Modeling of Clogging / Erosion of Nozzle Refractories

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Presentation

• Problem statement
• Model Description
• Model equation derivations and validations
• Post processing
• Picking diffusion coefficients
• Results and estimations
• Summary
Problem Statement

• Nozzle Clogging commonly plagues the steel industry
• Clogging and erosion leads to detrimental inclusions in the final product
• Many complex coupled phenomena govern the process: turbulent flow, multi-component multi-phase thermodynamics, ion-diffusion (in bulk, solid-phase, liquid-phase, and grain-boundaries), chemical reactions (e.g. graphite oxidation, spinel formation, etc.)

Keith Rackers thesis, 1995

Adding CaO can liquefy Al$_3$O$_3$ inclusions

Doloma nozzles utilize this concept to prevent clogging
**Nozzle Clogging & Erosion Mechanisms**

- Clogging: solid alumina (Al$_2$O$_3$) inclusion particles in the steel flow come in contact with nozzle walls.

- Doloma (CaO-MgO) nozzle: diffuses calcia (CaO) through nozzle to liquify the inclusions & prevent clogging.

- Liquid layers/regions form and particles are released and walls erode with time.

**Objectives**

- Develop Numerical model (using finite element analysis) to simulate multi-component ion-diffusion, nozzle reactions / phase transformations, erosion, and clogging.

- Use model to predict
  - The dissolution and sweeping away of alumina inclusions
  - Composition of released inclusions
  - Composition evolution and liquefaction of nozzle wall
  - Removal rate of CaO (wall erosion)
  - Particle removal rates
Model Description

- The nozzle erosion / clogging mechanism will be modeled in 3 microscopic stages:
  - Stage 1: Removal of inclusion particles that touch wall surface, diffuse, partially liquefy, and are carried away, eroding nozzle wall
  - Stage 2: Gradual liquidation of nozzle wall, entrainment of inclusions that touch, and formation of liquid/inclusion matrix layers in the wall
  - Stage 3: Inclusion build up on nozzle surface such that the nozzle wall can no longer liquefy all the inclusions present at the interface.
Stage 1:
Particle becomes liquefied

Nozzle – Stage 1

Stage 1:
Particle becomes liquefied

CaO Concentration Profile

Al$_2$O$_3$ Concentration Profile

Inclusion Particle

Nozzle Wall
Stage 1:
Liquefied inclusion removed by force of flow

Stage 2:
- Nozzle wall becomes liquefied
- Particles stick to liquid wall, form liquid/inclusion matrix
- Inclusions still liquefied (i.e. no solidification)
Nozzle – Stage 3

Stage 3
• Inclusions build up on nozzle wall preventing further liquefaction
• As a result, solidification of the liquid/inclusion matrix can take place.

Used Nozzles

Casting time = 191 minutes
Doloma Graphite SEN

- Original thickness ~ 20 mm
- Measurements taken at 50 mm intervals

Donald Griffin, Rob Nunnington LWB, 2007
Nozzle wall microstructure

Casting time = 191 minutes
Doloma Graphite SEN

~ 3 mm of wear/erosion

Region of lower wear (top of SEN)
Region of higher wear (near bottom of SEN)

Original surface
Relatively small wear

4 mm

1.3 mm

Donald Griffin, Rob Nunnington, LWB, 2007

Modeling Assumptions

• Diffusion equation is solved for activity
• Assume activity = concentration everywhere in the domain
• Diffusion based on Al₂O₃ concentration, assumed to govern the diffusion process due to low diffusivity
• 1-D assumption (3-D inclusion effects incorporated)
• Assume inclusion particle is initially 100% Al₂O₃
• Assume semi infinite mediums (particle not fully liquid upon release)
• Assume only CaO and Al₂O₃ move by diffusion
• Effects of steel flow not included
• Only MgO and CaO present in new nozzle wall
• Only 3 phase’s considered: Al₂O₃ “rich” (solid), CaO “rich” (solid) and liquid with associated diffusion coefficients
• Temperature gradients ignored across the domain
• Concentration on weight basis
Previous Work

• Roy Maske’s 1-D model of CaO-Al$_2$O$_3$ diffusion couple which used analytical approach to solve diffusion equations
• Analytical equations are limited in their ability to model other effects such as MgO content, etc.

