




5-2016

Cd Transport in Eutectic LiCl-KCl and Contamination of Zr Metal And Thermal Dehydration of Bulk LiCl-KCl

Nicholas Azoy Earle

University of Tennessee - Knoxville, nearle1@vols.utk.edu

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I am submitting herewith a thesis written by Nicholas Azoy Earle entitled "Cd Transport in Eutectic LiCl-KCl and Contamination of Zr Metal And Thermal Dehydration of Bulk LiCl-KCl." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Nuclear Engineering.

Steven E. Skutnik, Major Professor

We have read this thesis and recommend its acceptance:

Howard L. Hall, G. Ivan Maldonado

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

**Cd Transport in Eutectic LiCl-KCl and Contamination of Zr Metal
And Thermal Dehydration of Bulk LiCl-KCl**

**A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville**

**Nicholas Azoy Earle
May 2016**

Dedicated to Paulina

ACKNOWLEDGEMENTS

The Center for Advanced Energy Studies (CAES) and Idaho National Lab (INL) in Idaho Falls, ID, for hosting the internship program that began this work.

Michael Simpson, Supathorn Phongikaroon, Michael Shaltry, and Robert Hoover for their guidance and mentoring.

Steven Skutnik of the University of Tennessee for directing me towards and facilitating my entry into this field of study.

John Auxier of the University of Tennessee for his extensive input and consultation.

Edward Wright of the University of Tennessee for his extensive assistance with the ultrafiltration procedures.

ABSTRACT

Researchers at Idaho National Labs have noted unexpectedly high Cd content in empty cladding hulls after processing in the Mark-IV ER. It has been theorized that Cd metal is transporting from the LCC pool through the eutectic LiCl-KCl salt bath to the anode baskets containing the empty hull where it is retained as a Zr-Cd intermetallic. This study sought to replicate the Cd contamination in a dry Ar glovebox using small-scale analogue of the Mark-IV ER salt-Cd metal system.

Anhydrous eutectic LiCl-KCl was an essential reagent in this research and experiments were conducted to investigate the feasibility of dehydrating nominally anhydrous salt using a method requiring less equipment and labor than the currently accepted practice using HCl gas. It was found that the new method may prove sufficient with further development.

Studies by K.M. Goff suggested that the Cd species soluble in LiCl-KCl were highly dependent on the presence of carbon and oxygen gas contaminants. Experiments were performed to verify Goff's findings and distinguish between Cd species using stirred cell ultra-filtration and ICP-MS. These investigations yielded results that were consistent with Goff's interpretation of the salt chemistry.

The hypothesized retention of Cd by Zr as an intermetallic was investigated by immersing Zr pellets in the glovebox analogue of the Mark-IV ER. The pellets were then cross-sectioned and analyzed using SEM-EDS. Cd was found on the pellet surfaces and in their interiors, but more extensive analysis was not possible. There were concerns that the sample preparation procedure may have resulted in Cd from the pellet surface be smeared onto the interiors of the cross-sections.

TABLE OF CONTENTS

INTRODUCTION	1
Background on the EBR-II.....	1
The Mark-IV ER.....	1
Cd Contamination of Metal Waste Stream	3
Objectives	3
CHAPTER I: Thermal Dehydration of LiCl-KCl under Dry Ar Gas	4
Abstract	5
Introduction	5
Atmospheric Contaminants in LiCl-KCl Salt.....	5
Prior Research on Dehydration of LiCl-KCl.....	6
Materials and Procedures	9
Ar Glovebox for Thermal Dehydration of LiCl-KCl	9
Modification and Programing of Furnace	10
Electric Motors in Dry Argon Atmospheres	10
Final Forced Ar Gas Flow LiCl-KCl Dehydration Procedures.....	11
TGA-MS Analysis of LiCl-KCl Samples	14
Results	14
Assay of Untreated LiCl-KCl with TGA-MS.....	14
Effect of duration of heating on dehydration of LiCl-KCl	16
Dehydration of LiCl-KCl in Lower Strata of Salt without Force Ar Gas Flow	19
Effect of Forced Ar gas flow on dehydration of LiCl-KCl	19
Most Complete Achievable Dehydration of LiCl-KCl with Existing Set-Up... ..	20
Problems with the use of sealed Al sample pans with the TGA-MS	22
CHAPTER II: Cd transport in LiCl-KCl	23
Abstract.....	24
Introduction	24
Metal Solubility in Molten Salts	24
Cd species and transport pathways in LiCl-KCl.....	24
Concerns over use Li metal in Goff's studies.....	25
Aqueous Separation of Cd Species	26
Materials and Procedures	27
Experimental Procedures for Study of Cd transport in LiCl-KCl.....	27
Results and Analysis	29
INL Work.....	29
UTK Work	30
CHAPTER III: Cd uptake by Zr in LiCl-KCl	33
Abstract	34
Introduction	34
Zr-Cd Intermetallics	34
Experimental Procedures for Study of Cd uptake by Zr	34

Results and Analysis of Cd Uptake by Zr studies	35
CONCLUSIONS.....	38
Conclusions regarding the thermal dehydration of LiCl-KCl	38
Conclusions regarding Cd transport in LiCl-KCl	38
Conclusions concerning Cd uptake by Zr	40
REFERENCES	41
VITA.....	44

LIST OF TABLES

Table 1. TGA of weight loss of surface strata salt dehydrated at 150-200 °C without forced Ar gas flow	17
Table 2. Zr Sample immersion times	34

LIST OF FIGURES

Figure 1. The Mark IV ER (Argonne National Laboratory)	2
Figure 2. Internals of Aquarium Pump	11
Figure 3. Furnace during Drying Cycle	13
Figure 4. Ramp-rate = 10 °C/min, 18.0 amu = H ₂ O, 36.0 & 38.0 = HCl?	15
Figure 5. Mass loss correlates with 18.0 amu MS ion current peak	15
Figure 6. TGA-MS ramp-rate = 10 °C/min, 18.0 amu = H ₂ O, 36.0 & 38.0 = N/A	16
Figure 7. Longer heating cycle durations yield diminishing returns	17
Figure 8. TGA-MS ramp-rate = 10 °C/min	18
Figure 9. Dehydration restricted to upper salt strata without forced Ar gas flow	19
Figure 10. Forced Ar Gas Flow did not yield improved dehydration	20
Figure 11. Water content of salt in surface strata reduced to ~0.2 wt%	21
Figure 12. Experimental setup within the crucible	28
Figure 13. Cd Concentration as a function of time and addition of Li metal	29
Figure 14. Cd content of LiCl-KCl salt before the addition of Li metal	30
Figure 15. Cd content of LiCl-KCl salt after addition of Li metal	31
Figure 16. Cd content of control sample of Li; note the sample also shows non-trivial Cd content	32
Figure 17. SEM micrograph of Sample 1 with EDS counts	35
Figure 18. Sample 2 – Line Scan 1	36
Figure 19. Sample 3 - Line Scan 1	37
Figure 20. Mean plateau Cd-Zr Ratio vs Sample Immersion Time	37

INTRODUCTION

BACKGROUND ON THE EBR-II

The Experimental Breeder Reactor II (EBR-II) was a sodium-cooled fast breeder reactor that operated from 1965 to 1994. One of its features was the use of metallic U-Zr fuel, which has the advantages of being easier to form into desired shapes through casting and superior thermal conductivity compared to oxide fuel. The EBR-II core consisted of a central region of HEU-Zr driver pins encased in a blanket region of LEU-Zr pins for the purpose of breeding Pu-239.

To enable secure, on-site separation of the Pu and refabrication of U-Pu-Zr metal fuel, pyroprocessing was selected as the reprocessing technology. In this process, electro-refiners (ERs) are used to electrochemically separate the components of used metallic fuel by dissolving and transporting them through a molten salt electrolyte¹.

While EBR-II and the mission to develop an Integral Fast Reactor (IFR) system were shut down in 1994, R&D of pyroprocessing technology has continued for the purpose of stabilizing its fuel for permanent disposal. In the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL), the Mark-IV Electrorefiner (ER) is used to process the used driver fuel.

THE MARK-IV ER

The Mark-IV ER is a cylindrical, airtight stainless steel vessel with access ports located in its top cover to allow the insertion of electrodes and instruments (Figure 1). The ER is filled with eutectic LiCl-KCl (44.2 wt% LiCl, 55.8 wt% KCl) molten salt electrolyte that floats above a liquid Cd cathode (LCC) pool. The headspace of the vessel is filled with dry argon (Ar) gas. Chopped sections of used EBR-II driver fuel containing U, Pu, fission products and minor actinides are loaded into baskets, which are then immersed in the salt.

An electrical potential is then applied between the anode baskets and solid cathode mandrels also immersed in the salt. The uranium, actinides, and fission products electrolyze into the salt and leave zirconium and other noble metals behind. The uranium is electrodeposited onto the solid cathodes as very pure metallic dendrites. The growth of these dendrites must be constrained by mechanical scrapers to prevent them from coming in contact with the vessel walls and shorting to ground. The LCC pool serves to dissolve these fallen scrapings and prevent HEU from piling up under the solid cathodes and creating a criticality hazard. Dissolved Pu and minor actinides are also absorbed from the salt bath by the LCC to keep them from co-depositing with U onto the solid cathodes. Active metal fission products accumulate in the salt and must eventually be removed and discarded as waste².

The cladding hulls remaining in the anode baskets contain undissolved actinides, noble metals, and zirconium. Adhering salt is distilled off and the hulls are then processed in a metal waste furnace to consolidate the metal into an ingot waste form.

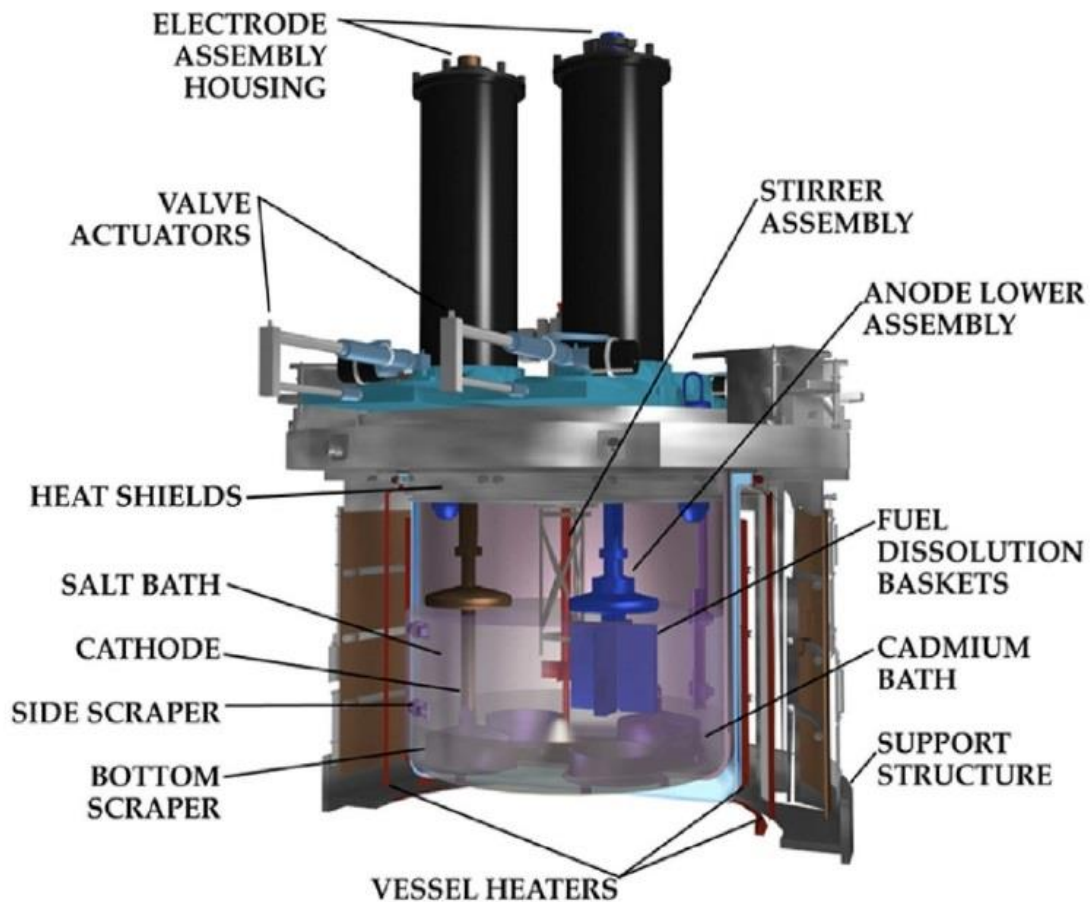


Figure 1. The Mark IV ER (Argonne National Laboratory)

CD CONTAMINATION OF METAL WASTE STREAM

While the LCC fulfills several important functions in the Mark-IV ER, Cd is a RCRA-listed toxic metal with a low melting point and high vapor pressure. Analysis cladding hulls from the anode baskets by INL researchers³ has found significant Cd contamination. Cadmium in the empty hulls is problematic because it once removed from the Mark –IV ER, it will contaminate subsequent stages of the metal waste stream.

Empty hulls are stripped of adhering salt in the salt distillation furnace, in which some or all of the Cd may vaporize and either be collected with the recovered salt or deposit inside the furnace and potentially foul it as was once an issue in the Mark-IV ER. If any Cd is retained by the hulls after being stripped of salt, it may then volatilize when the hulls are cast into ingots in the metal waste furnace, once again potentially fouling it. If these ingots manage to retain any Cd during casting, they would need to be classified as mixed-waste products warranting higher disposal costs. Any attempts to recover Zr from the ingots would also be complicate by Cd contamination. Lastly, in all scenarios the LCC pool would need to be replenished periodically to make up for this loss of Cd.

