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A research partnership between Boise State University, Idaho National Laboratory, Idaho State University and University of Idaho.

ZONE FREEZING STUDY FOR PYROCHEMICAL PROCESS WASTE MINIMIZATION

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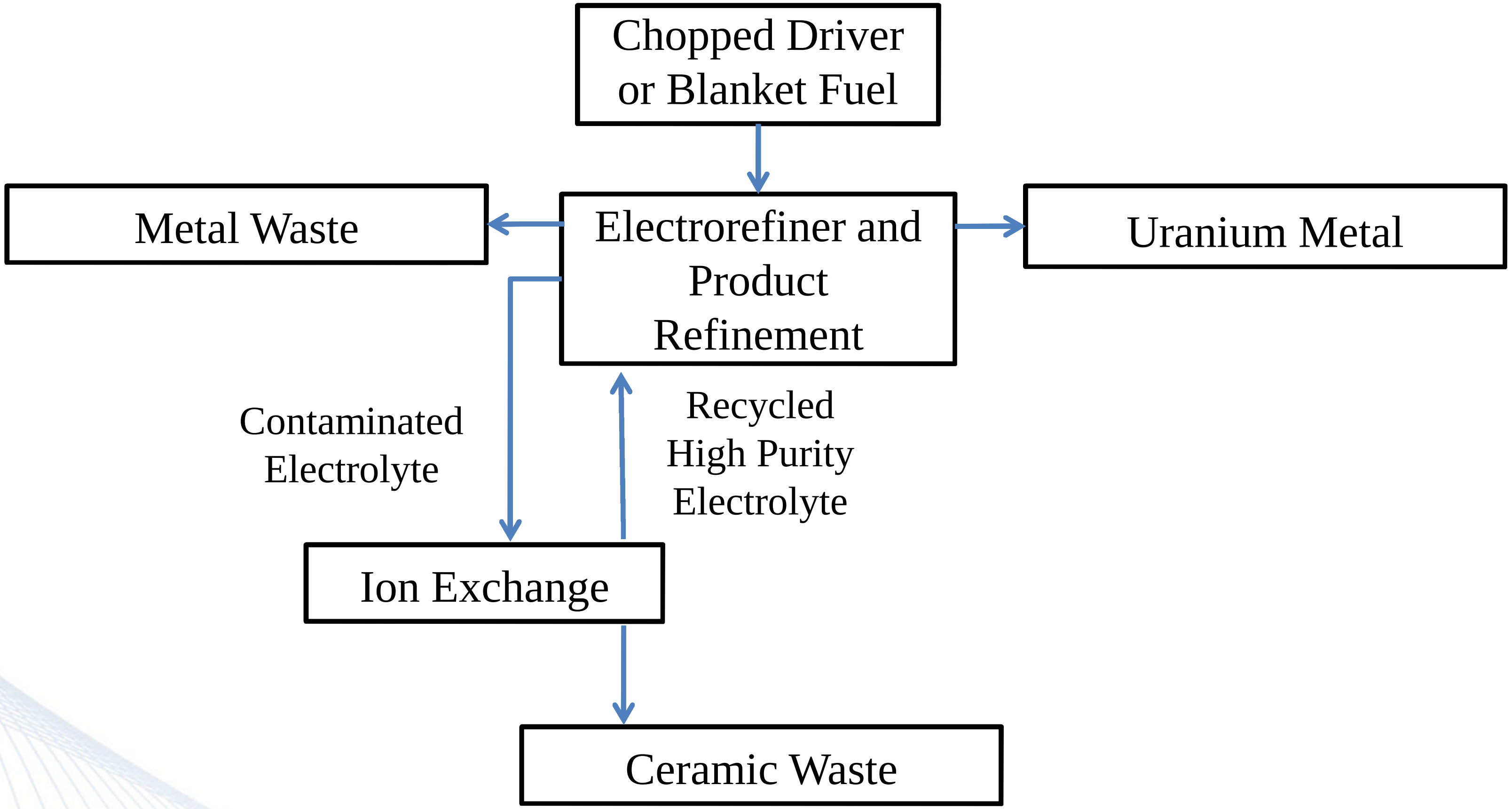
CAES Center for Advanced Energy Studies

Outline

- Background, Motivation, and Goals
- Experimental Method
- Experimental Results
- Model Development
- Modeling Results
- Conclusions and Recommendations
- Acknowledgments

Concept of Advanced Pyrochemical Process

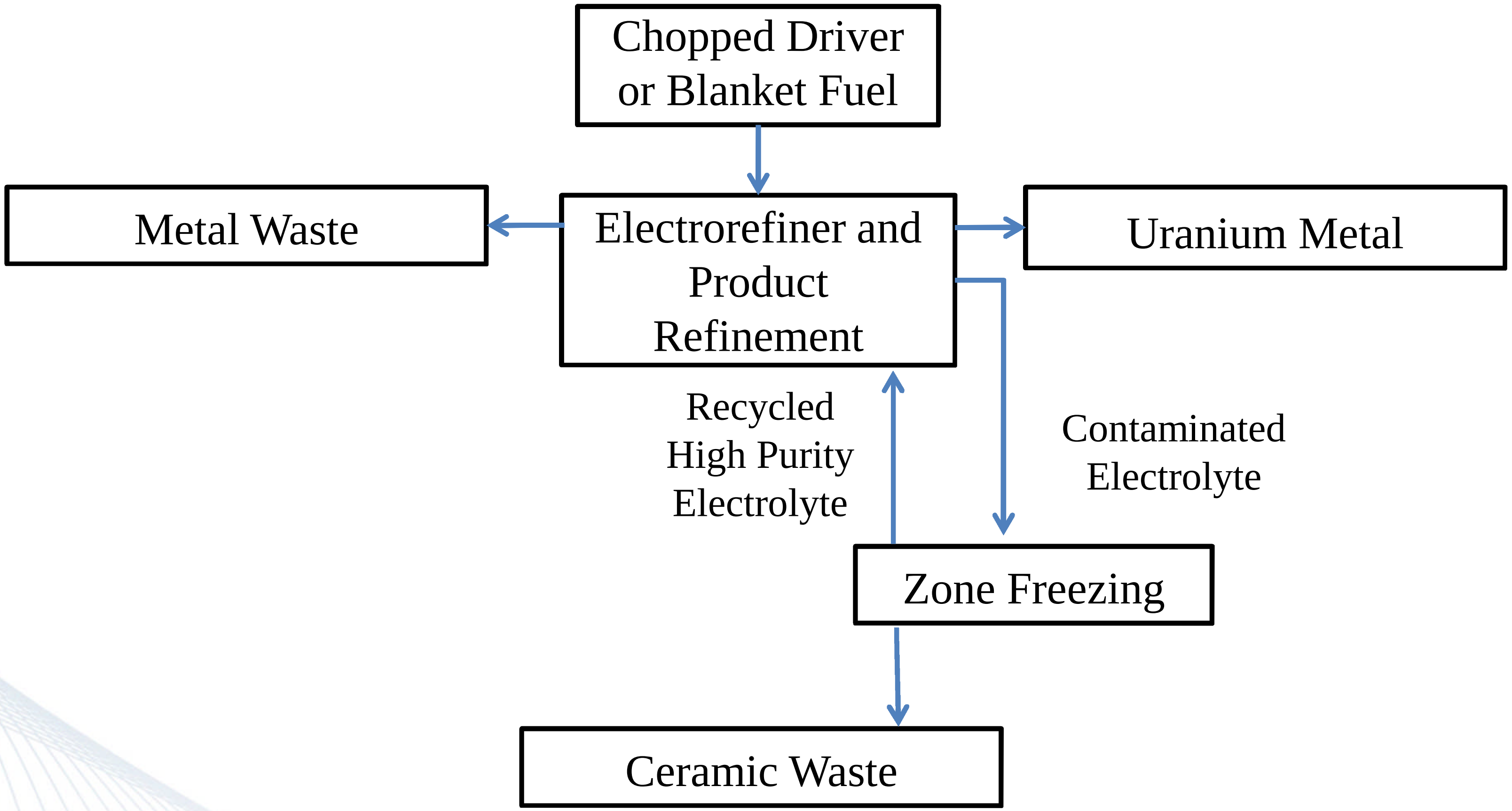


- An ion exchange process has been proposed as a method of removing fission products from the electrolyte salt. †

† D. Lexa and I. Johnson, *Metallurgical and Materials Transactions B*, 32B, 429-435, (2001).

