Experimental Studies of Oxygen Sparging in Molten Salt Through a Transparent Furnace

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Alternative Proposed Processes

- Chopped Fuel
  - Metal Waste
    - High Purity Electrolyte
  - Electrorefiner and Product Refinement
    - Contaminated Electrolyte
      - Rare Earth Oxidative Precipitations
        - Ion Exchange
        - Zone Freezing
          - Ceramic Waste
  - Uranium Metal
    - High Purity Electrolyte
Motivation and Approach

Korea Atomic Energy Research Institute (KAERI) observed gravity separation of oxides in molten salt.¹

Motivation
There is a lack of fundamental study to provide insight into systematic parameters in molten salt

Approach
Use transparent cell, high speed camera and O₂ sensor to obtain concentration data, bubble distribution and reaction rates.

\[
\begin{align*}
(1) \quad \text{RECl}_3 + \frac{1}{2} \text{O}_2 & \rightarrow \text{REOCl} + \text{Cl}_2 \\
(2) \quad \text{RECl}_3 + \text{O}_2 & \rightarrow \text{REO}_2 + \frac{3}{2} \text{Cl}_2 \\
(3) \quad \text{RECl}_3 + \text{O}_2 & \rightarrow \frac{1}{2} \text{RE}_2\text{O}_3 + \frac{3}{2} \text{Cl}_2
\end{align*}
\]

Experimental Setup and Plans

- Melt 150 g of LiCl-KCl eutectic salt (58.5 mol% LiCl, 41.5 mol% KCl) at 500°C under an argon environment.
- \( \text{O}_2 \) Sparging Rates: \((8.33 \times 10^{-7}, 1.67 \times 10^{-6}, 2.50 \times 10^{-6}, 3.33 \times 10^{-6})\) m\(^3\)/s. Note: (0.05, 0.10, 0.15, 0.20) L/min.
- Record bubble images (250 fps) and \( \text{O}_2 \) concentration data (± 3%).
- Sparge until salt is \( \text{O}_2 \) saturated.
Obstacles

Corrosion Issues

304 Stainless Steel

Inconel 600

Solution

Non-porous Alumina
(Aluminum oxide)
3/16” OD 0.031” holes.
Bubble Dispersion Video

Temperature: 500⁰ C
Sparging Rate: 8.33 \times 10^{-7} m^3/s
Camera Speed: 250 fps
Sample Size: 150 g
Transparent Study Analysis

\[ V_{\text{Ellipsoid}} = \frac{\pi}{6} b_{\text{Large}} b_{\text{Small}}^2 \]

\[ b_{\text{Equivalent}} = \left( \frac{6}{\pi} V_{\text{Ellipsoid}} \right)^{1/3} \]

Bubble velocity is also observed.

<table>
<thead>
<tr>
<th>Sparging rate, ( Q ) (m(^3)/s)</th>
<th>Number mean diameter, ( b_{10} ) (m)</th>
<th>Number standard deviation, ( \sigma_{10} ) (m)</th>
<th>Volume mean diameter, ( b_{30} ) (m)</th>
<th>Sauter mean diameter, ( b_{32} ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 8.33 \times 10^{-7} )</td>
<td>0.00263</td>
<td>0.00073</td>
<td>0.00301</td>
<td>0.00304</td>
</tr>
<tr>
<td>( 1.67 \times 10^{-6} )</td>
<td>0.00368</td>
<td>0.00112</td>
<td>0.00421</td>
<td>0.00438</td>
</tr>
<tr>
<td>( 2.50 \times 10^{-6} )</td>
<td>0.00383</td>
<td>0.00118</td>
<td>0.00466</td>
<td>0.00455</td>
</tr>
<tr>
<td>( 3.33 \times 10^{-6} )</td>
<td>0.00407</td>
<td>0.00103</td>
<td>0.00451</td>
<td>0.00459</td>
</tr>
</tbody>
</table>
Bubble Shape Validation

Conditions of Curve
- Log $M = -10$
- Eotvos Number 0.2-40
- Reynold’s Number 300-4000

Experimental Results
- Log $M = -10.1304$
- Eotvos Number 0.54-8.94
- Reynold’s Number 344-2406