Finite Element Equations

• 1-D diffusion equation

$$\frac{\partial C_\alpha}{\partial t} = \frac{\partial}{\partial x} \left( D_\alpha \frac{\partial C_\alpha}{\partial x} \right)$$

Where: $D_\alpha$ is the diffusivity of phase $\alpha$
- $C_\alpha$, Concentration of a particular specie in phase $\alpha$
- $dx$, is the nodal spacing
- $dt$, is the time step
Finite Element Equations

- Galerkin Finite Element Equation (analogous with heat transfer):

\[
[C]\{\dot{C}_\alpha\} + [k]\{C_\alpha\} = \{F\}
\]

\[
\{\dot{C}_\alpha\} = \frac{\{C_{\alpha\text{new}}\} - \{C_{\alpha\text{old}}\}}{\Delta t}
\]

\[
\{C_\alpha\} = \theta\{C_{\alpha\text{new}}\} + (1-\theta)\{C_{\alpha\text{old}}\}
\]

\(\theta\) determines the time-step method.

\([k] = \sum \int [B]^T [D][B] dV\) Diffusivity Matrix

\([C] = \int [N]^T [N] dV\) Capacitance matrix

\([F] = \sum \int [N]^T F dV\) Force matrix

\([D] = D_a\)

---

**Finite Element Equations**

**Domain**

\[
\begin{bmatrix}
1 - \frac{s}{L} & \frac{s}{L}
\end{bmatrix}
\]

Shape Function(N)

\[
[C_j] = \begin{bmatrix}
\frac{1}{2} & 0 \\
0 & \frac{1}{2}
\end{bmatrix} A_j L_j
\]

Lumped capacitance matrix

\[
[k] = \int \begin{bmatrix}
\frac{1}{L} & \frac{1}{L} \\
\frac{1}{L} & \frac{1}{L}
\end{bmatrix} D_a \begin{bmatrix}
\frac{1}{L} & \frac{1}{L} \\
\frac{1}{L} & \frac{1}{L}
\end{bmatrix} dV = \frac{A_j D_a}{L_j} \begin{bmatrix}
1 & -1 \\
-1 & 1
\end{bmatrix}
\]

Diffusivity matrix
From Galerkin Equation

\[
\begin{bmatrix}
\frac{\partial^2 (AL)}{2} & 0 & 0 \\
0 & \frac{\partial^2 ((AL)_{i+1})}{2} & 0 \\
0 & 0 & \frac{\partial^2 (AL)}{2}
\end{bmatrix}
\begin{bmatrix}
C_i \\
\vdots \\
C_n
\end{bmatrix} = 
\begin{bmatrix}
\frac{AD_i}{L_i} & \frac{AD_{i+1}}{L_{i+1}} & 0 \\
\frac{AD_{i+1}}{L_{i+1}} & \frac{AD_{i+2}}{L_{i+2}} & \frac{AD_{i+3}}{L_{i+3}} \\
0 & \frac{AD_{i+3}}{L_{i+3}} & \frac{AD_{i+4}}{L_{i+4}}
\end{bmatrix}
\begin{bmatrix}
C_i \\
\vdots \\
C_n
\end{bmatrix} + \begin{bmatrix}
\frac{AD_i}{L_i} \\
\frac{AD_{i+1}}{L_{i+1}} \\
\frac{AD_{i+2}}{L_{i+2}}
\end{bmatrix}
\begin{bmatrix}
C_i \\
\vdots \\
C_n
\end{bmatrix} + \begin{bmatrix}
0 \\
\frac{AD_{i+1}}{L_{i+1}} \\
\frac{AD_{i+2}}{L_{i+2}}
\end{bmatrix}
\begin{bmatrix}
\theta C_i \\
\vdots \\
\theta C_n
\end{bmatrix} + \begin{bmatrix}
0 \\
0 \\
\theta C_n
\end{bmatrix}
\]