OBJECTIVES

The purpose of this study was to replicate and investigate the Cd contamination of anode basket material observed in the Mark-IV ER using a small scale analogue in a dry Argon filled glovebox.

The first chapter of this text will discuss the preparation and assay of anhydrous LiCl-KCl salt. This salt was an essential reagent for the latter experiments and its sensitivity to atmospheric contaminants require that it be stored and worked with only under dry and inert ($[H_2O] < 10\text{ppm}$, $[O_2] < 10\text{ppm}$) gas. Towards these ends, the equipment used will also be introduced and discussed.

The second chapter shall discuss prior work on the solubility and transport of Cd species in LiCl-KCl salt and the investigations made as part of this study. Because the anode basket in the Mark-IV ER is not in contact with the LCC pool, the observed Cd contamination must therefore be a two-stage process consisting of the transport of Cd through the LiCl-KCl salt followed by retention in the cladding hulls. This investigation therefore seeks to characterize the mechanism of Cd transport within the salt by investigating the solubility and chemical form of Cd within the LiCl-KCl salt.

Finally, the INL researchers who first observed Cd contamination of the cladding hulls theorized that Cd was being retained by Zr as an intermetallic. This hypothesis was tested in a small scale analogue of the Mark-IV ER. The experiment and its findings are discussed in the final chapter of this study.

CHAPTER I
Thermal Dehydration of LiCl-KCl under Dry Ar Gas

ABSTRACT

The Mark-IV ER uses eutectic LiCl-KCl molten salt as solvent for the dissolution of driver fuel from the EBR-II. This salt is very susceptible to atmospheric contamination due to LiCl being highly hygroscopic. This is problematic because hydrated LiCl-KCl will undergo hydrolytic decomposition when heated to fusion. This will contaminate the binary chloride salt with hydroxide products that compromise its utility in pyroprocessing applications.

The established method for preparing anhydrous LiCl-KCl has been to heat the salt to the point of fusion while saturating it with $\text{HCl}_{(g)}$ to inhibit hydrolysis. Studies by Parash and Masset have discovered that LiCl can be fully dehydrated at temperatures below the range over which hydrolytic decomposition occurs. This study investigated the potential for dehydrating bulk quantities LiCl-KCl without the use of $\text{HCl}_{(g)}$. Parash and Masset's findings were confirmed using TGA-MS and it was determined the dehydration of bulk salt was limited by the diffusion of water vapor out of the material.

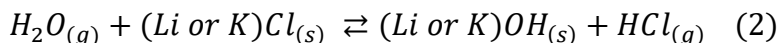
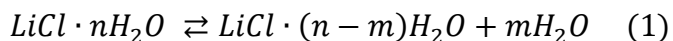
INTRODUCTION

Atmospheric Contaminants in LiCl-KCl Salt

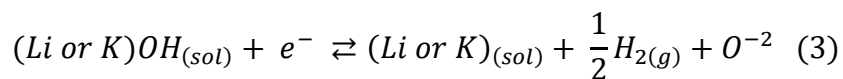
The LiCl-KCl salt used in these experiments is susceptible to several contaminants found in air that necessitate it being stored and worked with in an inert atmosphere glovebox. For the purposes of this experiment, this consisted of a dry (>10 ppm H_2O) argon atmosphere.

Both O_2 and N_2 will oxidize molten LiCl-KCl, releasing Cl_2 and contaminating the salt with oxides and nitrides. Fortunately this problem is restricted to elevated temperatures and the salt does not retain either contaminant at room temperatures, so once the ambient gas is free of N_2 and O_2 there is no further cause for concern.

A more problematic contaminant is H_2O , as LiCl is highly hygroscopic and retains water as hydrates at STP. These hydrates will decompose and release water vapor when the salt is heated (eq. 1), but heating in the presence of water can also result in the hydrolytic decomposition of LiCl and KCl (eq. 2). This process yields hydroxide products and HCl gas.



These hydroxide products fundamentally change the salt chemistry and are corrosive. The hydroxide ions are also particularly problematic in electrochemical applications because they can be converted into oxygen ions at an anode which can then react with the salt or the electrodes (eq. 3). The now neutral Li and K can additionally deposit onto the cathode in place of a targeted element. Prolonged exposure to HCl can also degrade vulnerable equipment.



For these reasons, LiCl-KCl must be dehydrated before it is useable for high-temperature applications. Anhydrous LiCl-KCl⁴ is commercially available from vendors, but at cost of more than \$6000/kg and more than four times as expensive as nominally anhydrous grades⁵. This motivates investigating the potential for dehydrating small batches of nominally anhydrous salt using equipment commonly available to researchers that use the salt.

Prior Research on Dehydration of LiCl-KCl

To dehydrate LiCl-KCl, the salt or its precursors (LiCl and KCl) must be heated under a dry inert gas atmosphere to decompose hydrates and the resultant H₂O_(g) must be expelled from the bulk material. The difficulty lies in preventing or avoiding simultaneous hydrolytic decomposition. Prior work by Gardner, Latinen, Parash, and Masset has yielded anhydrous LiCl-KCl as well as analytical techniques for measuring the purity (absence of hydroxides) and water content of treated salt. The following sections will provide a review of prior techniques investigated to dehydrate LiCl-KCl salts in preparation for the investigations carried out within the scope of this work.

Gardner's Studies of Vacuum Drying and Flushing LiCl-KCl with Inert Gas

Gardner et al⁶ were able to dehydrate KCl, LiCl, and NaCl salts used in their studies by heating ~20 g samples in sealed Pyrex vials under a 10⁻⁶ mm Hg vacuum pressure and then flushing with dry Ar or N₂. The vacuum drying was done in stages with progressively increasing temperature, starting at 25°C and then increasing in increments of 100°C up to the melting point of each salt. The salt samples were weighted in their vials prior to treatment and at the end of each stage. It was found that for LiCl and KCl, the temperature needed to be raised to 450°C and 300°C respectively for the samples to fully dehydrate as indicated by no further measurable mass loss. The error in weighing was estimated to be less than 1% for LiCl and less than 2% for KCl and NaCl.

To determine the potential for hydrolysis from any remaining water, Gardner heated 200 g samples of treated salt at 500 °C under high vacuum for 12 hours while collecting volatiles, HCl_(g), in a cold trap. The collected volatiles were dissolved in solutions of deionized water so that the HCl_(g) content could be estimated from the solution's pH. Based on this analysis, 0.00914 wt% of LiCl and 1.33x10⁻⁴ wt% KCl were estimated to have undergone hydrolysis.

Laitinen's Method of Heating to fusion under HCl/Cl₂ gas flow

Laitinen et al⁷ sought to inhibit hydrolysis by bubbling anhydrous HCl_(g) through a eutectic mixture of previously vacuum dried (at 300°C) LiCl and KCl as it was heated past the point of fusion (352°C) to a final temperature of 500 °C in a Pyrex glass cell.

The spontaneity of chemical reactions can be described by the Gibb's free energy of reaction ΔG_r , which is a function of the changes in enthalpy ΔE_r and entropy ΔS_r . Reactions without an activation energy will occur spontaneously if the sign of ΔG_r is negative. The value of ΔG_r (eq.4) can be determined from its value at STP ΔG_r^\ominus , the temperature T, and the reaction quotient Q (eq.5).

$$\Delta G_r = \Delta G_r^\ominus + RT \ln Q \quad (4)$$
$$Q = \frac{a_{HCl}}{a_{H_2O}} = \frac{f_{HCl}}{f_{H_2O}} \sim \frac{n_{HCl}}{n_{H_2O}} \quad (5)$$

Increasing the proportion of HCl_(g) to H₂O_(g) molecules drives $Q > 1$ and increases the ΔG_r of the hydrolysis reaction, inhibiting it. The HCl_(g) can then be flushed from the salt under moderate vacuum (0.1-0.2 mmHg).

Laitinen analyzed molten salt samples for water and HCl content using polarography, a method in which the current between inserted electrodes is measured across a range of voltages. Electroreactive impurities like water or HCl permit a current to flow at voltages below the break-down voltage of pure LiCl-KCl.

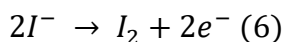
Laitinen reported that salt that had been untreated, only vacuum dried, or was not flushed with Ar to remove HCl would begin conducting at lower voltages than fully-treated salt. Glassware was also noted to suffer more extensive etching from molten salts that were not fully treated, indicating hydroxide contamination. A number of metal chlorides known to be insoluble at lower concentrations in hydroxide contaminated LiCl-KCl did not precipitate in the treated salt. Laitinen found that deviations from his detailed procedures failed to yield comparably uncontaminated salt. It is worth noting that this work was done using glassware outside of a dry Ar glovebox, and this may have made his task more difficult.

Parash's Thermochemical Analysis of Dehydration and Hydrolysis reactions in LiCl-KCl

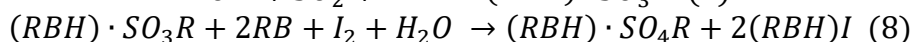
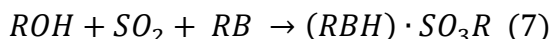
Laitinen's work yields a robust set of procedures for synthesizing anhydrous eutectic LiCl-KCl salt. However, it does not delve deeply into the quantitative thermochemical properties of the H₂O/Li-KCl system. The procedures also demand an investment of labor and equipment that may prove inconvenient to some researchers.

Work by Parash⁸ et. al. doubles back to basic science of the problem by making continuous measurements of partially hydrated LiCl-KCl samples (with MgO added as a binder) as they are heated to the mixture's melting point.

Parash used Karl Fisher coulometric titration to determine that the initial water content of her salt was ~2.0-3.0 wt%. This method uses a two-compartment titration cell separated by an ion-permeable membrane and containing an alcohol (ROH) solution of I^- , a base (B), and SO_2 . A salt sample is dissolved in the anodic compartment containing a pair of Pt measuring electrodes maintaining a constant current between them. I_2 is then coulometrically “titrated” into the cathodic compartment by a generator electrode with a small steady current (eq. 6).



The water in the sample will react with the I_2 (eq. 7 & 8) until it is entirely consumed (the equivalence point). This is detected via a sudden voltage drop across the measuring electrodes due to the presence of excess I_2 . The water content of the sample can then be determined from the charge introduced via the generator electrode.



A Karl Fisher coulometric titrator is a much more limited instrument than a TGA/DTA machine and cannot be used to analyze salt continuously as it is heated. However, it is much smaller and could be used in a glovebox without taking up excessive space and moved in and out via a modestly-sized transfer chamber.

Having established the initial water content of the salt, Parash then conducted TGA/DTA and electrical conductivity/polargraphic analysis on salt/binder samples as they were heated up to 500 °C in a dry Argon atmosphere.

The combined analytical methods revealed that dehydration occurred at two broad endothermic peaks at ~80°C and ~120°C. Hydrolysis, which could be distinguished from dehydration by DTA as exothermic, was found to only occur at temperatures over 200°C and peaking at ~250°C. Furthermore, the mass loss of dehydrated samples was found to be equal to the initial water content. These findings suggest that complete dehydration can be achieved at temperatures below those at which hydrolysis becomes spontaneous.

Masset’s Research on the Thermal Dehydration of $LiCl \cdot H_2O$ under Inert Gas

In his studies, Masset⁹ directly investigated the thermodynamics of the dehydration of monohydrate $LiCl$ (~12.5 wt% H_2O) using TGA/DTA. .

Masset heated 100mg samples of $LiCl \cdot H_2O$ at 1-10°C/min up to 620°C under dry (< 1 ppm H_2O) helium gas flow of 1.25cm³/hr. Under these conditions, he found that the $LiCl \cdot H_2O$ dehydrated into $LiCl$ in a two-step process with transitions at 99-110 °C and 160-186 °C. Between 190 and 500 °C no mass loss

was observed and a linear mass loss with temperature from 500 to 610 °C corresponding to the expected vaporization of LiCl as it neared its melting point.

Based on the pause in mass loss and good agreement of the measured melting point with that of pure LiCl (610°C), Masset conclude that dehydration had been achieved at 190 °C with no hydrolysis as hydroxide contamination would have altered the melting point of the samples. Furthermore, Masset found the activation energies of the two dehydration stages to be 240 and 137 kJ/mol.

Proposed Thermal Dehydration of gram quantities of LiCl-KCl under dry Ar_(g)

Parash and Masset's studies both found that in dry Ar_(g), LiCl·H₂O fully dehydrates at temperatures below those at which hydrolysis is observed to occur. It is hypothesized that the bubbling of HCl_(g) used in Laitinen's method was necessary due to the procedure being conducted outside of a dry Ar_(g) glovebox, albeit in sealed glassware, and exposed to gasses with a higher moisture content. Any additional moisture will increase the Gibbs free energy and temperature required for dehydration to occur. Given that dehydration is complete by 200°C and hydrolysis occurs at no more than 250°C, additional moisture could cause the minimum temperatures of the two reactions to overlap and necessitate the bubbling of HCl_(g).

To prepare and characterize the salt to be used in the Cd transport studies, experiments were preformed to investigate the feasibility of scaling up the methods used by Parash and Masset to yield gram quantities of anhydrous LiCl-KCl suitable for research needs. These experiments would seek to estimate the H₂O content of untreated salt and characterize the effectiveness of variations in the dehydration procedures.