Background

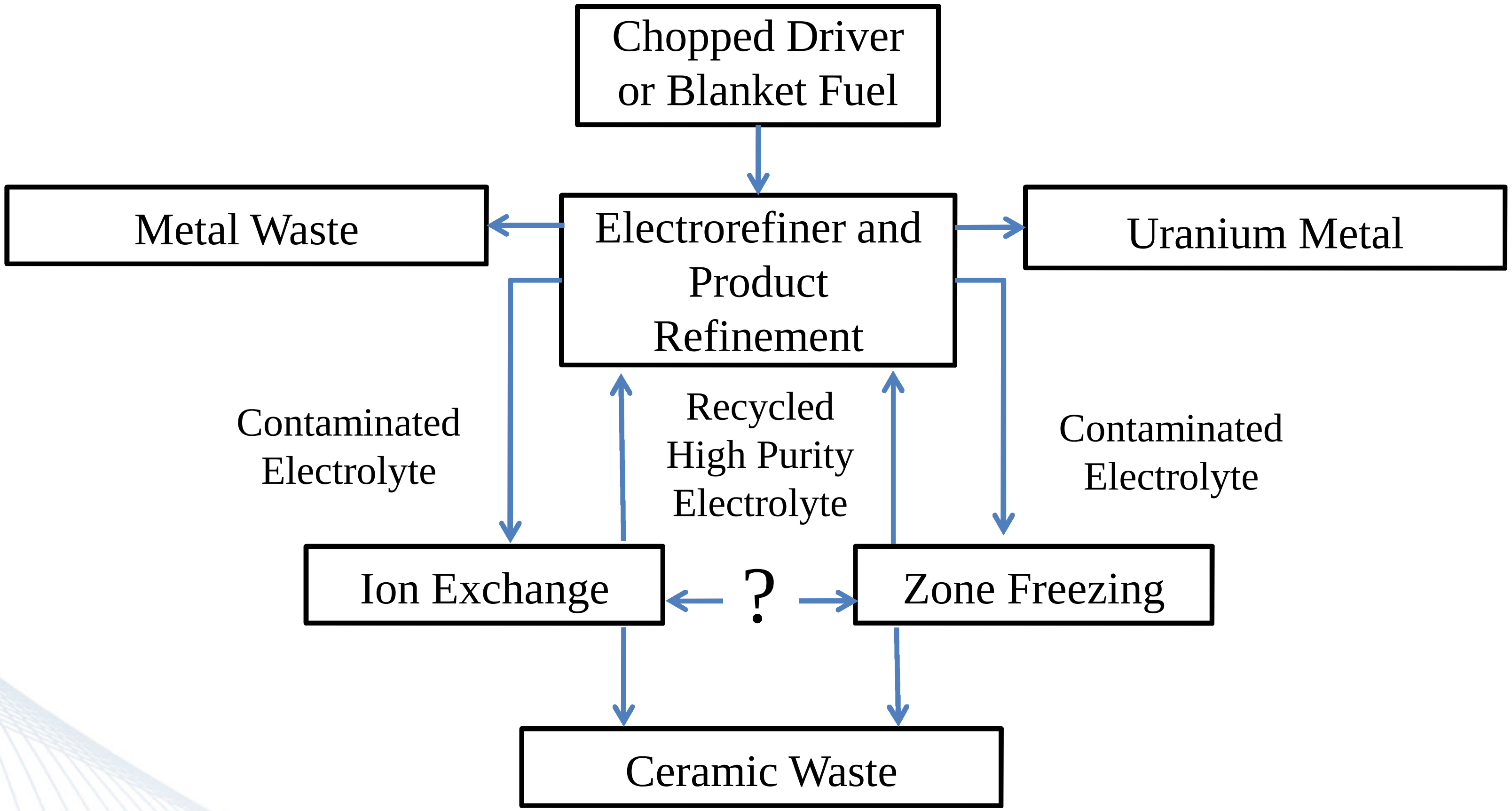
Concept of Advanced Pyrochemical Process



- The Korea Atomic Energy Research Institute (KAERI) proposed a zone freezing method as a potential alternative to the ion exchange process. †

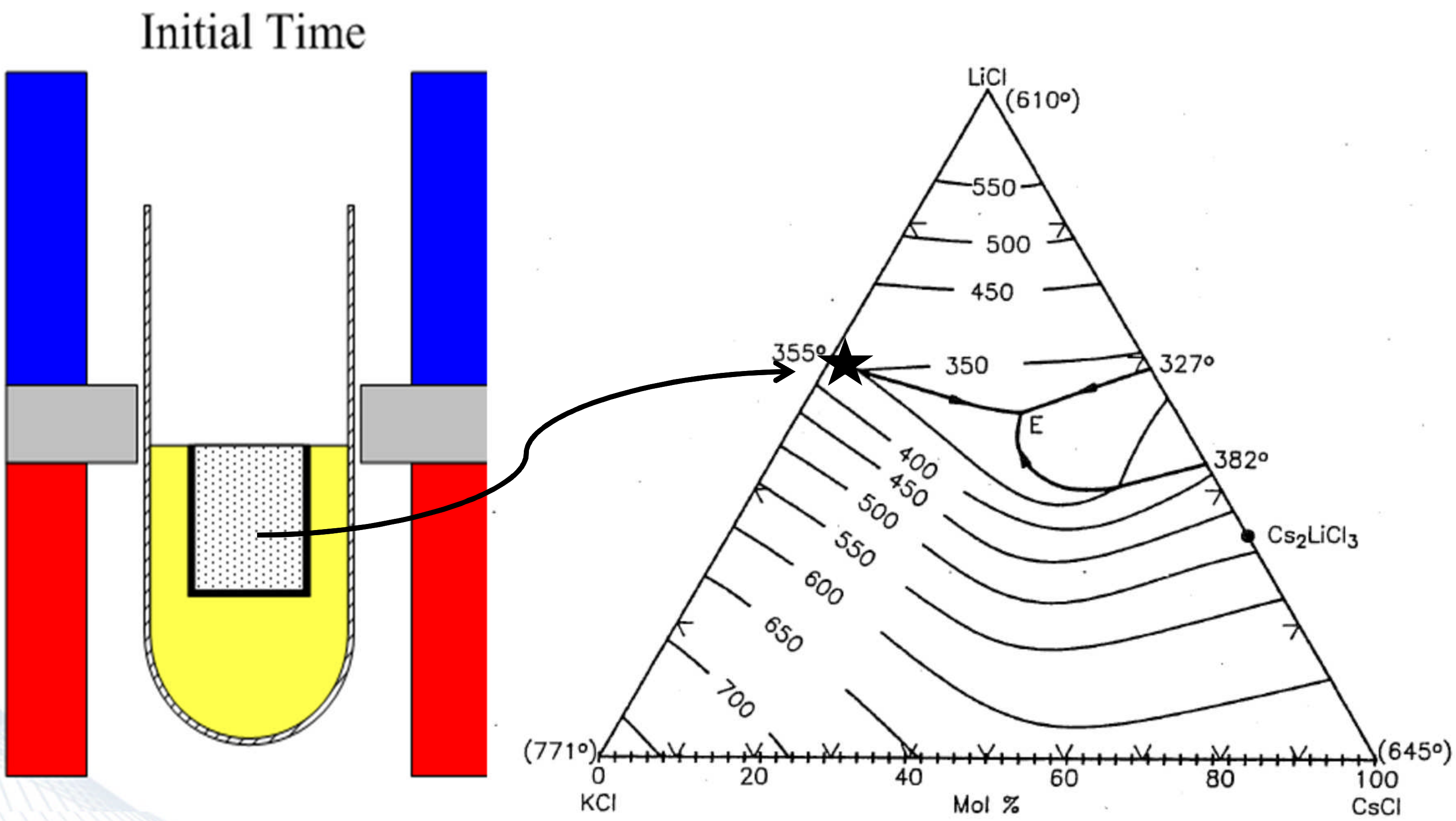
† Y. Z. Cho, G. H. Park, H. S. Lee, I. T. Kim, D. S. Han, *Nuclear Technology*, 171, 325-334 (2010).

Concept of Advanced Pyrochemical Process



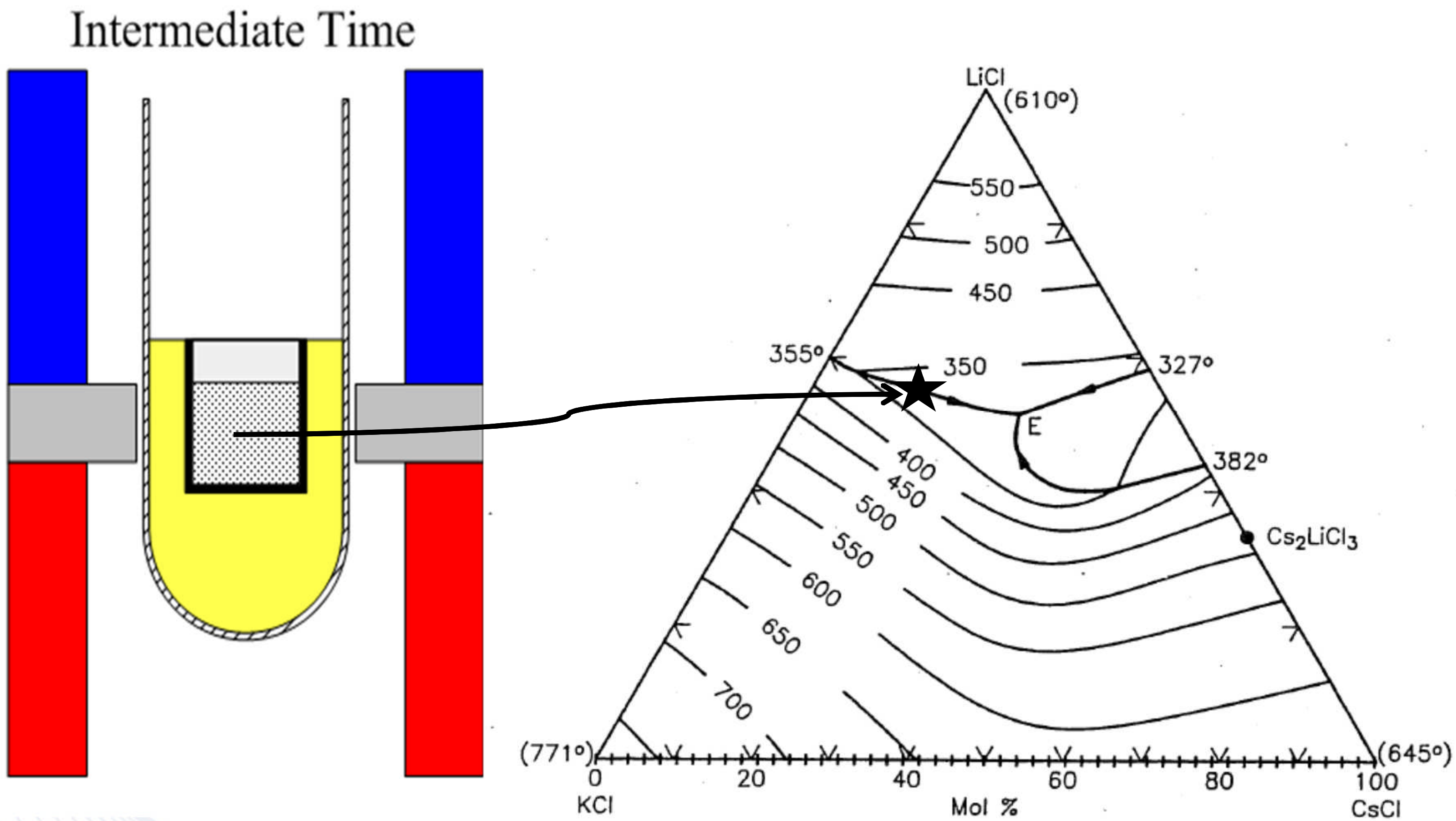
- Ion exchange and zone freezing were not directly compared in this work; however, results may help researchers determine the optimal process configuration.

