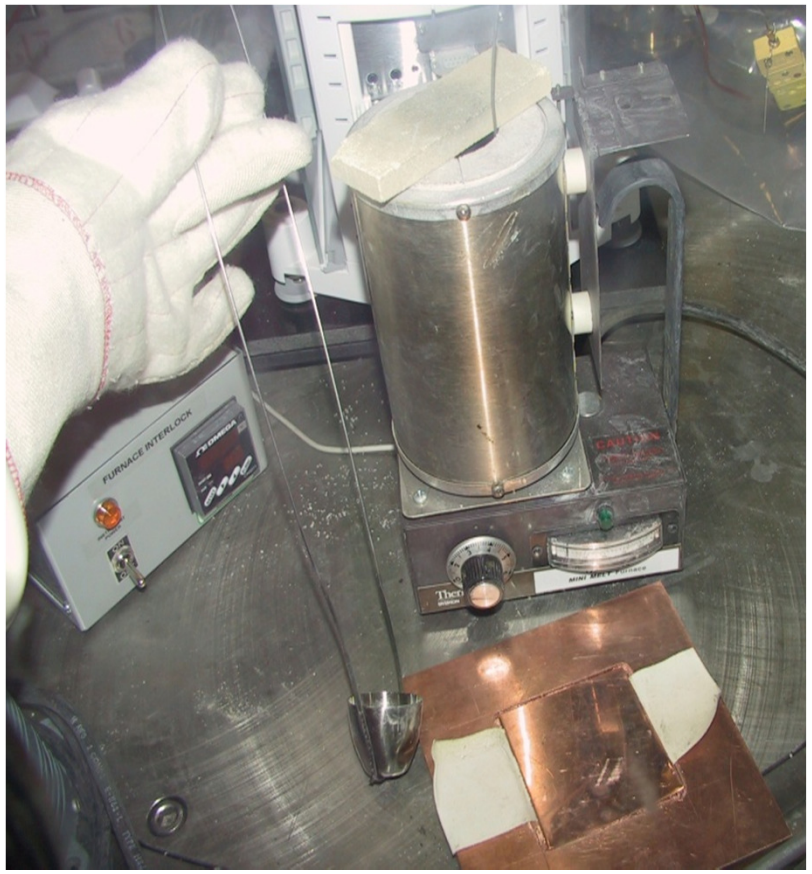
- Goal: Verify the existence of $KCl\text{-}UCl_3$ ternary phases in pseudo-binary phase diagram
- Published data on analagous compounds suggests existence of another $KCl\text{-}UCl_3$ ternary phase ($K_3U_5Cl_{18}$) not currently found in published pseudo-binary diagrams