MATERIALS AND PROCEDURES

Ar Glovebox for Thermal Dehydration of LiCl-KCl

The workspace was Labconco Protector Series combination glovebox using industrial-grade (99% purity) Ar gas. The H₂O and O₂ concentrations were maintained under 10.0 ppm by a gas purification system and monitored by a hydrometer and oxygen sensor. This glovebox was equipped with a single large transfer chamber, which while convenient for moving equipment also admitted outside gases during transfers. Proper transfer procedures could limit this ingress of gases and the purifier was normally able to lower the O₂ and H₂O levels below 10.0 ppm in less than an hour after transfer. Consultation with the manufacturer revealed that the glovebox could be damaged by internal temperatures in excess of 140°F. An air thermometer was installed to monitor this temperature and it was discovered to not rise above 100°F. It was also discovered that the furnace drew enough current to trip a 10A breaker, this was remedied (after consulting with the vendor) by replacing it with a 15A breaker.

Modification and Programing of Furnace

The salt used would be heated in a modified KerrLab Auto-Electro Melt furnace. This furnace incorporated a fail-safe switch connected to the lid such that power to the heating element was cut when it was lifted. This prohibited the operating the furnace with the lid open to allow the insertion of instruments and escape of water vapor; to overcome this, the fail-safe was reversibly disabled.

The default programming of the furnace's microcontroller was inadequate for its intended use and only capable of activating the heating element at full power until it reached a set-point in °F and then cutting all power. This resulted in unacceptable overshoots of the target temperature. The microcontroller was reprogrammed to use °C and to throttle power to the heating element to try a meet a preset ramp rate. When beginning work with a new configuration or in a new temperature range is advised to use initial set-point below the target temperature and then entering a 2nd set-point at the target temperature once the overshoot had peaked. By this method, overshoot can minimized to a few degrees.

Electric Motors in Dry Argon Atmospheres

Prior work used an inert gas flow (Ar or He) to remove dissociated water vapor from the bulk material. It hope that this could be accomplished using a 12" length of 3/16" ID alumina tube with vents cut on one end and connected by polyethylene tubing at the other to an gas compressor/blow/pump that could draw from the gas in the glovebox. The alumina tube could be inserted into the crucible to deliver Ar gas flow to the bottom from where it could flow upwards through a load of salt.

In sourcing an appropriate air gas pump, it was discovered that many commonly used electric motors will rapidly fail in dry Ar gas. ASTM C1615 standard guidelines¹⁰ specify that electric motors intended to function in this sort of environment must be designed/modified to compensate for the effects that low moisture has on lubricants, the lower thermal conductivity of Ar compared to air, and the lower dielectric coefficient of Ar (which can lead to arcing that would not happen in air). In this application, the only first two of these considerations are most relevant as the voltages required (120V) are low enough that arcing would be unlikely. The ideal motor would be brushless or use high-altitude brushes and have sealed-for-life lubricated parts. Certain motors may also need to be de-rated to have a useful service life.

As a stopgap and proof-of-concept, an aquarium air pump was used and discovered to tolerate the Ar atmosphere extremely well. The pump in question was able to deliver ~0.02 cfm of gas at ~2.9 psi. When examined internally (Figure 2) it was found to consist of a lever arm attach to a diagram at one end and with a permanent magnet at the other. An electromagnet was located a short

distance from the end of the lever arm with the permanent magnet such that it would actuate the lever as an alternating current was passed through it. It is believed that the simplicity of this design made it immune to the problems can plague more complex motors.



Figure 2. Internals of Aquarium Pump

Final Forced Ar Gas Flow LiCl-KCl Dehydration Procedures

An alumina thermocouple sheath and the alumina tube attached to the air pump were inserted into a 100ml alumina crucible. A ~50 gram quantity of -10 mesh LiCl-KCl sourced from Alfa Aesar was loaded into the crucible.

The empty furnace was turned on with the set-point at 0°C and the ramp-rate was then set to 200°C/hr. The furnace was generally not able to precisely meet this ramp-rate over such a short temperature range, but 200°C/hr yielded the most acceptable compromise between speed and minimal overshoot. The furnace was then given a set-point of equal to the target temperature plus a 50°C offset and then turned off.

The loaded alumina crucible was then placed in a larger graphite crucible already in the furnace. A k-type thermocouple connected to a digital multimeter

(DMM) was inserted into the sheath to measure the actual temperature of the salt. The top of the alumina crucible was then covered with several layers of folded quartz wool for insulation (Figure 3). The furnace and air pump were then turned on.

Once the thermocouple indicated that the temperature of the salt had reached the targeted temperatures $\pm 10^{\circ}\text{C}$, the start time for the drying cycle was noted. The salt was heated in the furnace for durations ranging from 4 to 20 hours, during which the crucible could be removed to take salt samples from the surface. After the heating cycle was completed, the furnace was turned off and the salt could be removed after being allowed to cool. Salt samples could then be taken from the layer at the bottom of the crucible, $\sim 3.0\text{cm}$ from the surface. To determine the effectiveness of the air pump, this procedure was repeated without it.

It was noted that the glovebox hydrometer reading would rise from around 2.0 ppm to as high as 8.0 ppm during drying cycles. While not a precise indicator of dehydration, it was clear qualitative evidence that it was occurring.

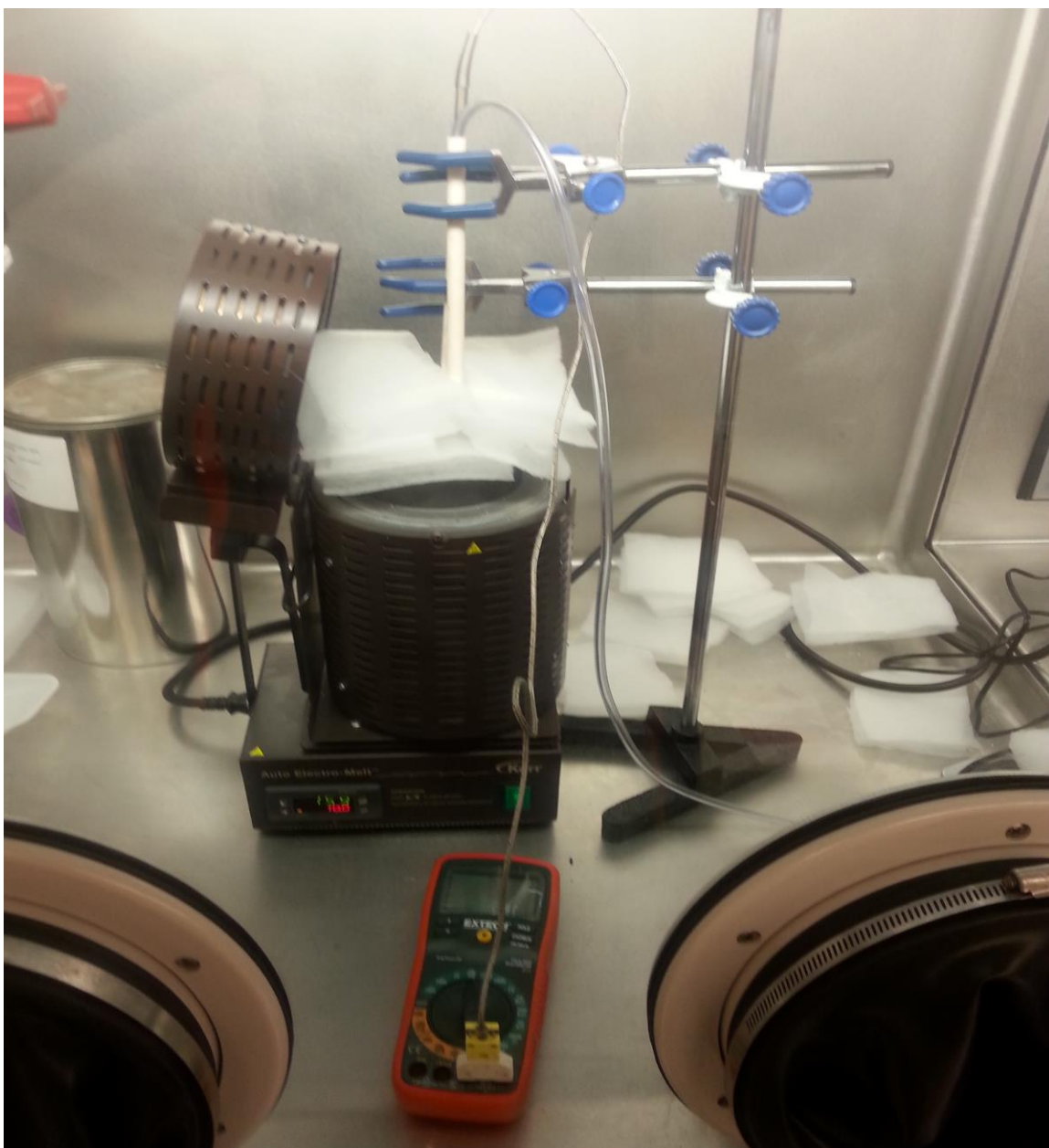


Figure 3. Furnace during Drying Cycle

TGA-MS Analysis of LiCl-KCl Samples

Milligram portions of the salt samples could then be loaded into hermetically sealed aluminum (Al) pans while still inside the glovebox. These sealed pans were then loaded into a TA Discovery Series combination TGA-Quadrupole mass spectrometer (TGA-MS) with a 40 eV electron ion source. The loading tray would press the lid of a pan against a force sensitive punch, and within 20 seconds load it into its furnace chamber under a 25.0ml/min flow of high-purity (99.9%) Ar gas. The TGA-MS would then heat the sample at a ramp-rate of 10 °C/min to a maximum temperature of 200°C. During the heating cycle, effluent gas from the sample would be collected by the quadrupole-MS. The mass spectrometer would then record the ion currents for preselected molecular weights over the course of the TGA cycle.

Both the dehydration and hydrolysis reactions would present themselves as an abrupt decrease in mass in the TGA data as either H₂O_(g) or HCl_(g) evolved from the sample during the heating cycle. The MS could distinguish these gases by their molecular weights. The evolution of water vapor, and a dehydration reaction, would be indicated by an 18.0 amu ion current channel peak at the same time of the mass loss. Peaks in the 36.0 and 38.0 amu ion current channels at the time of mass loss would indicate that the exhaust gas was composed of HCl_(g) and that hydrolysis had occurred.

This method needed to be applied indirectly as any HCl_(g) generated by the salt during a drying cycle would not be retained and escape well before any samples were loaded into the sealed Al pans. Instead TGA-MS would be used to analyze samples of untreated salt as they were heated up to 200°C, the maximum operating temperature of a drying cycle in the glovebox furnace. This would provide confirmation of Parash's and Masset's findings and give assurance that hydrolysis would not occur during the drying cycles.

RESULTS

Assay of Untreated LiCl-KCl with TGA-MS

The mean mass lost by five samples of untreated salt subject to TGA up to 200°C was 1.88 ± 0.523 % (RSD). While the error for this estimate of the water content of untreated salt was high, the mean was in good agreement with Parash's reported water content of ~2.0 wt%.

The atomic weights of interest in the MS data from untreated salt were 18.0 amu (corresponding to H₂O) and 36.0 and 38.0 amu (corresponding to HCl with two stable isotopes of Cl).

The MS data of untreated salt (Figure 4) was consistent across samples, with clear 18.0 amu/H₂O peaks that correlated well with the mass loss seen in the TGA data (Figure 5). There was also a 36.0 amu ion current that was initially feared to be indicative of HCl from hydrolysis.

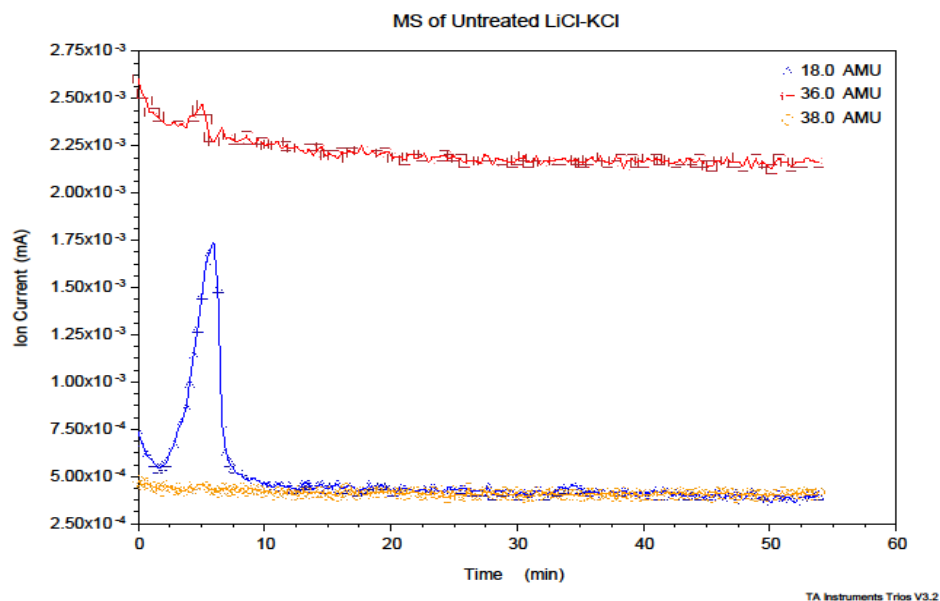


Figure 4. Ramp-rate = 10 °C/min, 18.0 amu = H₂O, 36.0 & 38.0 = HCl?