\[
\begin{bmatrix}
C_{i+1} \\
\vdots \\
C_{n+1}
\end{bmatrix} = \Delta t [\begin{bmatrix}
1 & 0 & 0 \\
-\frac{\lambda}{2} & \frac{\lambda}{2} & 0 \\
0 & -1 & \frac{\lambda}{2}
\end{bmatrix} - \Delta t [\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}] \begin{bmatrix}
C_{i+1} \\
\vdots \\
C_{n+1}
\end{bmatrix}
\]

Assuming constant area,

\[
\begin{bmatrix}
C_{i+1,1} \\
\vdots \\
C_{i+1,10}
\end{bmatrix} = \begin{bmatrix}
2\beta_l & 2\beta_l & 0 \\
2\beta_l & 2\beta_l & 0 \\
0 & 0 & 0
\end{bmatrix} + \begin{bmatrix}
\frac{D_{i+1}}{L_{i+1}} & \frac{D_{i+2}}{L_{i+2}} & 0 \\
\frac{D_{i+2}}{L_{i+2}} & \frac{D_{i+3}}{L_{i+3}} & 0 \\
0 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
C_{i+1} \\
\vdots \\
C_{i+1,10}
\end{bmatrix}
\]

\[
\beta = \frac{D_x \Delta t}{L^2}
\]
Finite Element Equations

- Diffusion coefficient based on phase
- Phase based on concentration (nodal property)
- Geometric averaging of Diffusivities used to determine diffusivity of elements

\[ D^j = \sqrt{D(C^i) \cdot D(C^{i+1})} \]

Nodes: \( i \quad j \quad i+1 \)

Element: 

Equation for LEFT most node in domain:

\[ C^α_i = (1 - 2 β_j) (C^α_i)_{old} + 2 β_j (C^α_{i+1})_{old} \]

Equation for INTERNAL nodes:

\[ C^α_i = β_j (C^α_{i-1})_{old} + (1 - β_j - β_{j+1}) (C^α_i)_{old} + β_{j+1} (C^α_{i+1})_{old} \]

Equation for RIGHT most node in domain:

\[ C^α_i = 2 β_j (C^α_{i-1})_{old} + (1 - 2 β_j) (C^α_i)_{old} \]
Model Validation 1

- Finite element solution compared analytical Solution for single species diffusion and single diffusivity

\[ C(x,t) = C_s + \text{erf} \left( \frac{x}{2\sqrt{\alpha t}} \right) (C_o - C_s) \]

- Analytical Solution,

\[ C(x,t) = C_s + \text{erf} \left( \frac{x}{2\sqrt{\alpha t}} \right) (C_o - C_s) \]

Model Validation 1

- Solutions match

Plot of Concentration as a function of distance and time
Model Validation 2

- Validation against previous analytical model:
  - Single diffusion species
  - Single Diffusivity

Model Validation 3

- Validation against previous analytical model:
  - Single diffusion species
  - Multiple Diffusivities (1 order of magnitude difference)
Post Processing: to model multicomponent materials

How to find compositions using data from diffusion data of single species?

i.e.

\[
\begin{align*}
\text{% Al}_2\text{O}_3 & \quad \text{Previous time step Composition} & \quad \text{Current time step Composition} \\
\text{% CaO} & \quad \text{(of Al}_2\text{O}_3) & \quad \text{% MgO}
\end{align*}
\]

Post Processing – mass flows

• Find mass flow rate, \( \dot{m} \)