What is Zone Freezing?



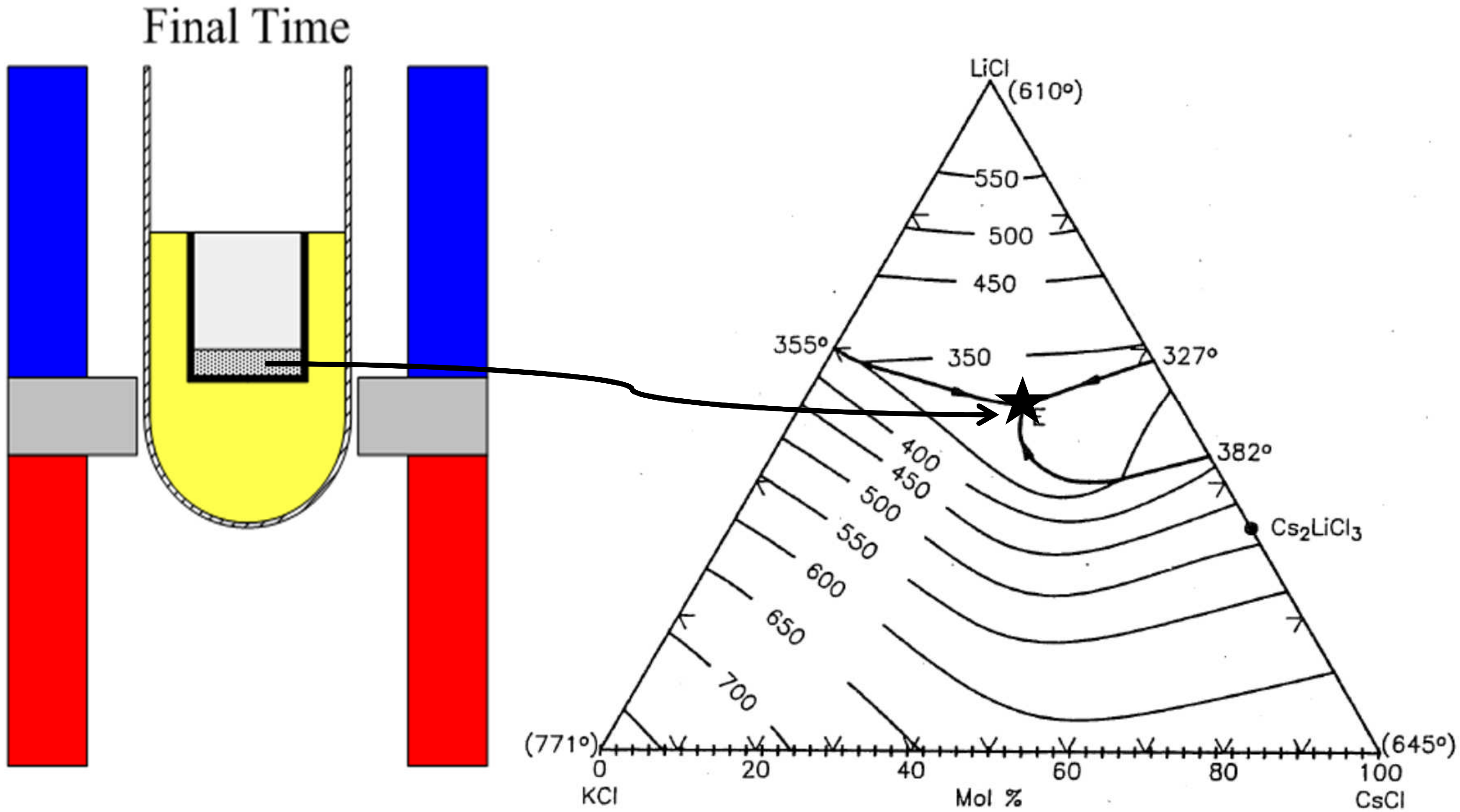
- Salt is completely liquid in the high temperature zone at typical electrorefiner exit compositions.

What is Zone Freezing?



- At some intermediate time, pure LiCl-KCl salt has solidified at the top surface, leaving a CsCl enriched liquid phase.

What is Zone Freezing?



- The ternary eutectic point has been reached and the bottom portion of the salt with the bulk of the CsCl finally solidifies.

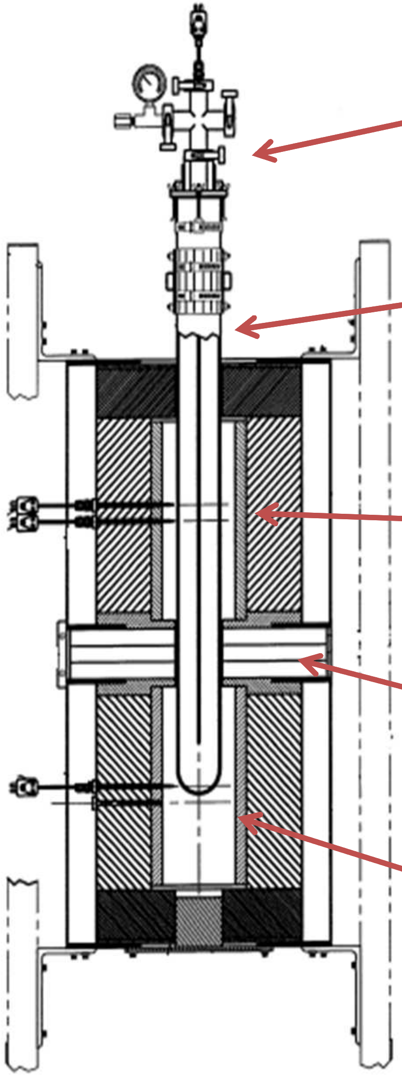
Motivation & Goals

- Results from Cho et al.[†] have proven that there are many parameters to be explored.
- To better understand the zone freezing process the following conditions were explored:
  - *Temperature*,
  - *Advancement and cooling rate*,
  - *Composition and amount of the salt*, and
  - *Crucible lid and no-lid configurations*.
- In addition, a modeling tool was developed to help describe zone freezing results.
- Success will help in optimizing zone freezing.

† Y. Z. Cho,, G. H. Park, H. S. Lee, I. T. Kim, D. S. Han, *Nuclear Technology*, 171, 325-334, (2010).

Crystal Growing Furnace

Cross-Sectional View



Inert Gas System

Alumina Retort Tube

Low Temperature Zone (LTZ)

Adiabatic Zone

High Temperature Zone (HTZ)

Variables & Conditions

- Initial compositions of salt.
- Amount of salt mixture.
- Temperatures of high and low furnace zones.
- Advancement rates.
- Lid Configurations.

	1 wt% CsCl	3 wt% CsCl				5 wt% CsCl
Advancement rate (mm/hr)	**50 g, No-Lid, ΔT = 200 °C**	**50 g, No-Lid, ΔT = 200 °C**	**400 g, No-Lid, ΔT = 200 °C**	**50 g, No-Lid, ΔT = 300 °C**	**50 g, Lid, ΔT = 200 °C**	**50 g, No-Lid, ΔT = 200 °C**
1.8		X	X	X	X	
3.2		X	X	X	X	
5.0	X	X	X	X	X	X