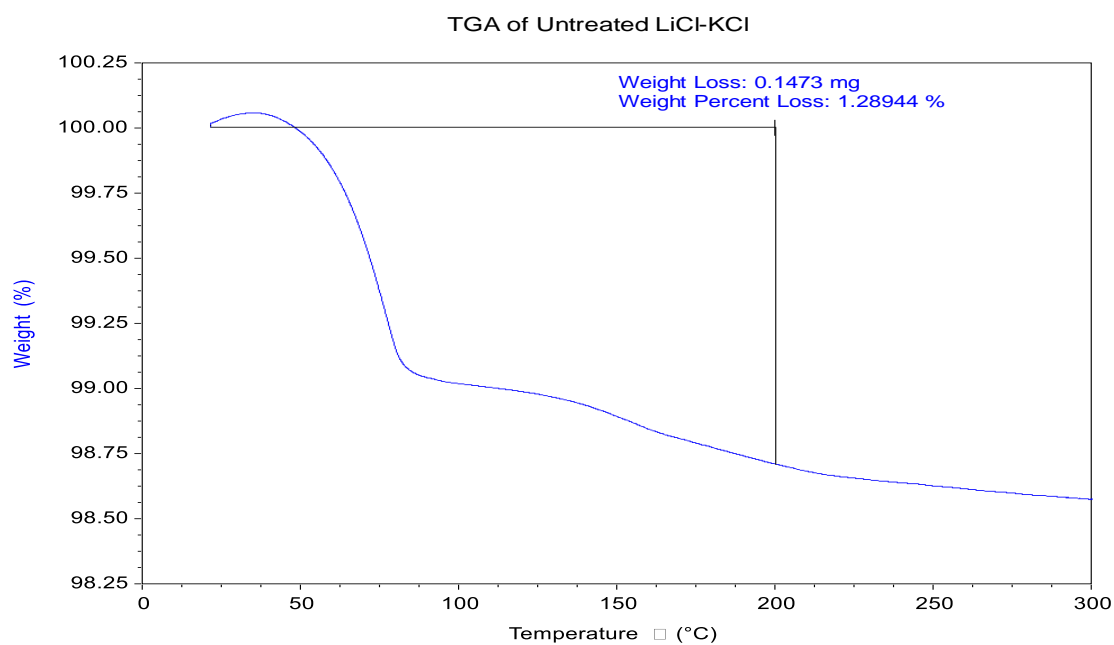


Figure 5. Mass loss correlates with 18.0 amu MS ion current peak

However, this ion current remained steady as the temperature rose during the TGA cycle. Had the ion current been due to HCl being emitted from hydrolysis, it should have had a peak around 250°C as had been seen with other studies. An alternative explanation would be that the ion current was due bimolecular H₂O ions, which would explain the small hump in the 36.0 amu ion current that paralleled the 18.0 amu peak. To test this theory, an empty platinum pan was put through a TGA-MS cycle and it was found that the 36.0 amu current persisted in the absence of salt (Figure 6). While its precise cause remains uncertain, it would be safe to conclude that it was not HCl being generated by hydrolysis in the salt sample.

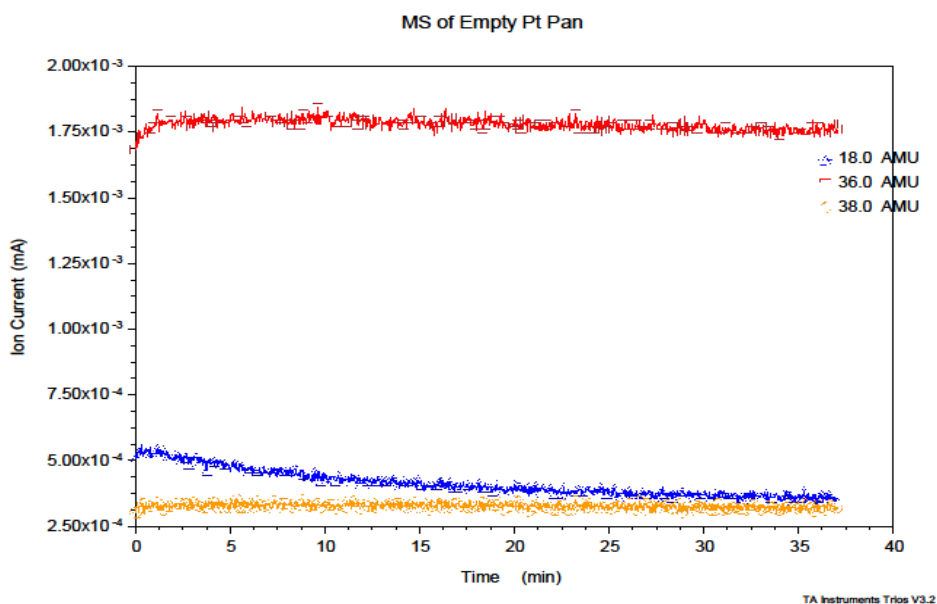


Figure 6. TGA-MS ramp-rate = 10 °C/min, 18.0 amu = H₂O, 36.0 & 38.0 = N/A

Effect of duration of heating on dehydration of LiCl-KCl

It was difficult to characterize the minimum amount of time required to achieve maximal dehydration in the surface salt layers with this experimental set-up. Beyond four hours, increasing the duration of heating cycles yielded at best diminishing returns with any additional reduction in water content being within the margin of error for the TGA instrument (Figure 7 and Table 1).

The MS data (Fig. 8) for treated salt showed that the 18.0 amu/H₂O ion current peak for treated salt was consistently smaller than for untreated salt, with the decrease in peak height being roughly proportional to the decrease in weight loss.

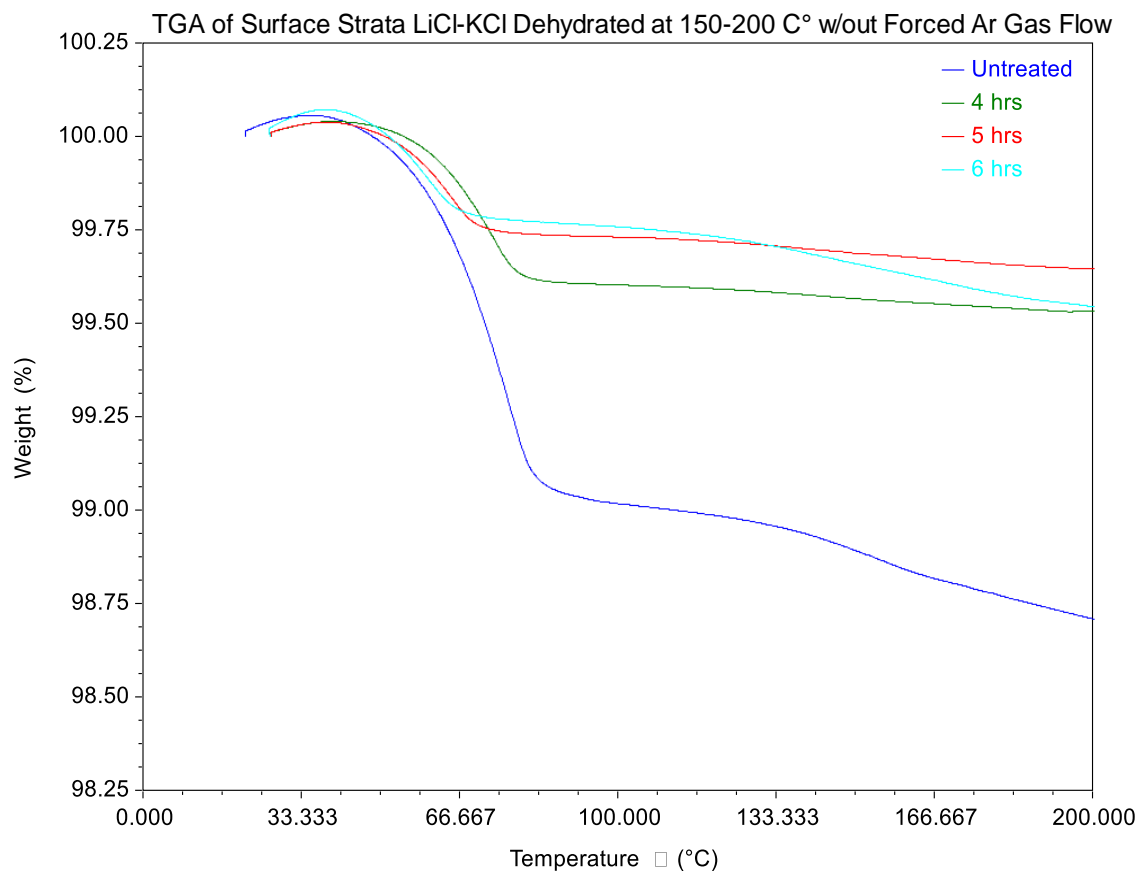


Figure 7. Longer heating cycle durations yield diminishing returns

Table 1. TGA of weight loss of surface strata salt dehydrated at 150-200 °C without forced Ar gas flow

Drying Duration (mins)	% weight loss at 200 °C (error = 0.1 wt%)
0	1.3
252	0.5
310	0.4
376	0.5

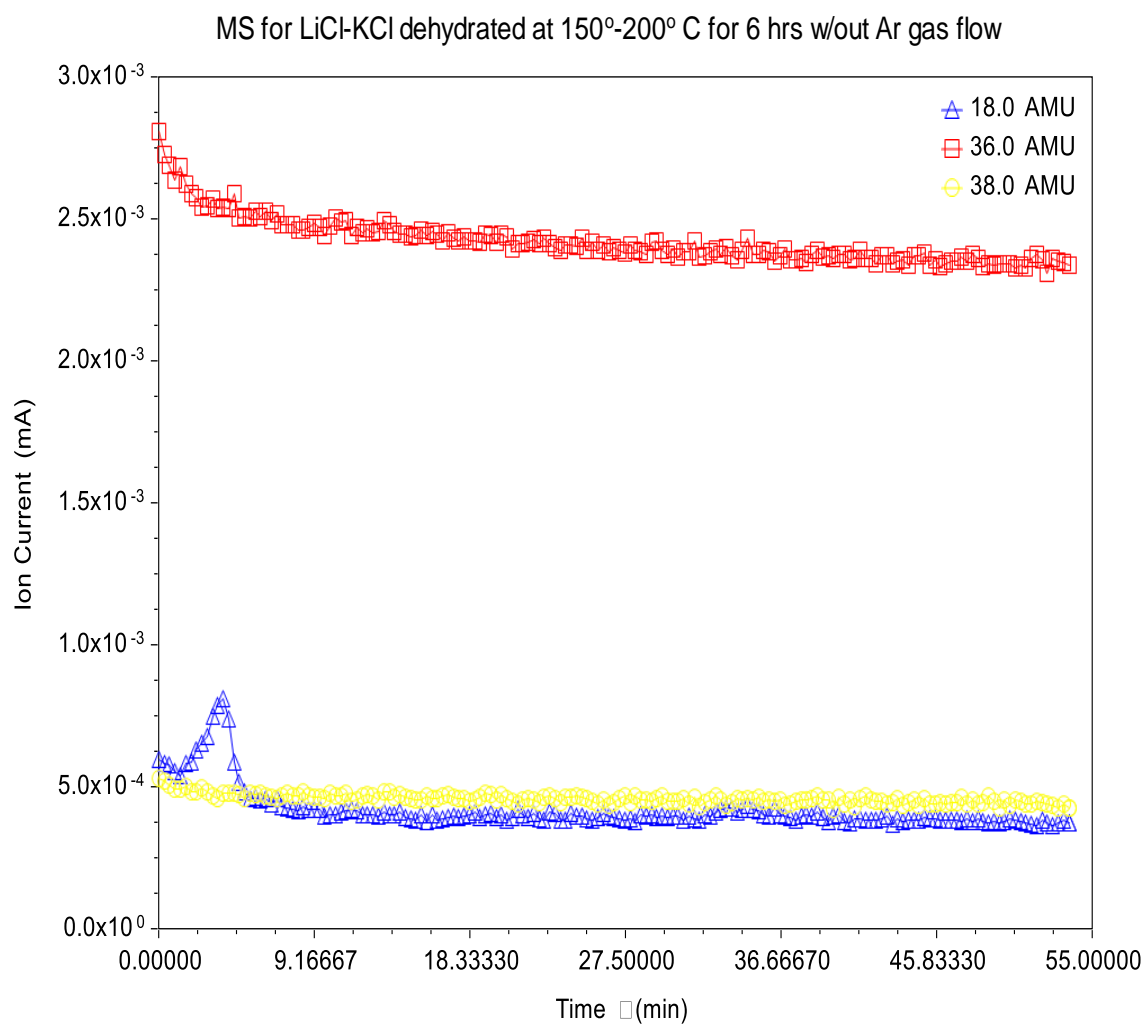


Figure 8. TGA-MS ramp-rate = 10 °C/min

Dehydration of LiCl-KCl in Lower Strata of Salt

While partial dehydration could be achieved for the surface strata of the salt, salt at the bottom the crucible was not being dehydrated appreciably (Fig. 9). This was not unexpected as the water vapor evolving from hydrates would need to diffuse through the ~3.0 cm of salt above it in order escape bulk material. It would appear that this rate of diffusion is the limiting step in the dehydration of bulk quantities of salt. The applied temperatures ($\leq 200^{\circ}\text{C}$) may have been sufficient to precipitate the decomposition of LiCl hydrates, but in this experimental setup they were inadequate for bulk dehydration.