From Finite element equations:

\[
\begin{bmatrix}
B_j & -B_j \\
-B_j & B_j + B_{j+1} & -B_{j+1} & B_{j+1} \\
-B_{j+1} & B_{j+1} & B_{j+1} & -B_{j+1}
\end{bmatrix}
\begin{bmatrix}
C_i \\
C_{i+1}
\end{bmatrix} =
\begin{bmatrix}
\dot{V}_i \\
\dot{V}_{i+1}
\end{bmatrix}
\]

Hence, for Node \( i \):

\[
\dot{m} = \dot{V} \times \rho_{\text{mix}}
\]

\[
\dot{m} = \rho_{\text{mix}} \left[ - (B_j) C_{i-1} + (B_j + B_{j+1}) C_i - (B_{j+1}) C_{i+1} \right]
\]

Where:

\[
\dot{V} = \text{Volume flow rate (mm}^3/\text{s)}
\]

\[
B = \frac{AD}{L}
\]

\[
\rho_{\text{mix}} = \text{Mixture Density (kg/mm}^3\text{)}
\]

\[
\rho_{\text{mix}} = \left[ \sum_{n=1}^{\text{species}} \frac{C_n}{\rho_n} \right]^{-1}, \text{for } n \text{ species}
\]

NB: +ve flowing into a node
**Post Processing - Criterion: charge balance**


**Molar Basis**

\[ 2 \text{Al}^{3+} (\text{kmol}) \iff 3 \text{Ca}^{2+} (\text{kmol}) \]

Assume Oxygen and Magnesium atoms have no net diffusion.

**Post Processing – mass ratio calculation**

- Charge balance converted to mass ratio

  **Mass Basis**

  \[ 2\text{Al}^{3+} (\text{kmol}) \times M_{\text{Al}} (\text{kg} / \text{kmol}) \iff 3\text{Ca}^{2+} (\text{kmol}) \times M_{\text{Ca}} (\text{kg} / \text{kmol}) \]

  where; \[ M_{\text{Ca}} = 40.08 \text{ kg/kmol} \quad M_{\text{Al}} = 26.98 \text{ kg/kmol} \]

- Hence, mass flow rate of Ca found as a function of mass flow rate of Al.

\[ \dot{m}_{\text{Ca}} = \dot{m}_{\text{Al}} \left( \frac{2 \times 26.98}{3 \times 40.08} \right) = \dot{m}_{\text{Al}} \times 2.228 \]
Post Processing –
new species composition calculation

• New Composition for species \( n \)

\[
\text{Concentration}_{n}^{\text{New}} = \frac{\text{Nodal mass}_{n}^{\text{Old}} + (\text{mass flow rate}_{n} \times dt)}{\text{Nodal mass}_{n}^{\text{New}}}
\]

Where,
\( dt = \) Time step size in seconds
\( \text{Nodal mass}_{n}^{\text{New}} = \text{Nodal mass}_{n}^{\text{Old}} + (\text{mass flow rate}_{\text{Ca}} + \text{mass flow rate}_{\text{Al}}) \times dt \)

‘\( \text{Old} \)’ = previous time step 
‘\( \text{New} \)’ = current time step

Spherical Assumption

• model single inclusion as a sphere

The normal length, \( b \), can be determine as a function of the distance \( x \) away from the sphere boundary, and the radius, \( R \), of the sphere
Spherical Assumption

• By geometry:

\[
\left(\frac{b}{2}\right)^2 + (R - x)^2 = R^2
\]

Hence,

\[
b = 2 \times \sqrt{R^2 - (R - x)^2}
\]

• Approximate sphere as a series of frustums:

\[
b_1 = 2 \times \sqrt{R^2 - (R - x_1)^2}
\]

\[
b_2 = 2 \times \sqrt{R^2 - (R - x_2)^2}
\]
Spherical Assumption

- Volume of frustums:

\[
Volume = \frac{\pi L}{12} \left( b_1^2 + b_1 b_2 + b_2^2 \right)
\]

\[
L = (x_2 - x_1)
\]