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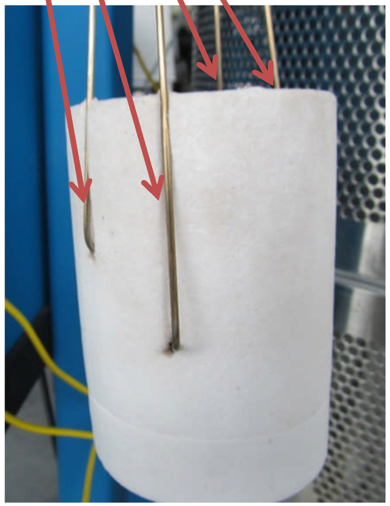
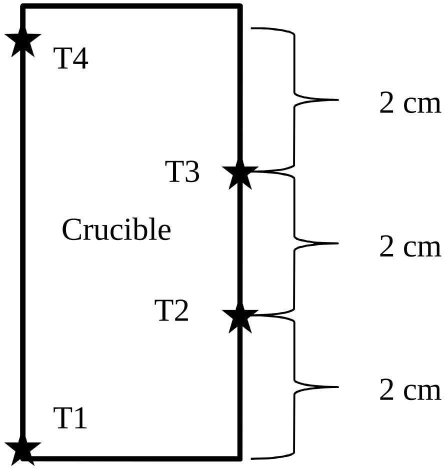
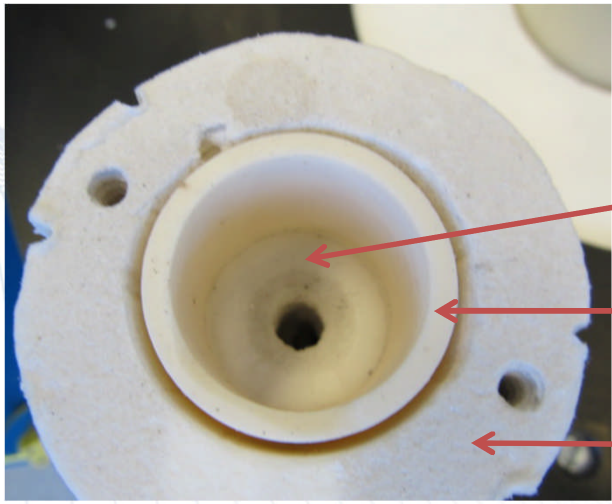
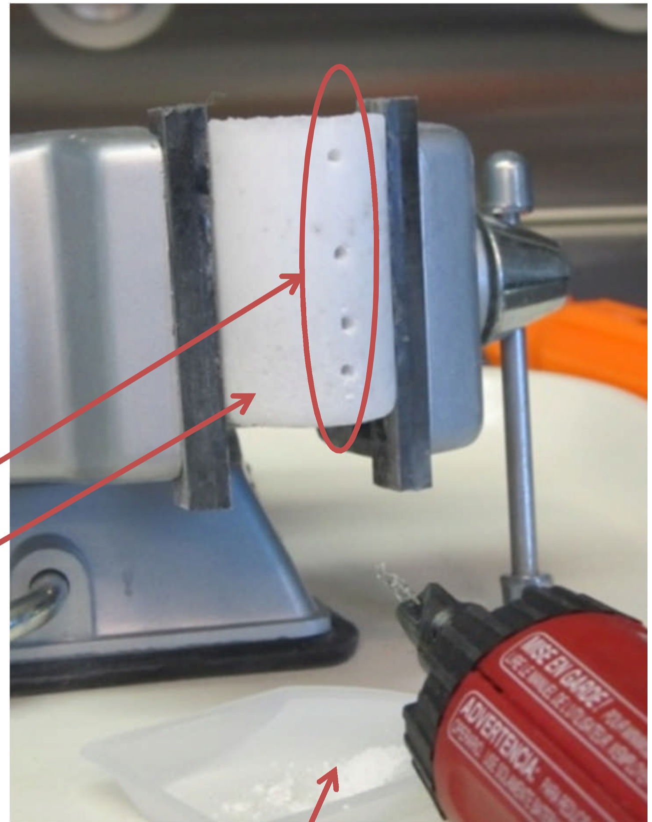
Material Configuration & Sampling

Thermocouples









Drilled Sampling Holes

Salt

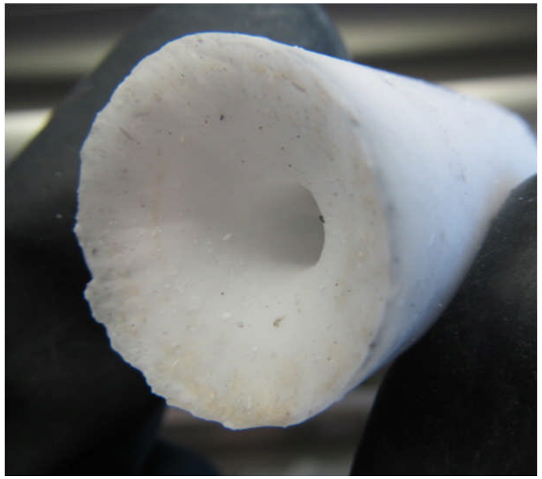
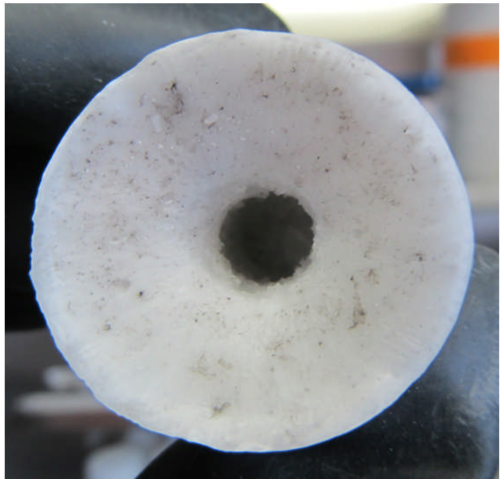
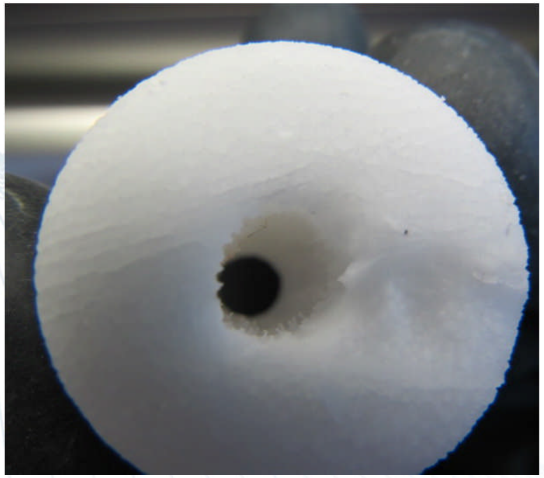
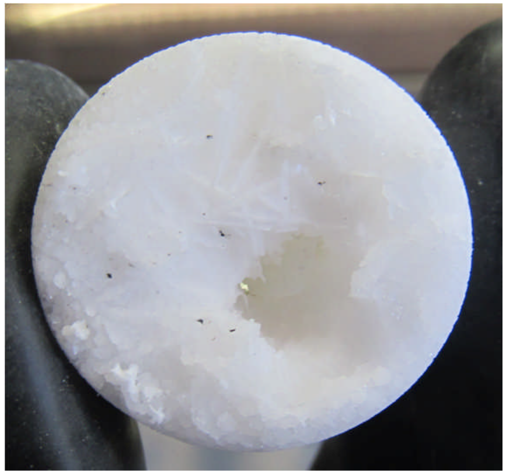
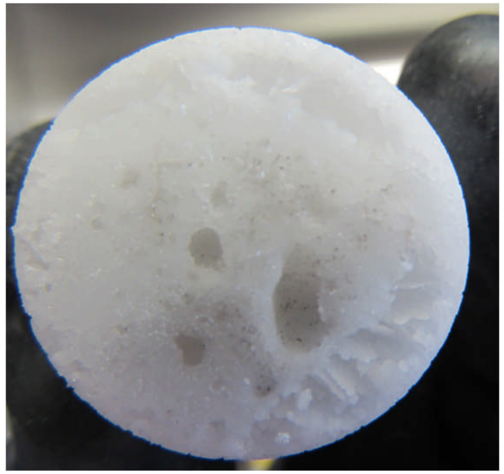
Alumina Crucible