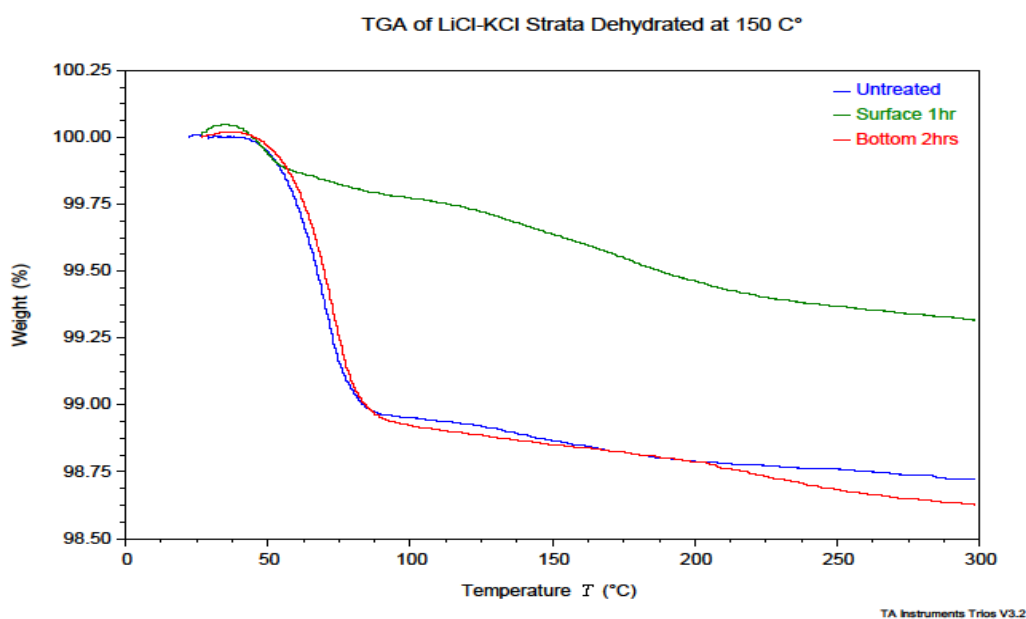


Figure 9. Dehydration restricted to upper salt strata without forced Ar gas flow

Effect of Forced Ar gas flow on dehydration of LiCl-KCl

The forced flow of Ar gas delivered via the alumina tube was intended to facilitate the dehydration of lower strata by improving the transport of water vapor. The data on the effectiveness of Ar gas flow from the aquarium pump indicated that it was not measurably improving the dehydration of the lower salt strata. Some sample salt samples that had been treated with the pump running showed lower mass loss than other samples that were treated without, but there

were also cases in which the opposite was true (Fig. 10) or there was no discernable pattern.

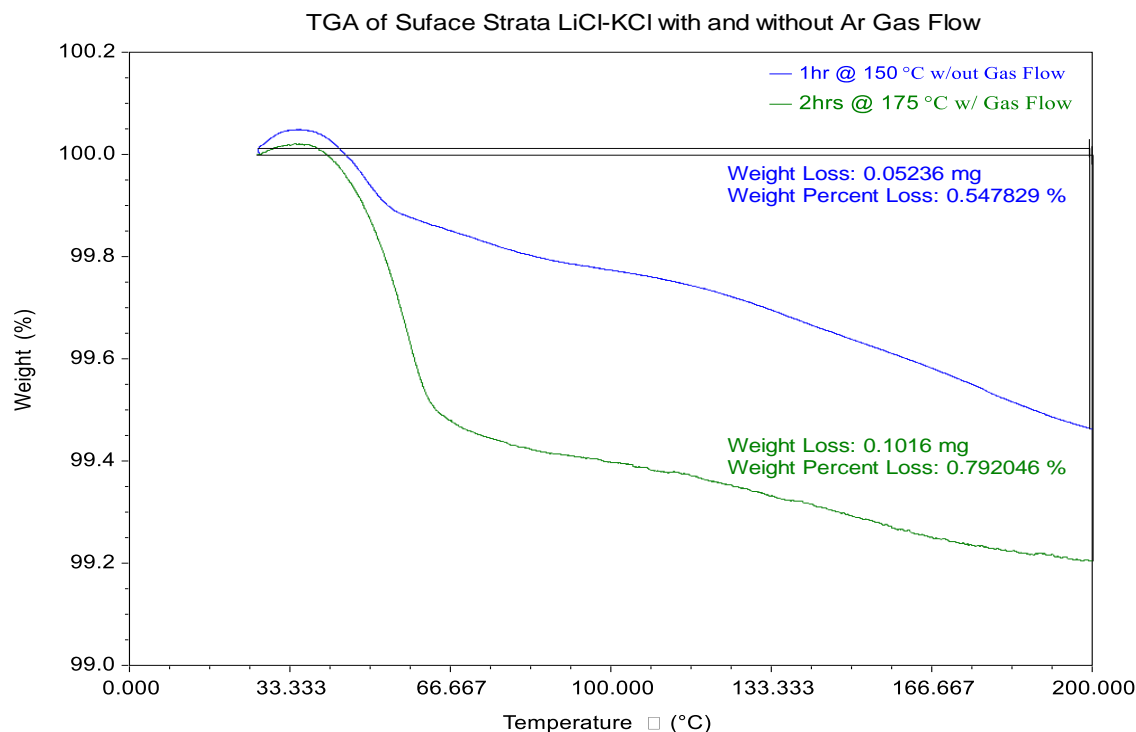


Figure 10. Forced Ar Gas Flow did not yield improved dehydration

The aquarium air pump used to supply the Ar gas flow could only produce limited pressure and flow-rate and was intended as a stand-in while refining the procedures. Unfortunately, the more powerful compressor that was to replace it quickly failed for the reasons discussed earlier. It is thought that the working pump was simply not powerful enough to deliver the necessary aeration of the bulk salt.

Most Complete Achievable Dehydration of LiCl-KCl with Existing Set-Up

The most complete dehydration was for a sample of surface strata salt that had been heated for 977 minutes at 200°C (Fig. 11) with the air pump running. It lost only 0.21364% of its mass in a TGA cycle running up to 200°C. As was the case with other drying cycles the bottom salt strata were unaffected, even after a lengthy drying cycle at 200° C.

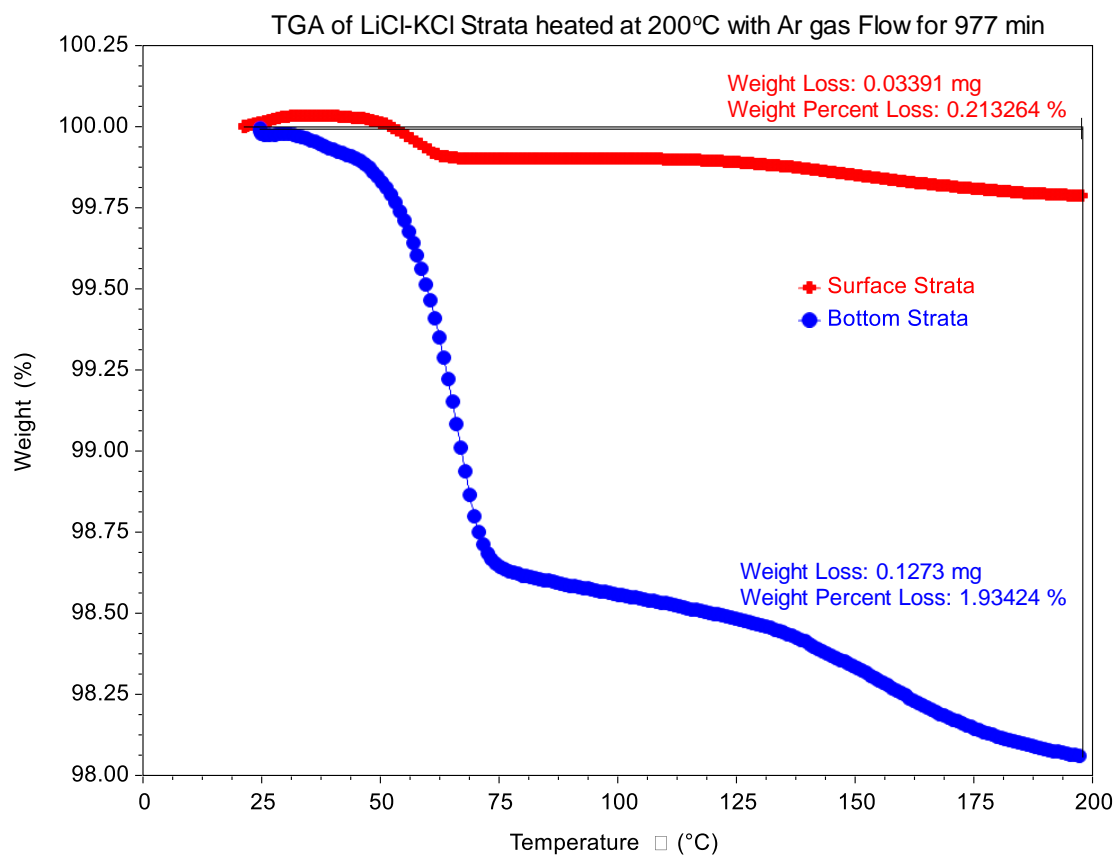


Figure 11. Water content of salt in surface strata reduced to ~0.2 wt%

Problems with the use of sealed Al sample pans with the TGA-MS

Initial TGA-MS runs proceeded rather smoothly despite some incidences of human error associated with loading the pans. But in latter runs, the pressure sensor for the punch which opened the pans often failed to register that the pan had been opened. It is unclear whether this was due to variations in the mechanical properties of individual pans or if there was something amiss with the sensor or the actuator that pressed the pans up against the punch. This malfunction would cause the preprogrammed series of TGA-MS cycles to terminate and greatly hindered work.

It was also noticed that depth the punch penetrated into the pans could vary greatly. Some pans were opened very gently and with only a hairline cut along the rim of the pan cover. Other pans had their covers forcefully pushed inward with an audible noise. It is feared that these more forceful punches could introduce water-laden air into the pans and have disturbed the layer of Ar resting above the salt samples.

In assessing the TGA data with these issues in mind, the measured mass losses should be viewed as an upper limit of the true water contents as air contamination during the 20+ seconds between the pans being punched and loaded into the TGA furnace chamber could only result in positive systematic error. Prior studies using TGA situated the instrument inside a dry Ar glovebox and did not have this concern. This practice is not ideal though as it confines the machine to the glovebox and takes up enough space to preclude the use of the glovebox for other purposes.

CHAPTER II

Cd transport in LiCl-KCl

ABSTRACT

To reach the contents of the anode basket in the Mark-IV ER, Cd from the LCC must transport through the LiCl-KCl salt bath. Prior work by K.M. Goff found that Cd is slightly soluble in molten LiCl-KCl and hypothesized to be present in two species, Cd metal vapor and CdCl₂. The formation of the later is not thermodynamically favorable in a simple salt-metal system, but may be so in one with C and O₂ contaminants. This study sought to replicate Goff's findings and independently measure the two proposed Cd species using stirred-cell ultrafiltration of aqueous solutions to achieve separation and analysis with ICP-MS. The results were consistent with a dominant CdCl₂ solute species in a system with C and O₂ contaminants.

INTRODUCTION

Metal Solubility in Molten Salts

Research on the chemistry of metals in molten salt solutions is most extensive for metals in solutions of their halides (i.e. Cd-CdCl₂ or Hg-HgI₂). M.A. Bradig¹¹ observed that metals in molten salts solutions interacted with their solvent to varying extents. Alkali, alkaline earth, and rare metals reacted the most extensively, sharing their valence electrons within the solution to impart to it a metallic character. Less reactive transitional and post transitional metals are thought to form sub-halides with a lower than normal oxidation state. Coulombic forces between the ions that make up molten salts impose a short-range lattice structure. This lattice may be deformed to complex sub-halides, substitute common ions into it, or accommodate single metal atom in preexisting holes.

Cadmium belongs to the 2nd group, but it is hypothesized that in LiCl-KCl solution Cd would be inhibited from forming sub-halides by the less electronegative Li and K ions (0.98 vs. 0.82 on the Pauling scale compared to 1.69 for Cd).

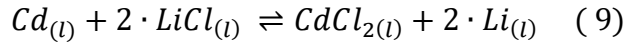
A study by Cubicciotti¹² supported this idea, finding that the addition of KCl (among other chloride salts) to a Cd-CdCl₂ solution lowered the solubility of Cd metal. Furthermore, he noted the decrease in Cd solubility correlated with the electropositivity of the chloride cations, with KCl having the most electropositive cation of the chlorides tested. Li has comparable electronegativity to that of K, so it would be a fair assumption to expect that LiCl would also negatively impact the solubility of Cd in a molten salt solution.

Cd species and transport pathways in LiCl-KCl

An extensive survey of the literature only yielded a study by K.M. Goff¹³ which directly addressed Cd transport in LiCl-KCl. A electrorefining cell like the Mark-IV ER was simulated with a low-carbon steel crucible loaded with LiCl-KCl eutectic and Cd metal. The crucible was heated in a tube furnace to 500 °C in the confines of an Argon (< 1.0 ppm O₂, < 0.1 ppm H₂O, and < 15.0 ppm N₂)

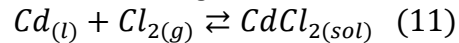
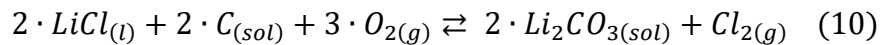
glovebox. The contents of the crucible differentiated into a bilayer of molten salt resting above a pool of liquid Cd.

Vapors emanating from the melt were collected with a cold chimney and salt samples were taken directly from the melt. Both the collected vapors and salt samples analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Goff estimated the diffusion coefficient of Cd in the salt based on the rate of Cd vaporization and found it to be comparable to literature values of Cd⁺² ions in LiCl-KCl at 500 °C. However, the Cd content of the salt samples was found to be greater than 0.1 wt% and much more than the 2·10⁻⁵ wt% expected from the redox of Cd by LiCl (eq. 9).