Anneal and Quench of KCl-UCl_3 Compositions

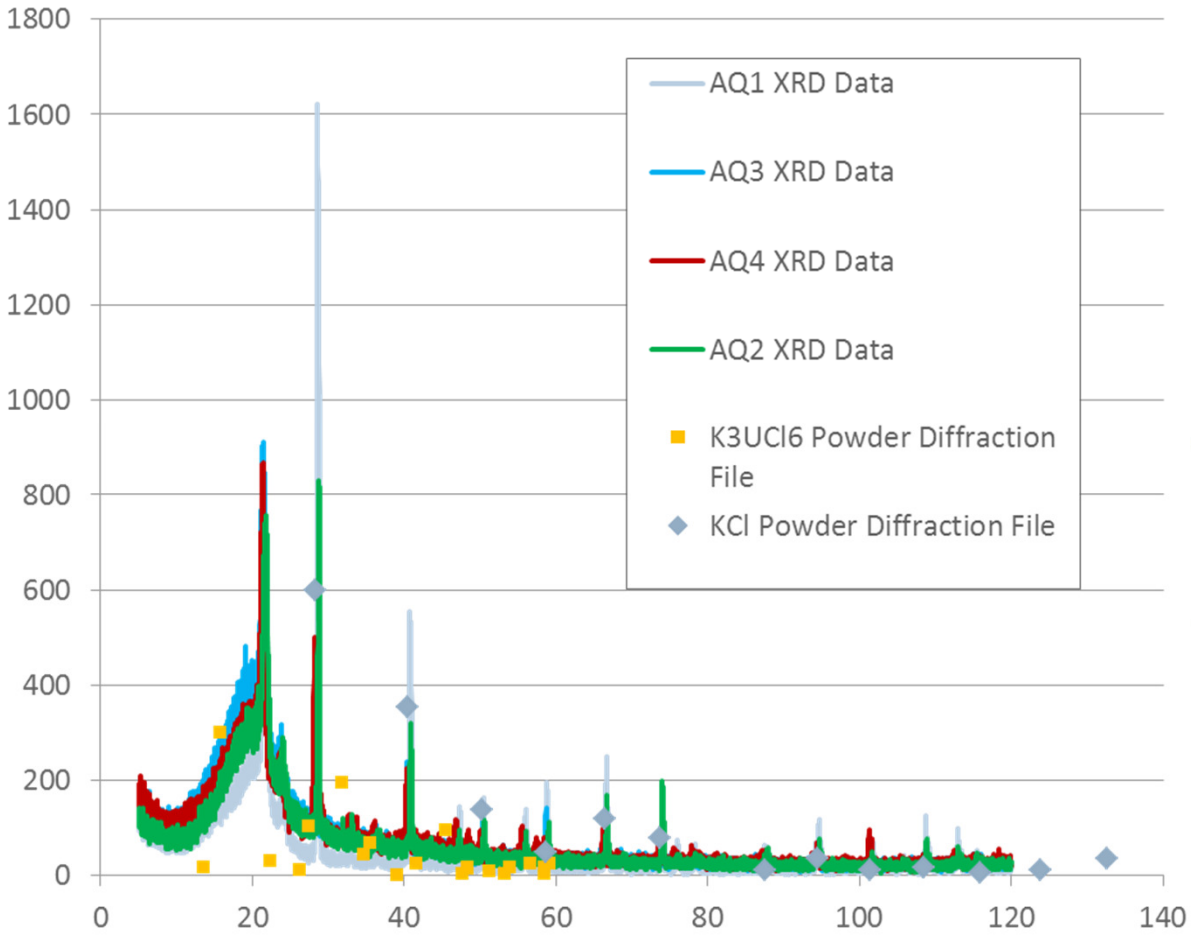
Approach

- Heat compositions to above liquid temperature, hold for >30 minutes
- Reduce to temperature corresponding to solid ternary phase of interest, hold for >2 hours
- Remove sample quickly and quench on copper freeze block
- Analyze sample using XRD and traditional analytical chemistry



Furnace, crucible, and freeze block used for anneal and quench experiments.

XRD Data for Anneal and Quench of KCl-UCl_3 Compositions



- All anneal and quench samples contain same 2Θ peak locations, but intensities differ (possibly due to slide quality)
- Peaks match very well with KCl peaks
- Secondary peaks do not match predicted complex, K_3UCl_6, or any other complexes with available powder diffraction files

Additional Comments on KCl-UCl_3 Anneal and Quench Experiments

- KCl-UCl_3 ternary phases or UCl_3 should also be identifiable, but are not evident in x-ray patterns
  - Large differences found between the predicted concentrations of unquenched samples and the analytically determined concentrations
  - Likely that samples were never taken to temperature above the liquidus for the projected composition

- Additional procedure modifications necessary to
  - Ensure homogeneity of sample during heating/quenching
  - Verify concentration of unquenched sample to ensure that liquidus temperature is reached prior to quenching

Summary

- LiCl-KCl results consistent with published values
  - demonstrates that the calibration and techniques used for preparing and testing samples are consistent and reliable

- LiCl-UCl_3 data show that eutectic temperature for system is 471 °C
  - Less than the published value of 495°C, probably due to methods used to determine transition temperature
  - Eutectic composition for LiCl-UCl_3 system is between 22.1 mol% and 29.4 mol% UCl_3, which is consistent with the published value of 25 mol% UCl_3, 75mol% LiCl

- Inconsistencies still exist between the limited literature on the KCl-UCl_3 system and ANL data
  - UCl_3-quartz reaction could be one reason for discrepancies

- Anneal and quench work in progress to determine identity of UCl_3-KCl ternary phases
  - Experimental procedures are being refined to ensure phase formation prior to quenching

Acknowledgements

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- This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under Contract DE-AC02-06CH11357.