Filler Material

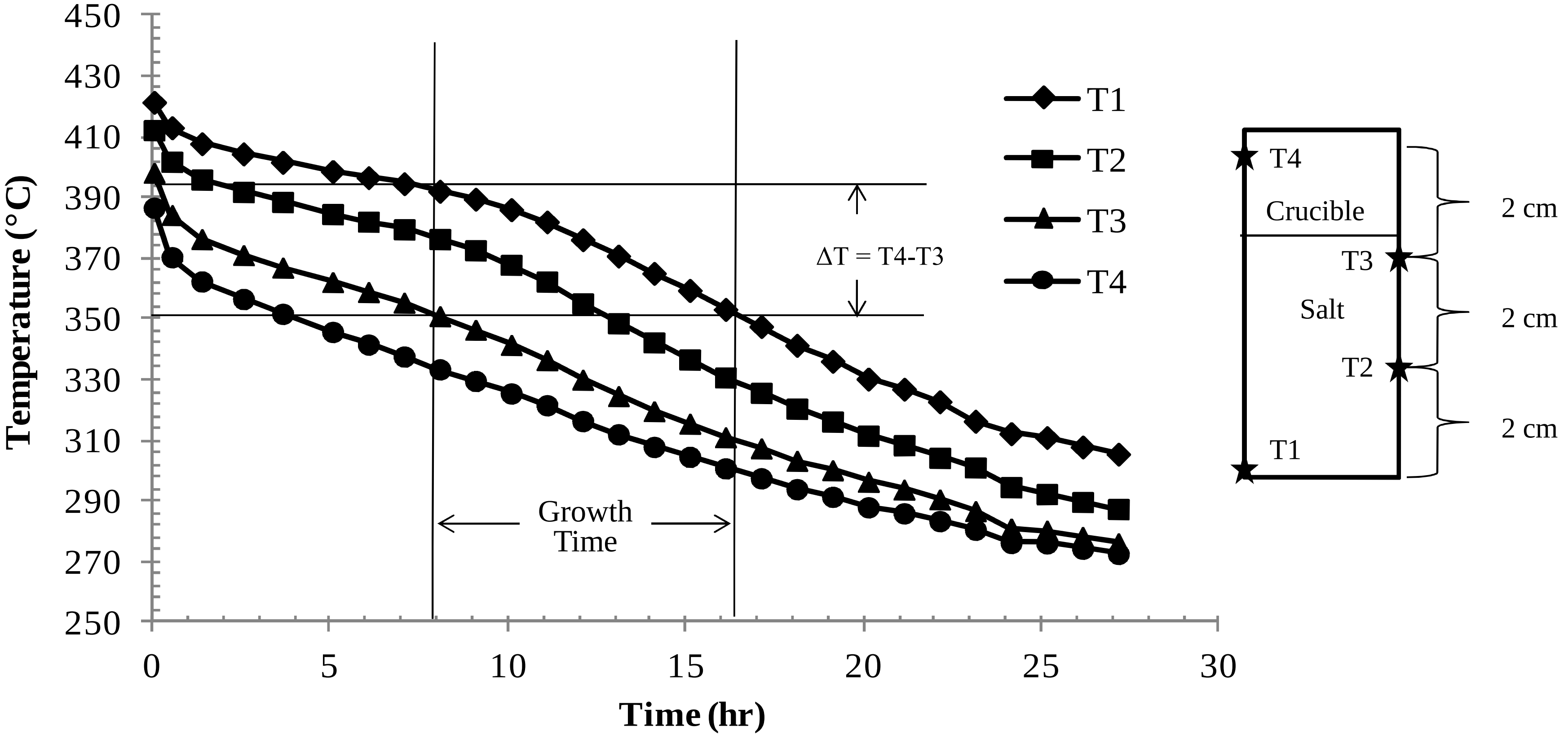
Collected Sample

Experimental Results

Grown Salt Crystals

	1.8 mm/hr (Lid)	3.2 mm/hr (Lid)	5.0 mm/hr (Lid)
Top View			
Bottom View			

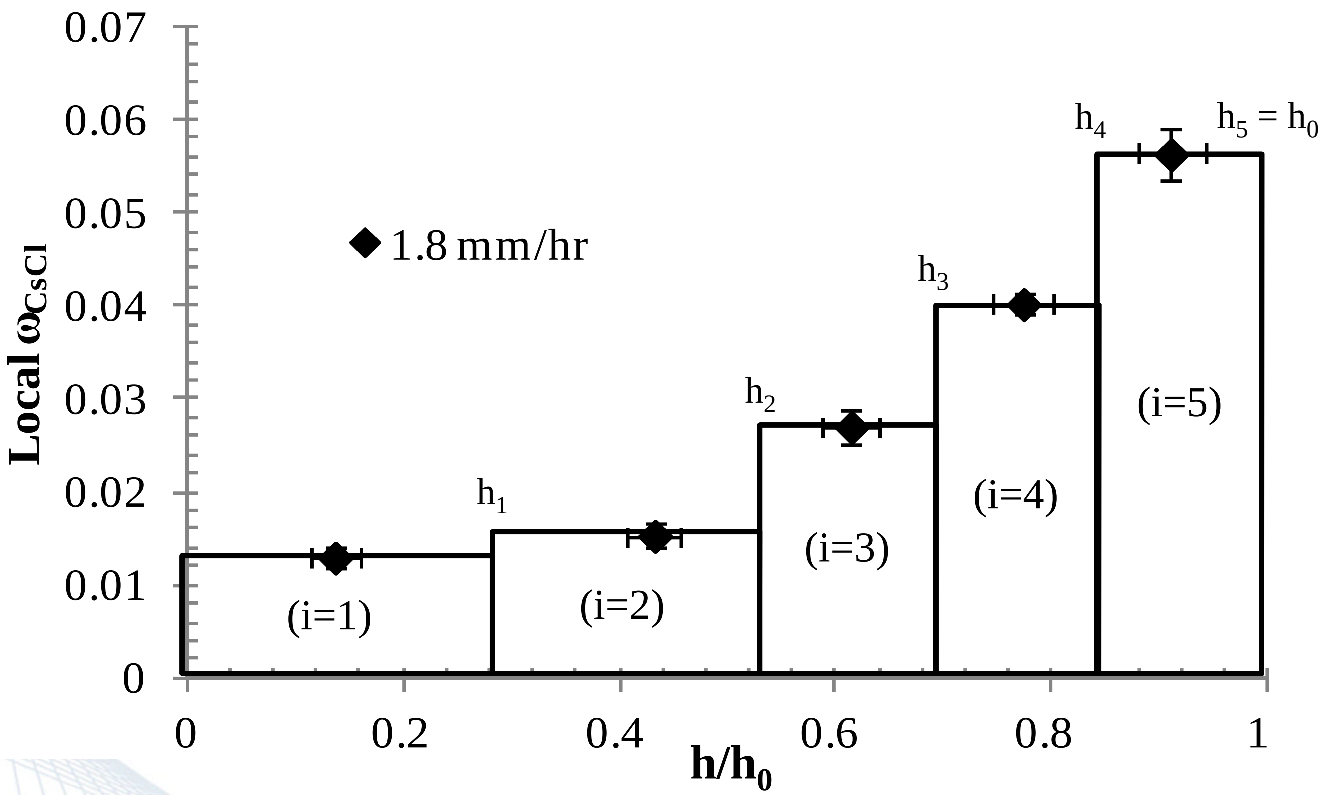
Temperature Profiles & Analysis

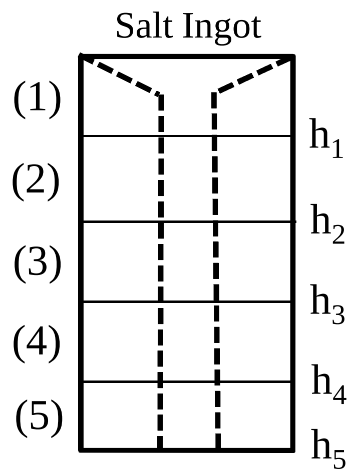


Growth Time: The amount of time passed from the onset to the termination of solidification. Used to determine the effective growth rate in the salt.

ΔT: The temperature difference between the top and bottom of the liquid phase. Used to calculate the Gr number and salt physical properties (ρ, ν, and D).

Concentration Profiles & Analysis





$$\text{Buildup Fraction}_n = \frac{\sum_{i=1}^{n} m_{CsCl_i}}{\sum_{i=1}^{n} m_{Salt_i}}$$

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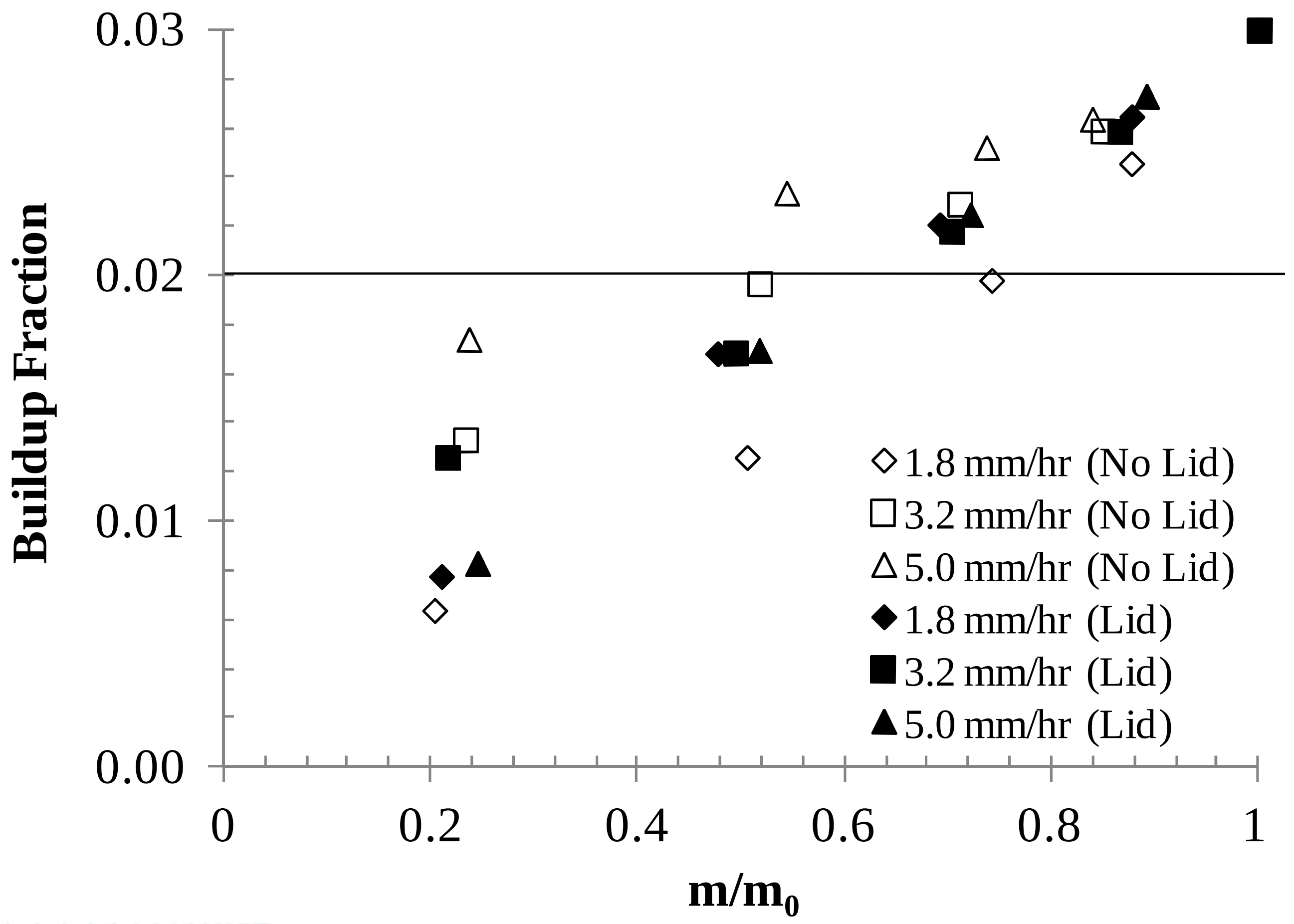
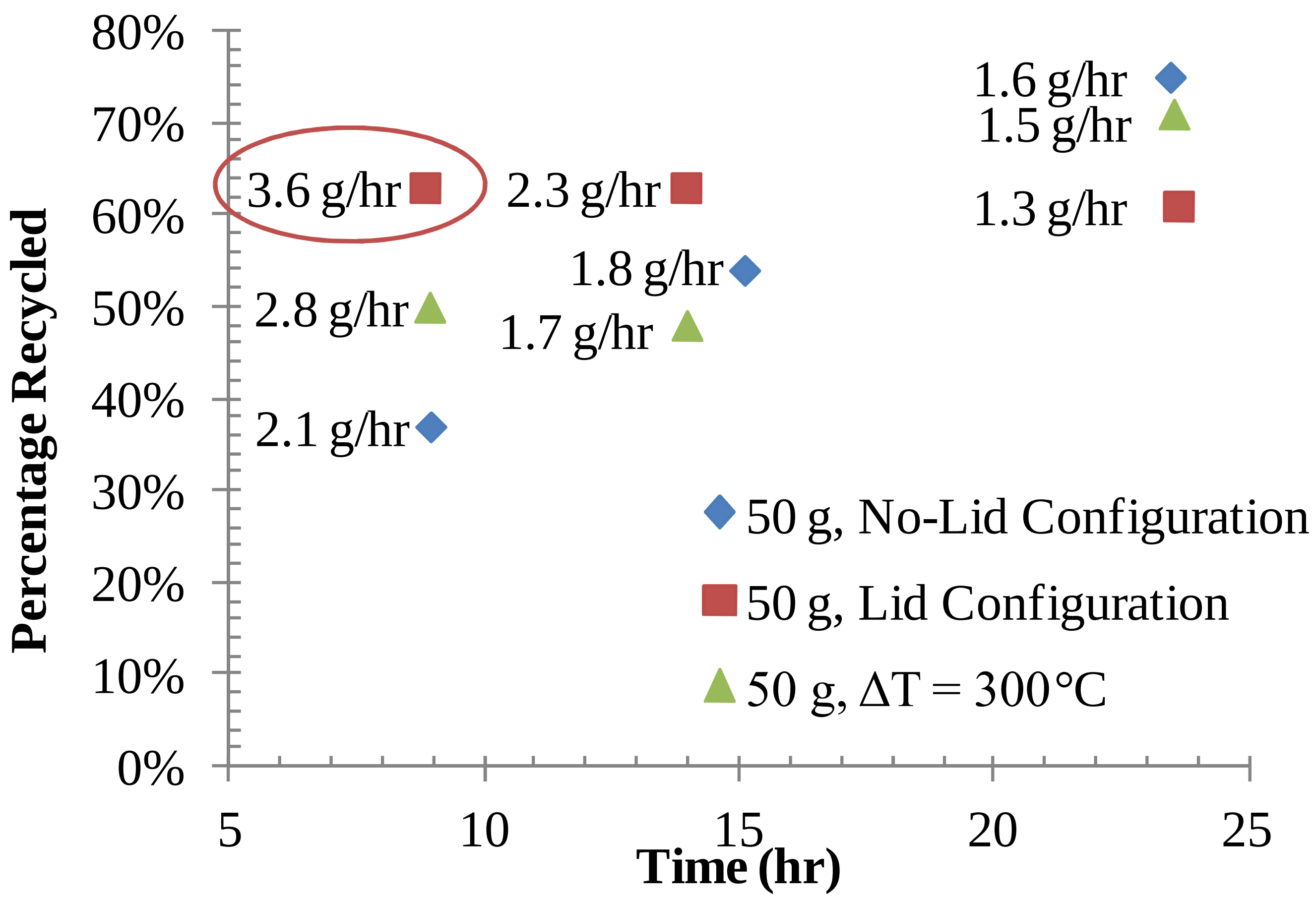
CsCl Buildup Profiles