To verify that Cd was dissolved in the salt as CdCl₂, Goff add Cd alloyed with 28.6 wt% Li metal to the melt to reduce any Cd⁺² ions and replicate the reducing effect of U present in the Mark-IV ER's salt bath. It is presumed (but not made explicit) that a Cd-Li alloy was used instead of pure Li as the latter is less dense than the salt ($\rho_{Li} = 0.484 \text{ g/cm}^3$ vs. $\rho_{LKE} = 1.62 \text{ gm/cm}^3$) and would therefore float. He found that this lowered the content of the salt samples down to 0.004 wt%. This same decrease in Cd solubility was also observed when a U rod was left inserted in the melt. This measured Cd content in the presence of reducing agents was still higher than the calculated concentrations for Cd in a melt with Li or U (5·10⁻¹⁶ wt% and 1·10⁻¹³ wt %).

Presented with this evidence, Goff concluded that CdCl₂ was present in the unadulterated melt and its formation was enabled by C and O₂ contaminants (C content in the salt ranging from 0.12-2.0 wt% and O₂ being available in trace amounts in the glovebox atmosphere). He proposed that these contaminants could react with LiCl to form Li₂CO₃ (Eq. 10) and that the liberated Cl could then react with Cd from the pool to form CdCl₂ (Eq.11).



Goff attributed the remaining 0.004 wt% of Cd in the melts to Cd metal vapor physically dissolved in the salt. He noted that the holes in the molten salt lattice were large enough to accommodate Cd atoms.

Concerns over use Li metal in Goff's studies

Introducing Li metal to the salt/Cd metal system would reduce Cd⁺² ions as Li⁺¹ is the more thermodynamically favored ion, but it may also have other undesired effects on the chemistry of the melt.

Studies of liquid Li-Cd alloys by Langen¹⁴ et al, found that the Gibbs free energies of mixing of Li-Cd liquid alloys were negative across all compositions. The implication being that Cd is more stable alloyed with Li than as pure Cd. This would reduce the fugacity (non-ideal vapor pressure) of Cd at the pool-salt

interface and consequently its equilibrium concentration in the salt. Li vapor could also displace Cd atoms from the salt matrix by occupying holes. There is good reason to believe that the addition of Li to the salt could negatively impact the solubility of multiple Cd species and not just the targeted CdCl₂.

It was also demonstrated by Seefurth¹⁵ that the addition of Li to a LiCl-KCl melt will result in a redox reaction between the Li metal and KCl. The equilibrium constant at 500°C was estimated to be only $K = 0.07323$, but reaction was accompanied by the vaporization of now metallic K which then escaped the system. The salt mixture would be left containing more LiCl than the true eutectic, straying from desired model.

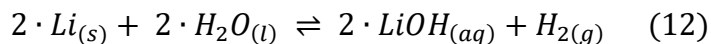
The significance of the effect produced by the immersion of a U rod into the melt is more defensible. The Mark-IV ER's LCC is in fact replenished with CdCl₂ in the knowledge that the U present will reduce it. Adding U to the system is also closer to the application this line of research attempts to model. However, the observed decrease in Cd content of sampled salt is still only circumstantial evidence for a dominant CdCl₂ species.

Aqueous Separation of Cd Species

Cd metal is insoluble in water¹⁸, while CdCl₂ is very soluble (119.6g/100ml @ 25°C)¹⁹. This difference in the chemical properties of these two Cd species provokes the question, "Could an aqueous separation procedure allow the two species to be measured independently in samples of LiCl-KCl?"

When a salt like CdCl₂ dissolves into an aqueous solution its lattice structure broken apart by the electrostatic action of polar water molecules. The molecules are then dissociated into ions to an extent quantified by its solubility product constant (K_{sp}). These ions and molecules disperse evenly and become complexed by water molecules, which electrostatically retain the solute in its dissolved state and keep it from settling or being filtered out.

Metals can also dissolve in aqueous solutions, but first need to be oxidized by some component of the solution such as is the case with Li metal (Eq. 12).



Cd metal does not oxidize readily in an aqueous solution with a neutral pH and thus does not dissolve. Instead it will exist in particulate or colloidal form, the distinction being that colloids consist of particles of a size sufficiently small to be subject to intermolecular forces in solution and thus resistant to settling. The size of metallic Cd particles in solidified salt sample is not known, but smaller ones would be more difficult to separate from an aqueous solution due to the aforementioned forces

Colloidal Cd was separated from dissolved Cd⁺² ions using stirred-cell ultra-filtration in a study by Cantwell²⁰. The colloidal Cd in the sample solutions was reduced by a factor of four as it passed through an ultra-filter rated to retain particles with molecular weights in excess of 1kDa (equivalent to 1,000 amu).

Filtered and unfiltered sample solutions could then be analyzed with ICP-MS to determine the concentrations of each Cd species.

It was decided to apply Cantwell's procedures to LiCl-KCl samples dissolved in water with a neutral pH. The success of this approach would be dependent on the significant portion of metallic Cd particles having masses in excess of 1,000 amu (8.9 Cd atoms). A positive result would consist of a significant decrease in Cd content of sample solutions after filtration and allow an estimate of the speciation of Cd. A negative result not have such a decrease and would indicate either that CdCl₂ was the dominant species or that the metallic Cd particles were too small to be caught by the filter.

MATERIALS AND PROCEDURES

Experimental Procedures for Study of Cd transport in LiCl-KCl

This work was performed in two phases. The first occurred at Idaho National Labs (INL) and was tasked with measuring Cd solubility in LiCl-KCl and effect the addition of Li metal had on it. The second phase was conducted at the University of Tennessee, Knoxville (UTK) using mostly identical equipment and procedures, but also attempted to differentiate between Cd species using stirred-cell ultrafiltration. The major difference in material was that anhydrous LiCl-KCl was used at INL and dehydrated nominally anhydrous LiCl-KCl was used at UTK.

INL work to establish Cd solubility in LiCl-KCl

A KerrLab Auto Electro Melt Maxi furnace was used to heat 100 ml alumina ceramic crucibles in these experiments. For some portions of the experiment, a stand was utilized to support a stainless steel basket that could be lowered into the crucible. All procedures using this equipment were carried out in an MBraun LABmaster glovebox filled with an industrial-grade argon gas (<10 ppm water and <10 ppm oxygen).

A high purity (99.99%) anhydrous eutectic LiCl-KCl mixture (44.2 wt% LiCl, 55.8 wt% KCl) from the stock used by the Mark-IV ER was used for the salt bath. Cd of 99.999% purity was supplied by Alfa Aesar as were 3-6mm Zr pellets (99.8% purity excluding Hf, 4% max Hf). In all experiments, the crucible was loaded with 60g of eutectic LiCl-KCl mixture and 20g of Cd metal (fig. 12). The first objective was to determine the solubility and rate of dissolution of Cd in the salt bath under lab conditions. The loaded crucible was heated at a rate of 10 °C per minute to 500 °C. A sample was taken from the surface of the salt once it had liquefied (also recording the current temperature) followed by four additional samples taken every hour thereafter. The temperature of the salt was directly measured with an alumina-sheathed thermometer at each sampling.

The next stage of the experiment investigated the hypothesized presence of CdCl₂ in the salt. Here, 0.08g of Lithium (Li) metal was added to the salt solution to reduce any CdCl₂ that may have been present. This amount was chosen to be sufficient to reduce the excess CdCl₂ hypothesized by Goff.

Samples of salt were taken from its surface every 30 minutes for 2.5 hours with measuring the temperature of the salt at each sampling. The Li metal formed a bead on the surface of the salt, the bead was swirled around gently after the second sampling and between the third and the fourth. The swirling did not appear to facilitate the bead's dissolution. The furnace was then set to cool to 300°C and turned off after reaching this temperature. The crucible was removed the following morning after it had cooled. The salt samples were then removed from the glove box and approximately 100mg from each sample were transferred to test tubes in a fume hood in a preparation for inductively coupled plasma mass spectrometry (ICP-MS) analysis to determine the relative weight fraction of Li, K, and Cd.

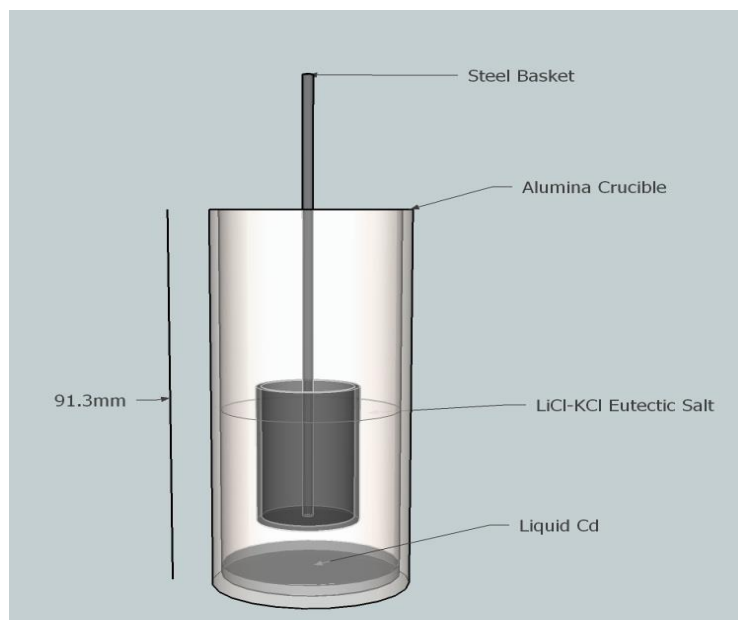


Figure 12. Experimental setup within the crucible

UTK work to differentiate between Cd species in LiCl-KCl

Work at INL had established that the Cd content of salt samples stabilized after the melt had been at 500°C for 5 hours. Such a melt was prepared using the treated salt acquired from Alfa Aesar as was Cd shot of 99.95 % purity. In a variation of procedures, the lid of the furnace was left open (covered with quartz wool) to allow the temperature of the melt to be monitored continuously with the alumina sheathed thermocouple. A salt sample was taken after the melt had been at 500°C for 5 hours, after which 0.08g of Li metal was added. A second salt sample was then taken 7 hours later, as experience at INL indicated that it would take more than 5 hours after adding Li metal for the system to come to equilibrium. After the furnace had been turned off and the melt cooled, the

remnant of the Li bead was chiseled out of the solidified salt melt to be analyzed via ICP-MS for Cd uptake.

The salt samples and Li beads were then weighted and dissolved in deionized water. One set of salt solutions samples was run through a stirred-cell fitted with a 1kDa Amicon ultrafilters once using $N_{2(g)}$ at 60-70 psi. A second set of salt solutions samples were then run through the stirred-cell twice so that the reduction factor might be calculated if the separation succeeded. The three sets of salt solution samples (one unfiltered, one filtered once, and one filtered twice) and the Li bead solutions were then analyzed using ICP-MS.

This procedure was repeated with a second melt due to concerns that loose graphite from the furnaces' integrated outer crucible was contaminating the first melt. The loose graphite could not be completely eliminated, but it was better controlled during the second melt. It was also noted that Cd metal vapor was depositing on the grip of the chem-stand.

RESULTS AND ANALYSIS

INL Work

Cadmium concentrations of the salt samples taken during the INL work were measured using ICP-MS. The results indicated that the addition of Li metal lowered the solubility of Cd in the molten salt (fig. 13). While it appears that the Cd concentration in the unadulterated salt was approaching a value of ~0.0055 wt%, the measurement duration was insufficient to ensure that equilibrium concentration had been reached; therefore hence the longer durations used in the latter work at UTK.

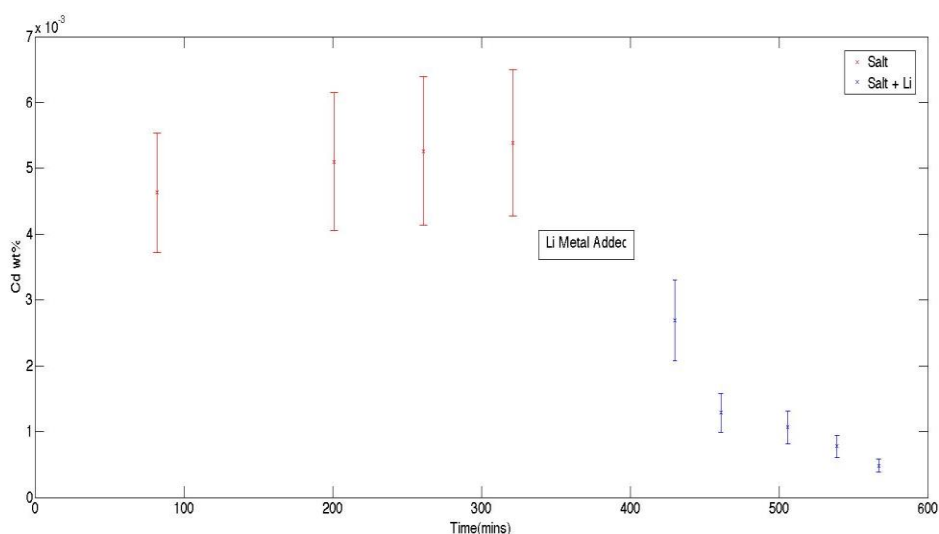


Figure 13. Cd Concentration as a function of time and addition of Li metal

UTK Work

The ICP-MS analysis of salt solutions from the first UTK melt subjected to ultrafiltration was compromised by high random and possibly systematic error (one filtered solution was estimated to have ~30wt% Cd) that precluded drawing any conclusions from it.

Results of Stirred Cell Ultrafiltration

However, the analysis of the solutions from the second melt indicated that the ultrafiltration had some success at separating out insoluble Cd species. The Cd content of the solutions made from the salt sample taken prior to the addition of Li metal all were all in excess of 1.0 wt% (the same range seen by Goff). The two ultrafiltered solutions showed a progressive reduction in Cd content (fig 14). The random error and limited number of data points precluded an estimate of relative proportion of insoluble Cd species compared to total Cd content.