$Eo = g \Delta \rho d_{\text{equiv}}^2 / \sigma$

$M = g \mu^4 \Delta \rho / \rho^2 \sigma^3$

$Re = \rho d_{\text{equiv}} V_b / \mu$

<table>
<thead>
<tr>
<th>Salt viscosity, $\mu_c$ (N s/m$^2$)</th>
<th>Salt density, $\rho_c$ (kg/m$^3$)</th>
<th>Surface tension, $\sigma_c$ (N/m)</th>
<th>Oxygen density, $\rho_b$ (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00223</td>
<td>1,621</td>
<td>0.126</td>
<td>0.457</td>
</tr>
</tbody>
</table>

[7]
The normally distributed probability density function:

\[ f(\beta) = \frac{1}{\sigma_\beta \sqrt{2\pi}} \exp\left[ -\frac{1}{2} \left( \frac{\beta - \bar{\beta}}{\sigma_\beta} \right)^2 \right] \]

\[ \beta = \frac{b}{b_{10}} = 1.004 \pm 0.027 \quad \text{and} \quad \sigma_\beta = 0.255 \pm 0.018 \]
Fanning Friction Ratio

<table>
<thead>
<tr>
<th>Sparging Rate, $Q$ (m$^3$/s)</th>
<th>Mean Bubble Rising Velocity, $V_b$ (m/s)</th>
<th>Standard Deviation (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.33 \times 10^{-7}$</td>
<td>0.262</td>
<td>0.0510</td>
</tr>
<tr>
<td>$1.67 \times 10^{-6}$</td>
<td>0.301</td>
<td>0.0998</td>
</tr>
<tr>
<td>$2.50 \times 10^{-6}$</td>
<td>0.299</td>
<td>0.0554</td>
</tr>
<tr>
<td>$3.33 \times 10^{-6}$</td>
<td>0.338</td>
<td>0.0770</td>
</tr>
</tbody>
</table>

\[
\frac{f}{Re_b} = \frac{4}{3} \frac{g \mu_c}{\rho_c} \left( \frac{\rho_c - \rho_b}{\rho_c} \right)
\]

Using this correlation, the rising velocity of a bubble can be estimated based on the equivalent diameter of a bubble.
Oxygen Gas Holdup, $\phi$

**Experimental Approach:**

$$\phi = \frac{V_S}{V_b} \quad \text{and} \quad V_S = \frac{4Q}{\pi D^2}$$

**Akita and Yoshida’s Correlation (1973):**

$$\frac{\phi}{(1-\phi)^4} = 0.32 N_{Bo}^{0.121} N_{Ga}^{0.086} \left(\frac{\rho_b}{\rho_c}\right)^{0.068} N_{Fr}$$

<table>
<thead>
<tr>
<th>Sparging rate, $Q$ (m$^3$/s)</th>
<th>Experimental (Dimensionless)</th>
<th>Akita and Yoshida (Dimensionless)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.33 \times 10^{-7}$</td>
<td>0.00169</td>
<td>0.00174</td>
<td>3.09</td>
</tr>
<tr>
<td>$1.67 \times 10^{-6}$</td>
<td>0.00294</td>
<td>0.00345</td>
<td>17.4</td>
</tr>
<tr>
<td>$2.50 \times 10^{-6}$</td>
<td>0.00427</td>
<td>0.00514</td>
<td>19.2</td>
</tr>
<tr>
<td>$3.33 \times 10^{-6}$</td>
<td>0.00523</td>
<td>0.00681</td>
<td>30.3</td>
</tr>
</tbody>
</table>

**Bond Number**

$$N_{Bo} = \frac{gD^2 \rho_c}{\sigma_c}$$

**Galileo Number**

$$N_{Ga} = \frac{gD^3}{\nu_c^2}$$

**Froude Number**

$$N_{Fr} = \frac{V_S}{(gD)^{1/2}}$$
O$_2$ Mass Transfer Coefficient

- Calculate the interfacial area of an average equivalent bubble:
  \[ a = \frac{6\phi}{b_{32}} \]

- Oxygenation model:
  \[ \frac{dC}{dt} = \frac{ka}{(1 - \phi)} (C^* - C) \]

- After integration with the I.C. $t = 0$, $C = C_0$:
  \[ \ln(C^* - C) = \ln(C^* - C_0) - \frac{ka}{(1 - \phi)} t \]