Experimental Results

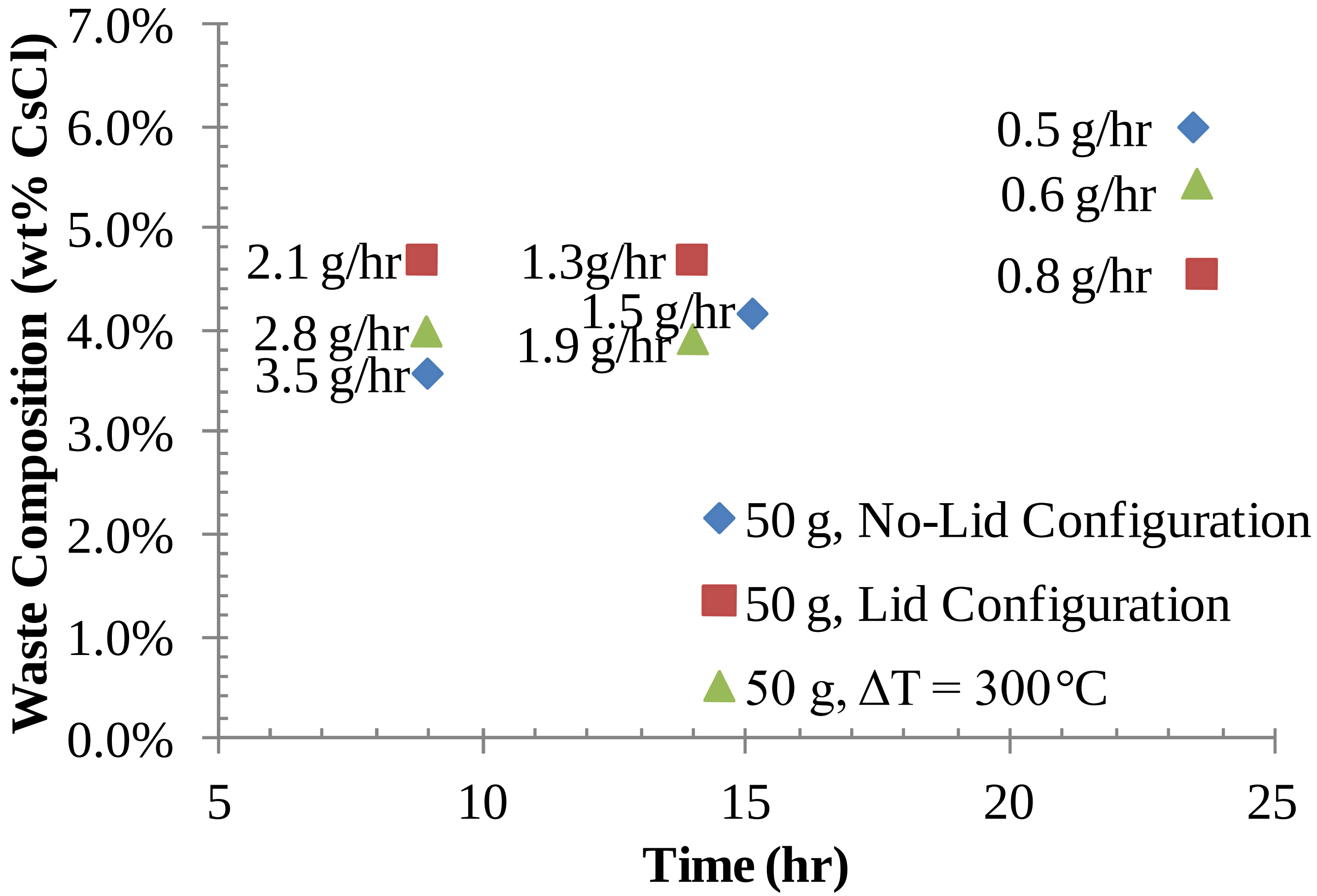
Percentage of Recycled Salt (2 wt % CsCl Purity, 50 g batches)



- The 400 g experiments showed increased recycle percentages and high throughputs.
- Assumed that all experimental conditions will have increased performance for larger mix sizes.

Experimental Results

Waste Composition (2 wt% CsCl Recycled Purity, 50 g batches)



- Recommend multiple stages to further reduce waste.