The addition of Li metal did not appear to result in the same precipitous drop in Cd solubility seen in the work at INL. There was a small, within the margin of error, reduction in the Cd content of the doubly filter salt solution compared to the unfiltered one (Fig. 15). However, the solution that had been filtered once greater was than either (with a suspiciously small estimated random error compared to the other two). Given the problems in the ICP-MS analysis of the solutions made from the first melt samples, there is cause to believe that systematic error was significant in this data set.

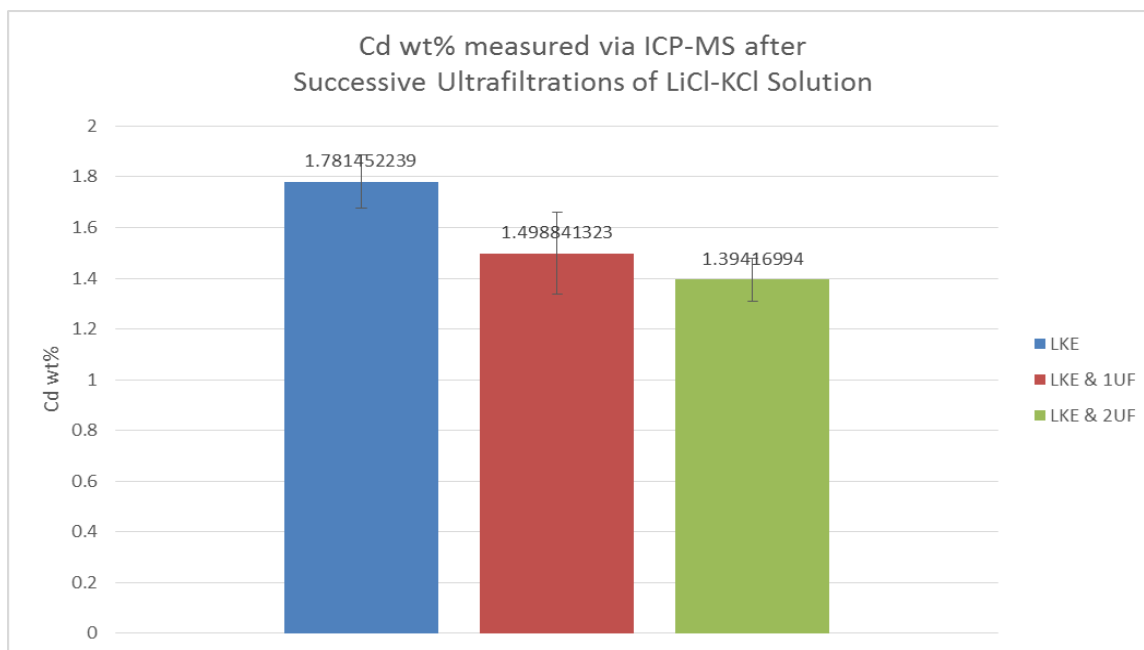


Figure 14. Cd content of LiCl-KCl salt before the addition of Li metal

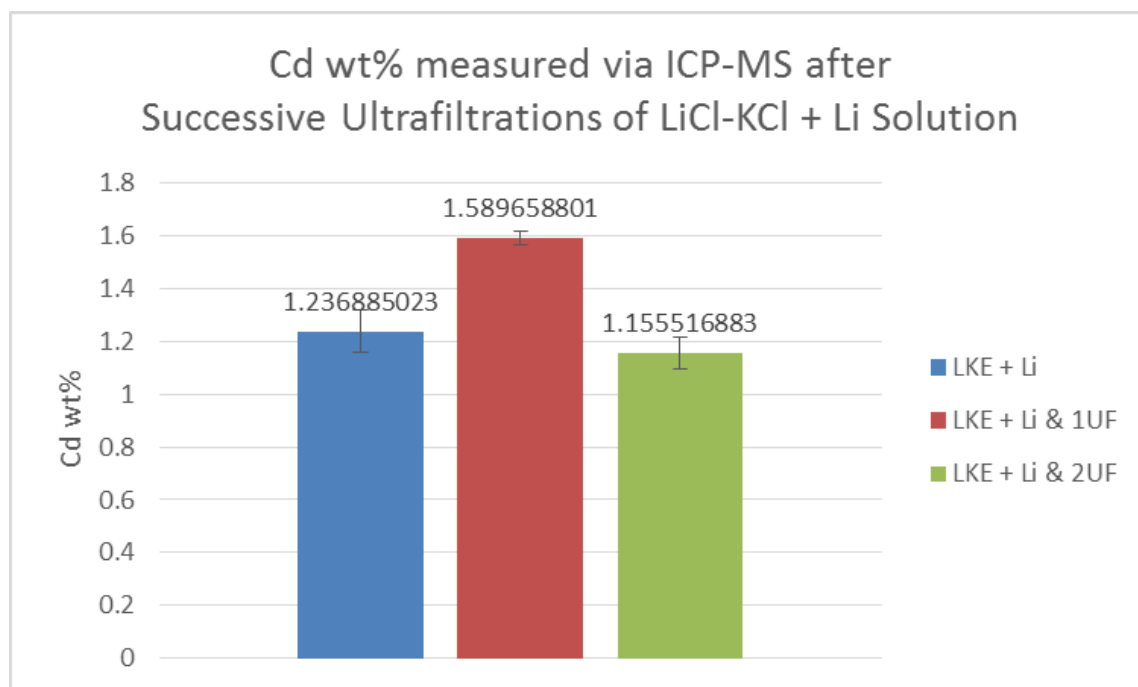


Figure 15. Cd content of LiCl-KCl salt after addition of Li metal

Results of Analysis of Li Bead from Melts

Analysis of remnants of the Li beads extracted from both melts (Fig.16) indicated that there may have uptake of Cd by the Li beads; however this finding is not trustworthy due to the ICP-MS also measuring the Cd content of a sample of reagent quality Li metal as on the order of 10 wt%. This is not a reasonable value as the metal is listed as 99% pure Li. Cross-contamination of from another sample during the ICP-MS analysis is a more likely explanation for this aberration.

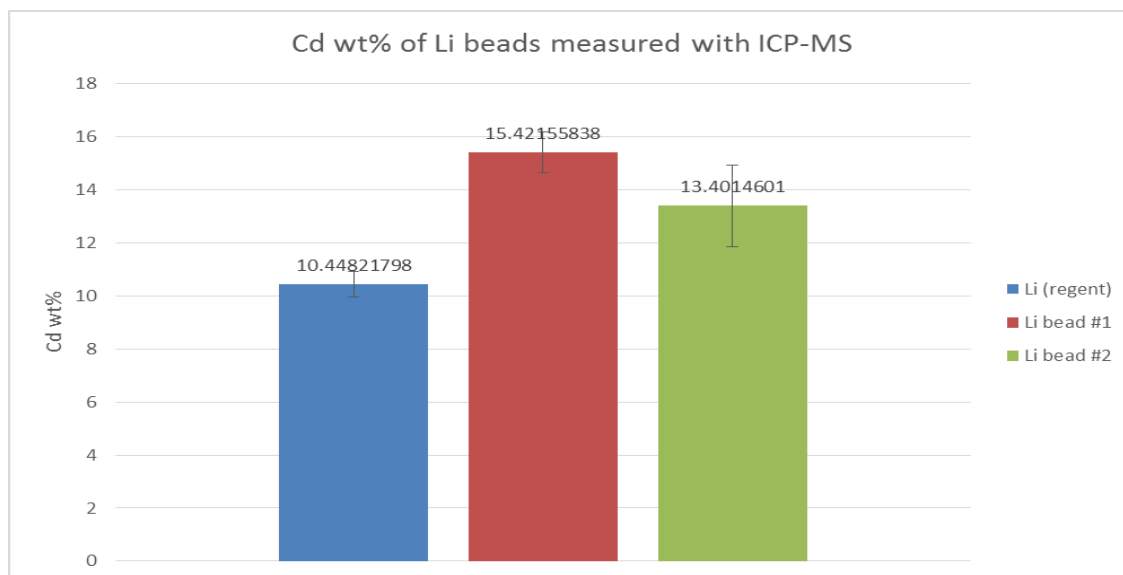


Figure 16. Cd content of control sample of Li; note the sample also shows non-trivial Cd content

CHAPTER III

Cd uptake by Zr in LiCl-KCl

ABSTRACT

Zr is the only major constituent of the contaminated cladding hulls that is known to form intermetallics with Cd at the operating temperature of 500 °C. To test the hypothesis that Cd was being retained in the hull as Zr-Cd intermetallics, Zr pellets were immersed in the salt bath of a small scale analogue for the Mark-IV ER at 500 °C for a range of durations. The immersed pellets were cross-sectioned and analyzed with SEM-EDS. Cd was detected both adhering to the surfaces of all pellets and in the interiors. The ratio of Cd to Zr was in the interiors was found to be constant, without respect to the duration of immersion. It is believe that interior Cd measured was dominated by Cd that was initially adhering to the surface but then smeared across the interior during sample preparation.

INTRODUCTION

Zr-Cd Intermetallics

Regardless of how Cd is being transported through the salt from the LCC to the anode basket, the situation becomes much clearer once Cd comes in contact with its contents. The hulls primarily contain Zr, U, and Fe, with other elements being present in only trace amounts. Work by Arunsingh¹⁶ and Frye¹⁷ have establish that Cd and Zr can form a range of intermetallics (of fixed stoichiometric ratios) and solid solutions at the operating temperature of 500°C. The same cannot be said for Cd with either Fe or U at 500°C. The amounts of Cd found in the hulls³ suggest that retention of Cd by Zr has not reached equilibrium (the most Cd rich compound, Cd₃Zr) and that process is rate-limited by the transport of Cd through the salt.

Experimental Procedures for Study of Cd uptake by Zr

After measuring the concentrations of Cd in the salt, tests were run to directly measure Cd contamination of the solid samples of Zr immersed in the salt bath. As in the Cd solubility tests, a crucible was loaded with 60g of eutectic LiCl-KCl mixture and 20g of Cd metal. The crucible was heated at a rate of 10 °C per minute up to 500 °C. It was then held at this temperature for 2 hours to allow the cadmium to saturate the salt. At this point 3.11 g of Zr pellets (3-6 mm diameter) was weighed and placed in the basket. The basket was then lowered into the molten salt so that the basket was just submerged in the salt and well above the liquid cadmium pool. The depth of immersion was held constant using marks on the stand and basket rod. At 66, 126, 192, and 256 minutes after immersion, several of the Zr pellets were sampled (see Table 1).

Table 2. Zr Sample immersion times

Sample	1	2	3	4
Time (mins)	66	126	192	256

After four samplings, the basket was removed and the furnace was set to cool back down to room temperature. The Zr samples were then removed from the glove box, and a Zr pellet was selected from each for Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis. The selected pellets were mounted in epoxy and then polished with an electric grindstone to expose a cross section to prepare them for the SEM. Three line-scans were made from each pellet at different sites perpendicular to the perimeter of the cross section.

RESULTS AND ANALYSIS OF CD UPTAKE BY ZR STUDIES

The SEM was used to measure the relative concentrations of Cd, Zr, and Cl via EDS line scans for samples of the Zr pellets as shown in Fig. 17. Note that the pellets were not washed to remove salt, thus they were all coated with LiCl-KCl.

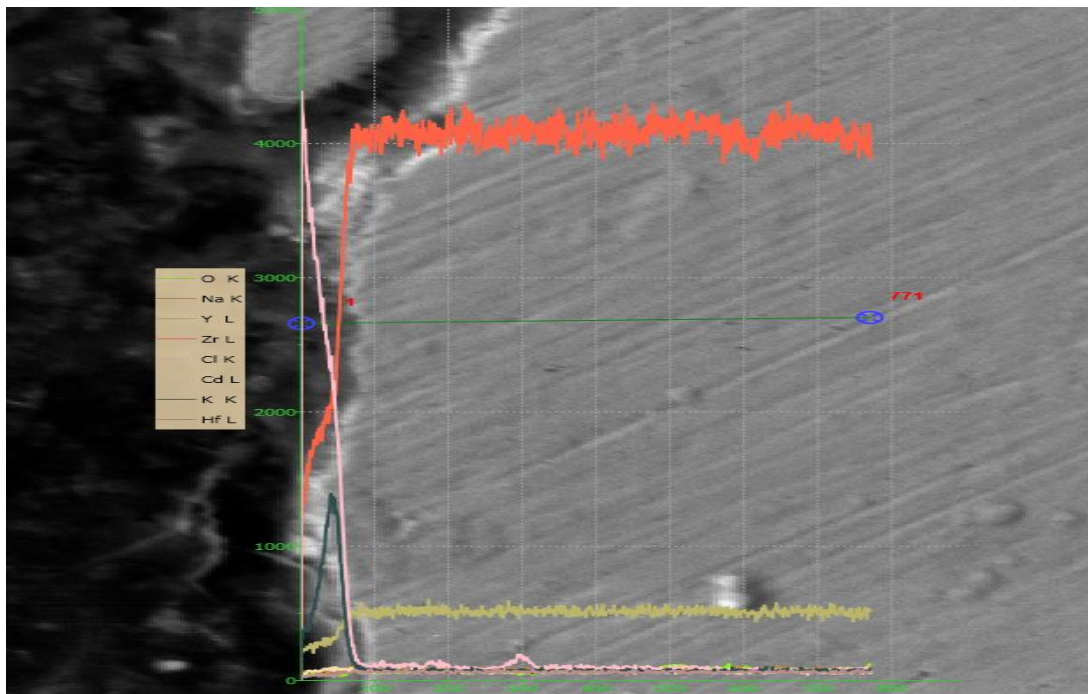


Figure 17. SEM micrograph of Sample 1 with EDS counts

The counts for Cd, Cl, and Zr vs. position were first normalized to their maximum values for each line scan so that they could be plotted and compared on the same scale. From each sample, the line scan with the least random variability in normalized Cd counts was selected as the “best”. The Cd counts vs. depth of these best line scans were then plotted together. Lastly, the mean plateau Cd/Zr ratios from the all line scans were plotted vs. time

The normalized Zr counts vs. position were consistent across line scans from all samples in that they rose sharply and then plateaued at the surface of the pellet, as seen in the SEM micrograph included in fig. 16. The position of the Zr count plateau “edge” was helpful in defining the surface of the pellet. The normalized Cl counts vs. position were also consistent in peaking at the nugget surface from adherence and then decreasing sharply to near zero in the interior.

