ZONE FREEZING STUDY FOR PYROCHEMICAL PROCESS WASTE MINIMIZATION

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Outline

• Background, Motivation, and Goals
• Experimental Method
• Experimental Results
• Model Development
• Modeling Results
• Conclusions and Recommendations
• Acknowledgments
An ion exchange process has been proposed as a method of removing fission products from the electrolyte salt.†

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

Experimental Methods

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.

<table>
<thead>
<tr>
<th>Advancement rate (mm/hr)</th>
<th>1 wt% CsCl</th>
<th>3 wt% CsCl</th>
<th>5 wt% CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>3.2</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>5.0</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Experimental Methods

Material Configuration & Sampling

Thermocouples

Drilled Sampling Holes

Salt

Alumina Crucible

Filler Material

Collected Sample
Experimental Results

Grown Salt Crystals

1.8 mm/hr (Lid)  
Top View

3.2 mm/hr (Lid)  
Bottom View

5.0 mm/hr (Lid)
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 ($\rho$, $\nu$, and $D$).
Experimental Results

Concentration Profiles & Analysis

![Graph showing concentration profiles](image)

- Local concentration $\omega_{CsCl}$ vs. $h/h_0$
- $1.8 \text{ mm/hr}$
- Fraction buildup

$$Buildup\ Fraction_{n} = \frac{\sum_{i=1}^{n} m_{CsCl_i}}{\sum_{i=1}^{n} m_{Salt_i}}$$
Experimental Results

CsCl Buildup Profiles

Buildup Fraction

$m/m_0$

1.8 mm/hr (No Lid)
3.2 mm/hr (No Lid)
5.0 mm/hr (No Lid)
1.8 mm/hr (Lid)
3.2 mm/hr (Lid)
5.0 mm/hr (Lid)
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.
Experimental Results

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

Cumulative $\omega_{\text{CsCl}}$ vs. $m/m_0$ for:
- 1 wt% CsCl (represented by black filled circles)
- 3 wt% CsCl (represented by black crosses)
- 5 wt% CsCl (represented by black plus signs)
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).

**Experimental Results**

![Graph showing buildup fraction against m/m₀, with data points for predicted 5 wt% CsCl (Lid) and 3 wt% CsCl (Lid).]
Model Development

Scheil Model

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

Governing Eqn.:
\[
(C_L - C_S)df_s = (1 - f_s)dC_L \quad \text{Eqn. 1}
\]

Solution:
\[
C_S = k_{\text{eff}} C_0 (1 - f_s)^{k_{\text{eff}} - 1} \quad \text{Eqn. 2}
\]

where,
- $C_S$ = Solid Conc., $C_L$ = Liquid Conc.,
- $C_0$ = Initial Conc., $k_{\text{eff}} = C_S/C_B$, and
- $f_s$ = Fraction Solidified

Model Development

Tiller Model

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

Governing Eqn.:
\[
D \frac{d^2C}{dx^2} + R \frac{dC}{dx} = 0 \quad \text{Eqn. 3}
\]

Solution:
\[
C_s = C_0 \left( 1 - k \left( 1 - \exp \left( -k \frac{R}{D} h \right) \right) + k \right) \quad \text{Eqn. 4}
\]
where,
\( C \) = Concentration, \( k = C_s/C_L \),
\( R \) = growth rate, and \( D \) = Diffusion Coefficient.

Modeling Results

Comparison Between Models

- 3.2 mm/hr, No-Lid Configuration
  - Tiller Model, $R^2 = 0.95$
  - Scheil Model, $R^2 = 0.92$
  - $\text{Gr} = 1.7 \times 10^4$

- 3.2 mm/hr, Lid Configuration
  - Tiller Model, $R^2 = 0.74$
  - Scheil Model, $R^2 = 0.84$
  - $\text{Gr} = 1.9 \times 10^4$

- 3.2 mm/hr, $\Delta T = 300°C$
  - Tiller Model, $R^2 = 0.66$
  - Scheil Model, $R^2 = 0.71$
  - $\text{Gr} = 2.1 \times 10^4$

- 3.2 mm/hr, 400 g
  - Tiller Model, $R^2 = 0.53$
  - Scheil Model, $R^2 = 0.95$
  - $\text{Gr} = 14.2 \times 10^4$
Hybrid Model

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

\[
C_{Hybrid} = C_{Tiller}\left(1 - \frac{h}{h_0}\right) + C_{Scheil}\left(\frac{h}{h_0}\right)
\]

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.
Hybrid Model

Modeling Results

Hybrid Model

- Tiller Model
- Scheil Model

Mass Fraction CsCl, $\omega_{CsCl}$

- 5.0 mm/hr, No-Lid Configuration
  - Tiller Model, $R^2 = 0.92$
  - Scheil Model, $R^2 = 0.93$
  - Hybrid Model, $R^2 = 0.96$

- 3.2 mm/hr, 400 g
  - Tiller Model, $R^2 = 0.53$
  - Scheil Model, $R^2 = 0.95$
  - Hybrid Model, $R^2 = 0.94$
Conclusions

• 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.
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Thank you for your attention!