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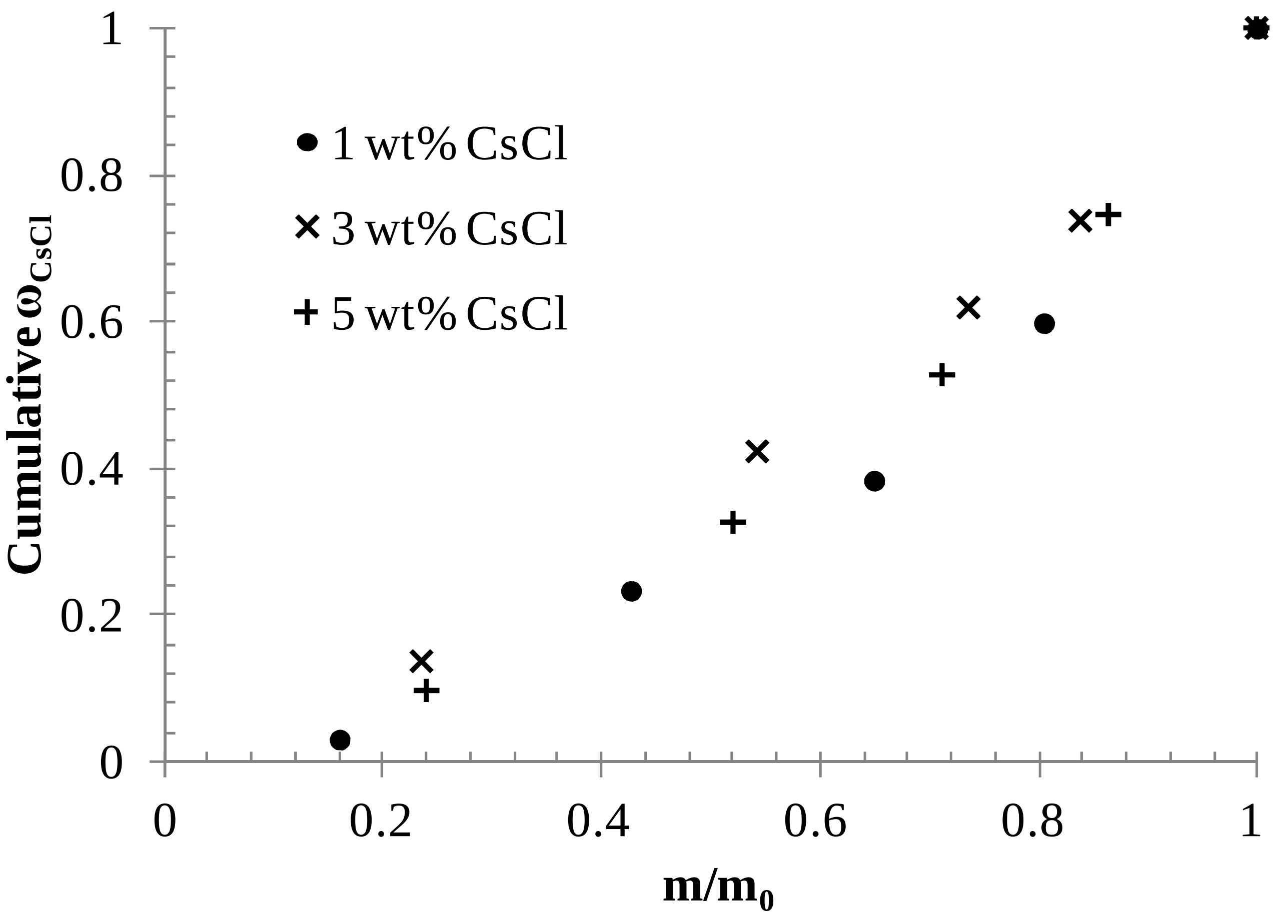
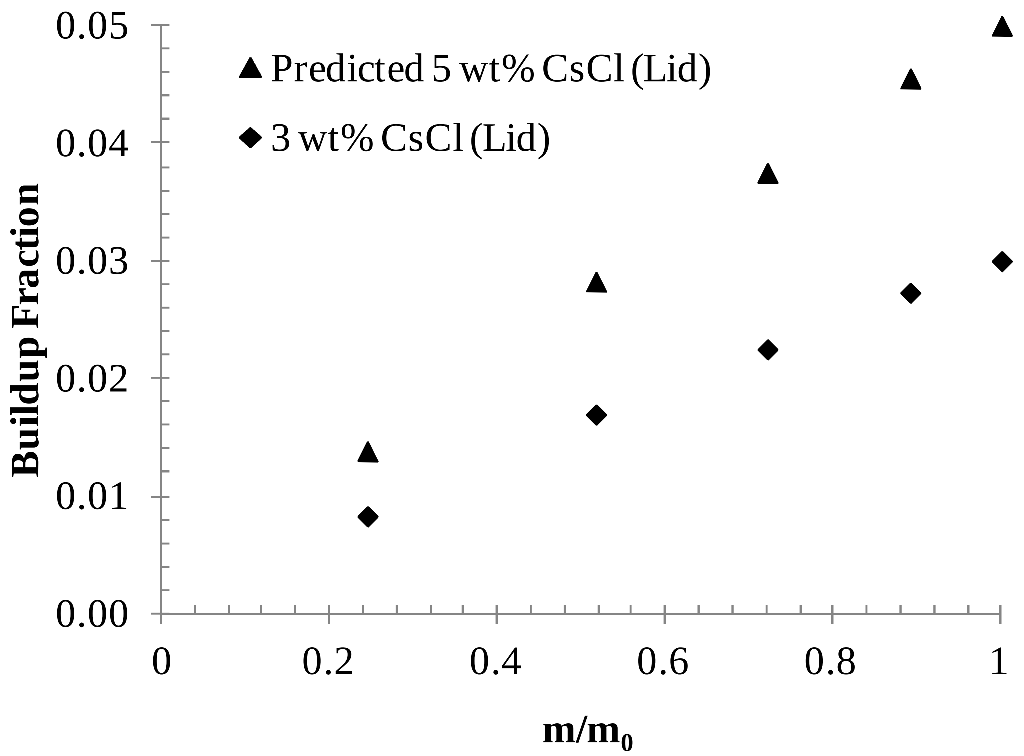
1 wt%, 3 wt%, and 5 wt% CsCl Experiments



Multiple Stages?



- ↑ initial compositions → diminishing returns.
- Recommended Conditions:
  - 5.0 mm/hr rate with a lid configuration with 4 stages.
  - Total recycle percentage of 86% and recycle throughput of 2.75 g/hr (waste = 0.44 g/hr at 9 wt% CsCl).

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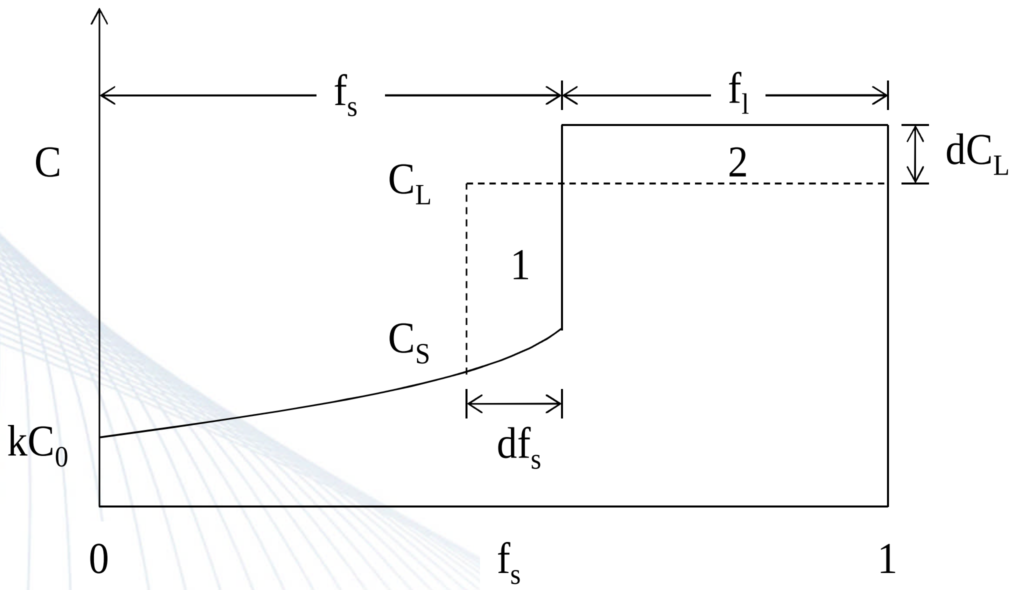
Scheil Model

- Model Assumptions:
  - Segregation coefficient (k_{eff}) is constant.
  - No concentration gradient in the liquid (**well-mixed**).
  - Equilibrium prevails at the interface.



Governing Eqn.:

$$(C_L - C_S)df_S = (1 - f_S)dC_L \qquad \text{Eqn.1}$$

Solution:

$$C_S = k_{eff} C_0 (1 - f_S)^{k_{eff} - 1} \qquad \text{Eqn.2}$$

where,
C_S = Solid Conc., C_L = Liquid Conc.,
C_0 = Initial Conc., k_{eff}= C_S/C_B, and
f_S = Fraction Solidified

E. Scheil, Zeitchrift fur Metallkunde, 23, 237, (1931) and W. G. Pfann, Journals of Metals, 4, 747 (1952).

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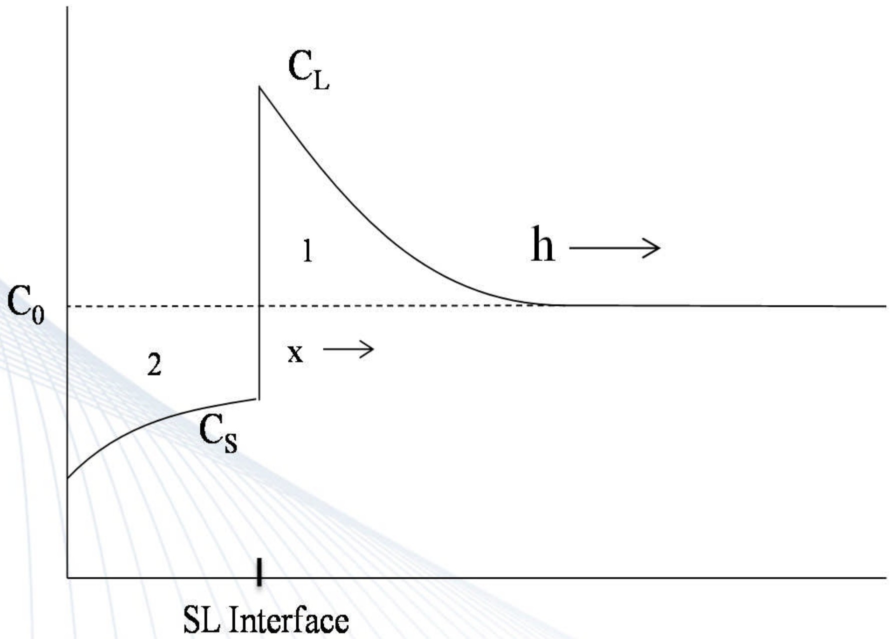
Tiller Model

- Model Assumptions:
  - Segregation coefficient (k) is constant.
  - A concentration boundary layer (δ) exists with **no mixing**.
  - Equilibrium prevails at the interface.
  - Neglects end effects.