The normalized Cd counts vs. position were, in contrast, highly variable between line scans but still revealed several trends. Normalized Cd counts either peaked at the surface or decreased to a non-zero plateau value in the interior (Fig. 18) or simply plateaued at the surface with no clear surface peak (Fig. 19). For all line scans, the normalized Cd counts varied greatly for small changes in position along the line scan. Line scans with a surface Cd peak generally had less variability in counts for small changes in position.

The mean Cd/Zr ratios in the interior-plateau regions of all line scans (fig. 20) were remarkably consistent. Across all samples and line scans, the Cd-Zr ratio was approximately 0.0152 (+/-) 0.0006. This data shows that the Cd-Zr ratio in the interior of the Zr pellets (to the depths measured by the line scans) was constant over the time period studied.

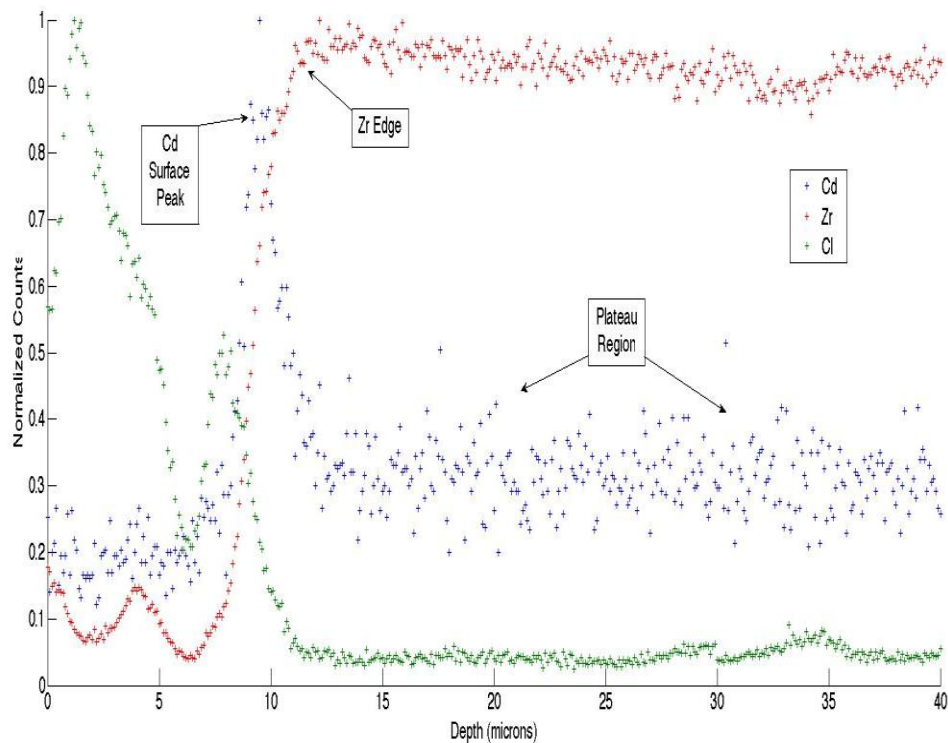


Figure 18. Sample 2 – Line Scan 1

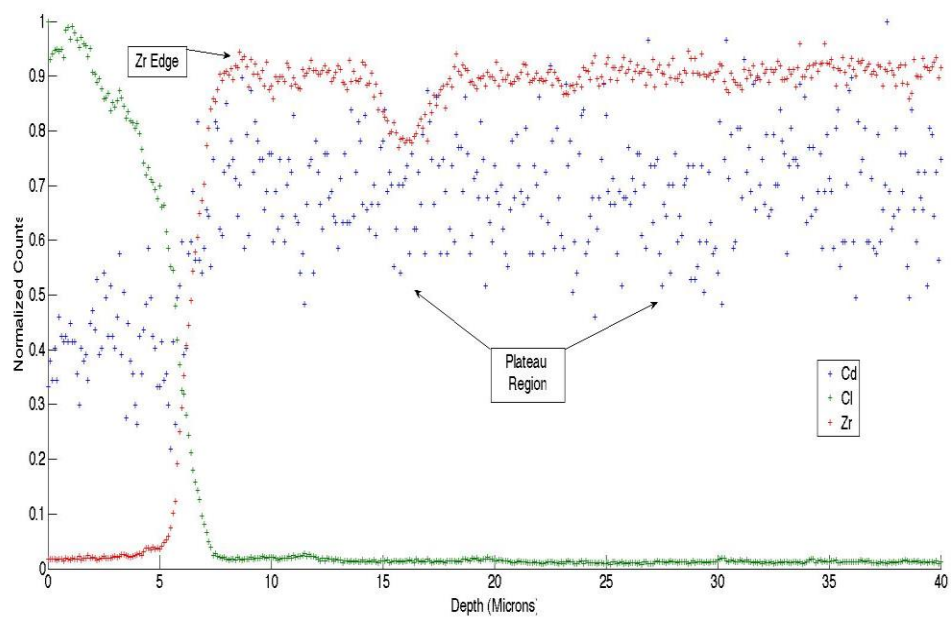


Figure 19. Sample 3 - Line Scan 1

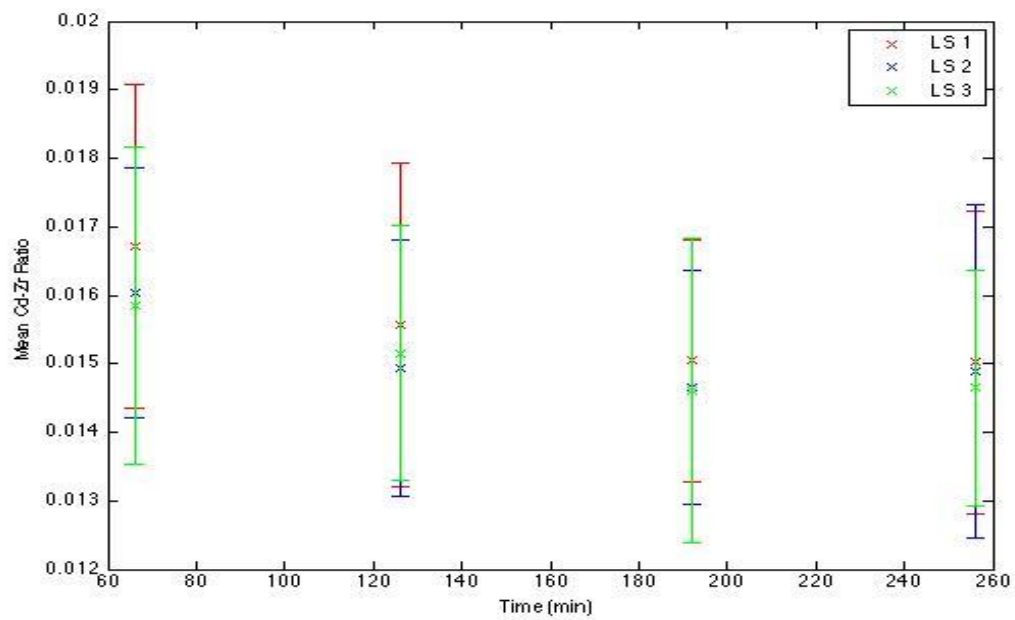


Figure 20. Mean plateau Cd-Zr Ratio vs Sample Immersion Time

CONCLUSIONS

Conclusions regarding the thermal dehydration of LiCl-KCl

From these experiments it's possible to draw several reasonable conclusions.

The water content of the cheaper, nominally anhydrous LiCl-KCl is ~2 wt%. This alone was important to know if the salt was to be used in the Cd transport studies. Heating this salt at 200°C can lower this to as low as ~0.2 wt% for the surface strata, but only has minimal impact on the subsurface strata. It seems that the major obstacle in dehydrating LiCl-KCl is the rate of diffusion of water vapor out of the bulk material.

The effect of the application of forced Ar gas flow was not adequately determined as the pump used was underpowered for the application. Despite this, the experience did provoke deeper thinking about how forced Ar gas flow might be applied to the salt as it is heated.

Given that extensive dehydration achieved for salt in the surface strata, a logical progression would be to try and increase the surface area-to-volume ratio of the bulk material during drying. One potential configuration towards these ends would be a series of concentric fine steel-mesh baskets holding the salt in thin layers with gas channels between them. Ar gas could then be flowed up over the salt by a pump/compressor or by natural convection.

Another option would be to adapt existing fluidized bed technology to operating in a dry Ar gas environment. This may require a greater investment in equipment, but agitating the salt as it is heated by mechanical means or just high pressure dry Ar gas would vastly increase the exposed surface area. The major obstacle would be procuring sufficiently powerful electric motors that would tolerate the environment.

It was found that the TGA-MS instrument was not sufficiently reliable at preventing air contamination when opening and transferring the sealed Al pans to the furnace chamber. If the operation of a TGA machine in a dry Ar glovebox is not practical for future studies, it would be advisable to investigate the use of Karr-Fisher titration for measuring the water content of salt samples. The practice has been successfully used in Parash's studies and the equipment is small in dimensions compared to a TGA machine.

The salt that was partially dehydrated in this part of the study was used in subsequent experiments investigating Cd transport in LiCl-KCl. The extent to which the ~2.0 wt% water content of the salt affected those experiments shall be discussed in appropriate chapter.

Conclusions regarding Cd transport in LiCl-KCl

The measurements made at INL of Cd solubility in LiCl-KCl before Li was added were on the same order as those that Goff found after he added a reducing agent (0.0055 wt% vs. 0.004 wt%). After adding Li, the Cd the content decreased precipitously to values well below what was found in Goff's studies.

The measurements made at UTK indicated Cd solubility in LiCl-KCl over 1.0 wt% before the addition of Li; in agreement with Goff's findings. However, the addition of Li did not seem to significantly impact the solubility of the Cd in this set of experiments, contradicting both Goff's work and that performed at INL.

The ultrafiltration procedures yielded results consistent with the removal of insoluble Cd metal from the salt sample solutions. Those results indicated that majority of the Cd in those samples was either water soluble or in the form of particles with masses less than 1,000 amu. Insight into the size distribution of Cd particles originating from solidified vapors in the salt would be important in further assessing ultrafiltration's utility in this application.

Initially the results of the work performed at UTK would seem to be at odds with both the work done at INL and Goff's findings. However, during the experiments done at UTK it was noted that the new outer graphite crucible was shedding far more loose graphite than was seen with the older equipment used at INL. If Goff's theory that C and O₂ contaminants facilitate the formation of CdCl₂ is correct, then contamination by loose graphite at UTK that was not present at INL would result in higher total Cd solubility in LiCl-KCl, dominated by the CdCl₂ species.

A gross excess of C contamination could also explain the why the Cd concentration in the UTK salt melts did not drop precipitously after the addition of Li metal. The Li metal could have immediately reacted with C and O₂ contaminants to form Li₂CO₃ instead of reducing CdCl₂.

The ICP-MS analysis of the extracted Li bead remnants is probably not trustworthy as it measured the Cd content of sample of reagent-grade Li metal as containing 10 wt% Cd. It is suspected that there was either some Cd contamination of the Li sample solution during preparation/dilution, Cd contamination in the ICP-MS instrument, or it was subject to improper calibration/operation. The validity of the ICP-MS analysis of the salt solution samples may also be undermined they were run alongside the Li solution samples.

Ultimately it seems that the ultrafiltration procedure shows some promise as a means of distinguishing between Cd species and that Goff's hypothesized CdCl₂ may have some merit. In light of the issues with loose graphite, it is strongly suggested that graphite not be used as a refractory material in any further studies. It is also thought that the use of quartz wool to cover the top of an open crucible is not an ideal practice. The Mark-IV ER uses a sealed vessel and so should crucibles used as small scale analogues. Beyond the practical concerns over Cd depositing on equipment, the escape of Cd vapor from the crucible may prevent the salt-metal system from coming to the same equilibrium state as a sealed crucible. This uncertainty could be avoided through the use of an alumina crucible cover with access ports machined for sampling/instruments.

No problems were identified during the course of the Cd transport experiments that could be attributed to the use of nominally anhydrous LiCl-KCl. Further studies using both anhydrous and nominally anhydrous salt in with the same equipment are needed to assure that the salt chemistry of interest is not being adversely affected.

Conclusions concerning Cd uptake by Zr

The data would support the hypothesis Cd is being retained by Zr, but is insufficient to say what intermetallics may be forming or what the rate of uptake might be. The uniform Cd-to-Zr ratio in the interior of the cross-sections raise concerns that the decision not to wash the Zr pellets may have led to the smearing of Cd adhering to the surface during cross-sectioning and polishing.

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Vita

Nicholas Azoy Earle was born in Washington, DC and grew up overseas on account his father's career in the US Foreign Service. He earned a B.S. in Physics from George Mason University and later attended the University of Tennessee in Knoxville where he has since completed a Master's Degree in Nuclear Engineering for which this thesis is written.