- $k$ = Mass Transfer Coefficient
- $C^*$ = Concentration at saturation
- $C_0$ = Initial concentration
- $C$ = Concentration at specific time
- $\phi$ = Gas hold up
- $a$ = Interfacial area
- $V_s$ = Superficial gas velocity
- $V_b$ = Bubble rise velocity
- $Q$ = Gas flow rate
- $D$ = Crucible diameter
- $b_{32}$ = Sauter mean diameter
Plot and Resulting $k$ values

<table>
<thead>
<tr>
<th>Sparging rate, $Q$ (m³/s)</th>
<th>Slope, $ka(1-\Phi)$ (s⁻¹)</th>
<th>Interfacial area, $a$ (m⁻¹)</th>
<th>Mass transfer coefficient, $k$ (m/s)</th>
<th>95% Confidence Interval (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.33 \times 10^{-7}$</td>
<td>0.0032</td>
<td>3.33</td>
<td>0.00096</td>
<td>18.9</td>
</tr>
<tr>
<td>$1.67 \times 10^{-6}$</td>
<td>0.0029</td>
<td>4.03</td>
<td>0.00072</td>
<td>18.9</td>
</tr>
<tr>
<td>$2.50 \times 10^{-6}$</td>
<td>0.0035</td>
<td>5.63</td>
<td>0.00068</td>
<td>26.2</td>
</tr>
<tr>
<td>$3.33 \times 10^{-6}$</td>
<td>0.0027</td>
<td>6.82</td>
<td>0.00039</td>
<td>14.7</td>
</tr>
</tbody>
</table>
**Diffusion Coefficient**

- Use the experimental k value to predict $D_L$.
- Use 3 correlations based on two different frames of preferences: (1) physics of the bubble and (2) systematic physical properties.

**Penetration theory:**

$$D_L = \frac{\pi k^2 b_{32}}{4 V_b}$$

**Calderbank and Moo-Young (1960):**

$$D_L \propto k^2 \mu_c^{1/3} \rho_c^{1/3} / (g\Delta\rho)^{2/3}$$

**Akita and Yoshida (1973):**

$$D_L \propto k^2 D^{0.26} \sigma_c^{0.24} \phi^{0.06} / (g^{0.66} \mu_c^{0.16} \rho_c^{0.08})$$

<table>
<thead>
<tr>
<th>Sparging Rate (m$^3$/s)</th>
<th>Penetration Theory</th>
<th>Calderbank and Moo-Young</th>
<th>Akita and Yoshida</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.33 \times 10^{-7}$</td>
<td>$8.40 \times 10^{-9}$</td>
<td>$1.28 \times 10^{-8}$</td>
<td>$2.43 \times 10^{-8}$</td>
</tr>
<tr>
<td>$1.67 \times 10^{-6}$</td>
<td>$5.89 \times 10^{-9}$</td>
<td>$7.21 \times 10^{-9}$</td>
<td>$1.42 \times 10^{-8}$</td>
</tr>
<tr>
<td>$2.50 \times 10^{-6}$</td>
<td>$5.82 \times 10^{-9}$</td>
<td>$6.43 \times 10^{-9}$</td>
<td>$1.30 \times 10^{-8}$</td>
</tr>
<tr>
<td>$3.33 \times 10^{-6}$</td>
<td>$1.65 \times 10^{-9}$</td>
<td>$2.12 \times 10^{-9}$</td>
<td>$4.44 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
Conclusion

- Both bubble size and rise velocity increase with an increase in oxygen sparging rate.
- $b_{10}$ ranged from 0.00263 m to 0.00407 m.
- These bubbles form an ellipsoidal shape and the equivalent bubble diameters of the populations observed were normally distributed.
- The bubble rise velocities can be predicted using a Fanning friction factor-Reynolds number correlation.
- $k$ can be calculated experimentally using the oxygenation model and ranged from $3.94 \times 10^{-4}$ m/s to $9.61 \times 10^{-4}$ m/s.
- The results show a downwards trend with an increase in sparging rate or an increase in bubble size which is supported by observations reported by previous researchers (Calderbank et al., 1960; Kulkarni, 2007).
- Diffusion coefficients were calculated using three correlations and compared.
- Penetration theory is the most robust of these models yielding diffusivity values between $1.65 \times 10^{-9}$ m$^2$/s and $8.40 \times 10^{-9}$ m$^2$/s, which is supported by literature (Cussler, 1984; Sada et al., 1984).
Acknowledgement

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Questions?