Governing Eqn.:

$$D\frac{d^2C}{dx^2} + R\frac{dC}{dx} = 0 \qquad \text{Eqn. 3}$$

Solution:

$$C_S = C_0\left((1-k)\left[1-\exp\left(-k\frac{R}{D}h\right)\right]+k\right) \qquad \text{Eqn. 4}$$

where,

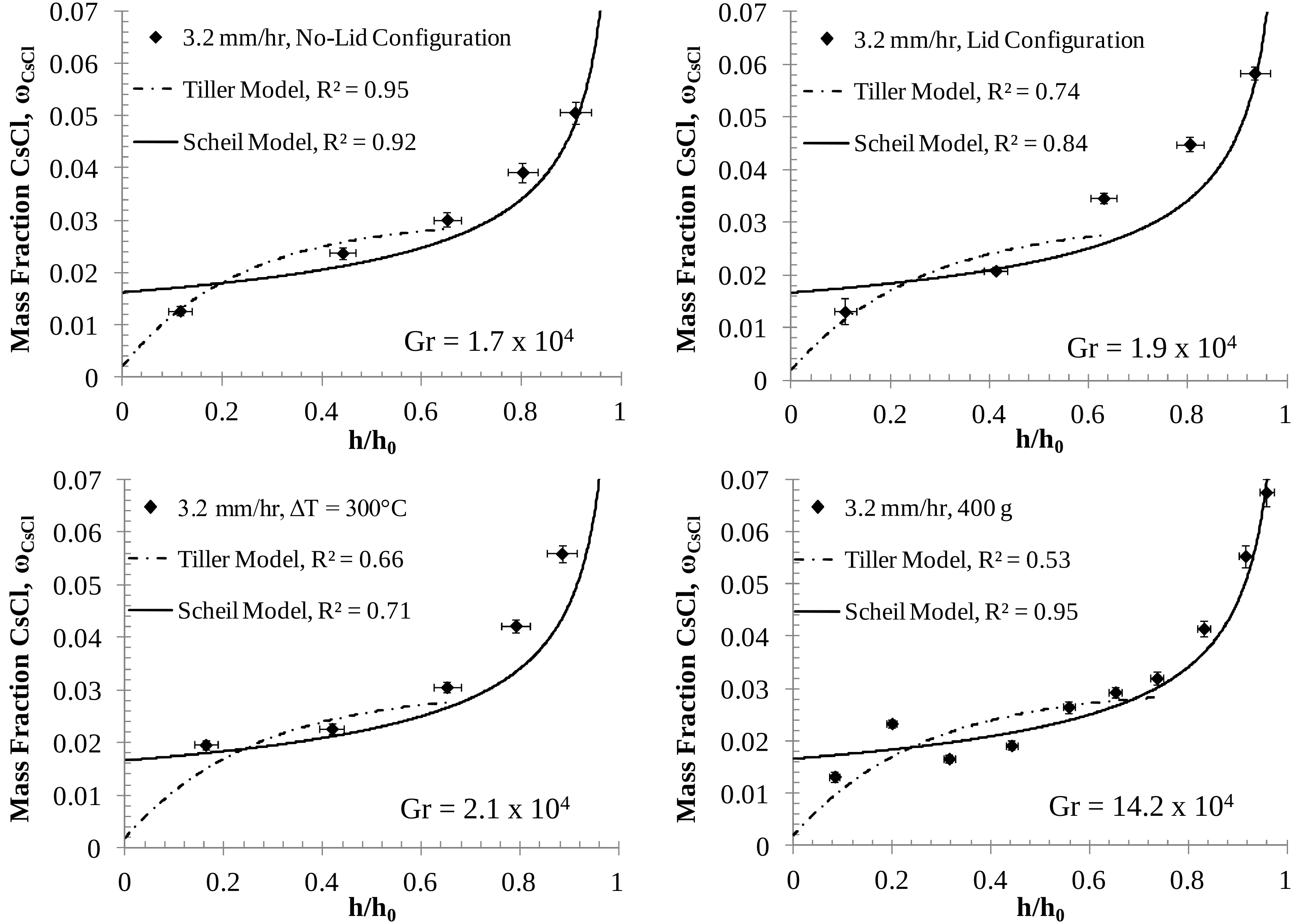
C = Concentration, $k = C_S/C_L$,

R = growth rate, and D = Diffusion Coefficient.

W. A. Tiller, K. A. Jackson, J. W. Rutter, B. Chalmers, Acta Metallurgica, 1, 428-437 (1953).

Modeling Results

Comparison Between Models



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Hybrid Model

- Use a simple weighted average method between the two models to get:

$$C_{Hybrid} = C_{Tiller}\left(1 - \frac{h}{h_0}\right) + C_{Scheil}\left(\frac{h}{h_0}\right) \qquad \text{Eqn. 5}$$

- k and k_{eff} are the same for parameters used in their respective equations.
- Simulates a system transitioning from a diffusion dominant to convection dominant regime.

Modeling Results

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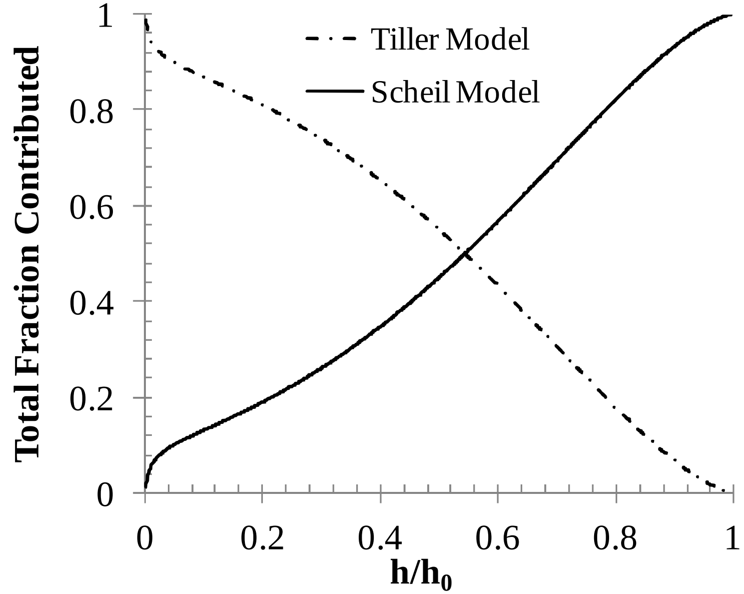
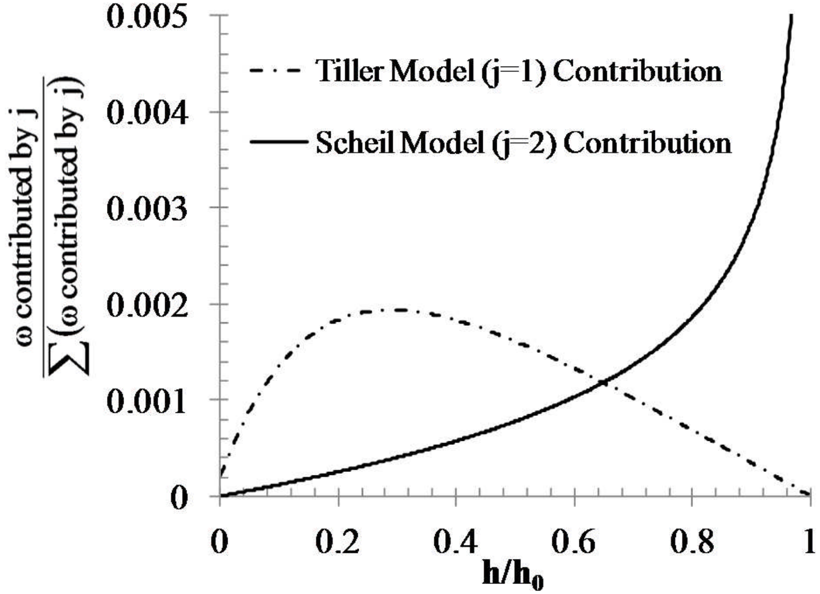
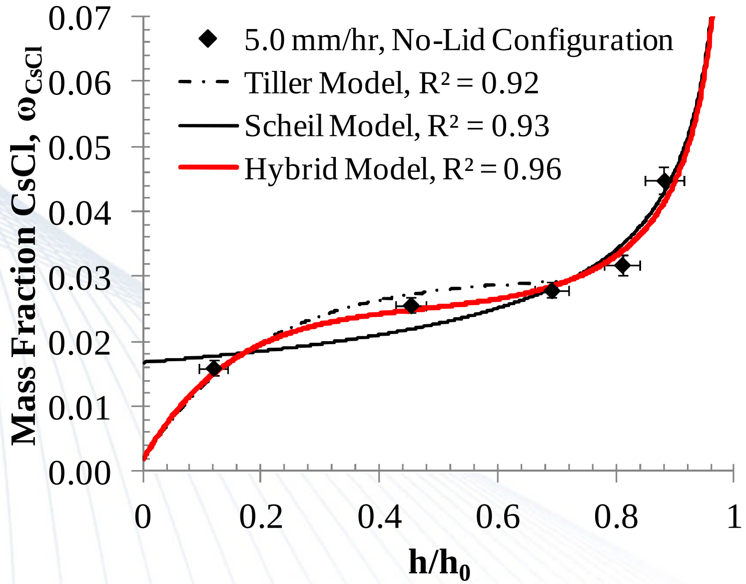
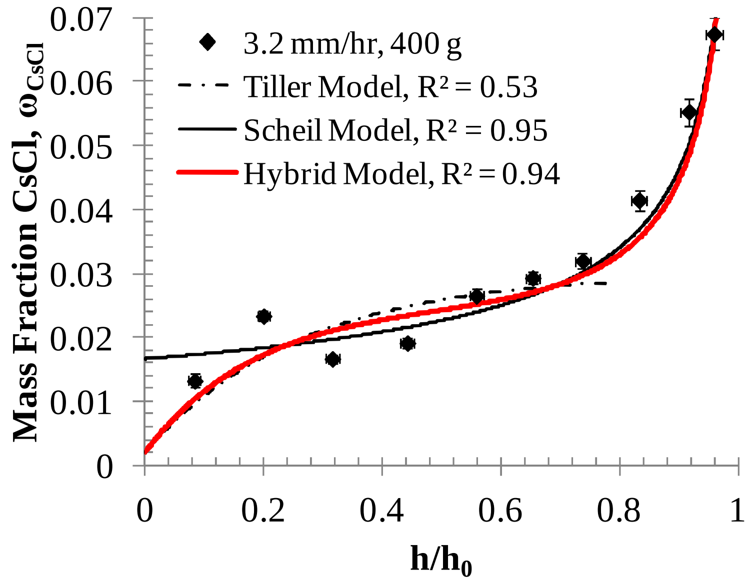
Hybrid Model









Conclusions

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- Optimal operating parameters are:
  - 400 g mixture,
  - 5.0 mm/hr,
  - $\Delta T = 200^{\circ}C$,
  - Lid Configuration.
- Multiple stages can be used to decrease waste volume.
- The Scheil model fits best the 400 g and $\Delta T = 300^{\circ}C$ cases.
- The hybrid model fits best the 50 g, lid and no-lid configurations, but can be used for all cases.

Acknowledgments

A Special Thanks:

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Thank you for your attention!