- Area,

\[
Area = \frac{\pi}{12} \left( b_1^2 + b_1 b_2 + b_2^2 \right)
\]

Choosing Diffusivities

- Published diffusion coefficients vary substantially

Up to 6 orders of magnitude difference

<table>
<thead>
<tr>
<th>Element</th>
<th>Diffusion Coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1.0 x 10^{-6}</td>
<td>J. Electrochem. Soc. 1955</td>
</tr>
<tr>
<td>C</td>
<td>5.0 x 10^{-6}</td>
<td>J. Electrochem. Soc. 1955</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0 x 10^{-6}</td>
<td>J. Electrochem. Soc. 1955</td>
</tr>
<tr>
<td>Fe</td>
<td>1.0 x 10^{-6}</td>
<td>J. Electrochem. Soc. 1955</td>
</tr>
</tbody>
</table>

Partly due to solid vs. liquid diffusion

Liquid diffusion coefficient highest

Rob Nunnington, LWB
Choosing Diffusivities

- However CaO on average has the highest diffusivity:
  - CaO movement by diffusion “easier” than Al2O3 movement by diffusion
  - Hence, calculate Al2O3 diffusion only (model)
  - Assume CaO diffuses fast enough to satisfy charge balance, based on local Al2O3 concentration (post processing)

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Choosing Diffusivities

- Diffusivities used:
  - \( D_1 \) (CaO “rich” solid) = \( 1 \times 10^{-6} \) mm\(^2\)/s
  - \( D_2 \) (Liquid-rich) = \( 5 \times 10^{-4} \) mm\(^2\)/s
  - \( D_3 \) (Al\(_2\)O\(_3\) “rich” solid) = \( 1 \times 10^{-9} \) mm\(^2\)/s
Choosing Diffusivities

• Assume liquid diffusivity, D₂, acts on compositions with 50% liquid and above

Isotherm section: 1600°C

100% liquid region

50% Liquid line

Choosing Diffusivities

• Assume a single liquid layer and associated diffusion coefficient.

Single 'liquid' region

\(D_2 = 5 \times 10^{-4} \text{ mm}^2/\text{s}\)

Isotherm section: 1600°C
Choosing Diffusivities

- Single diffusivities for Al₂O₃ “rich” and CaO “rich” regions

Al₂O₃ “rich” region
(D₃ = 1x10⁻⁹ mm²/s)

CaO “rich” region
(D₁ = 1x10⁻⁶ mm²/s)

Isotherm section:
1600 C

Geometric averaging used to determine diffusion coefficients when not in liquid, CaO “rich” or Al₂O₃ “rich” regions

\[ D = D_2 \left( \frac{c-c_1}{c_2-c_1} \right) \times D_1 \left( \frac{c_2-c}{c_2-c_1} \right) \]

\[ D = D_2 \left( \frac{c_4-c}{c_4-c_3} \right) \times D_3 \left( \frac{c-c_3}{c_4-c_3} \right) \]

C = Al₂O₃ Concentration
c₁ to c₄: Al₂O₃ Boundary Concentrations
Choosing Diffusivities

Plot of Diffusion coefficient against $\text{Al}_2\text{O}_3$ concentration MgO concentration = 10% $\times 10^{-4}$

- Log scale

$D_1$ (Nozzle)
$D_2$ (liquid)
$D_3$ (inclusion)

Geometric Averaging region
Results – Stage 1

Model Inputs:
- Model inclusion as spherical particle
- Inclusion diameter = 100 microns
- Contact region with nozzle wall = 20 microns diameter
  (Ratio of max inclusion area to contact area = 25:1)
- Initial nozzle wall composition is 90% CaO, 10% MgO
- Critical liquid layer thickness before particle detachment = 20 microns
- All liquid removed with particle
- Removed particle immediately replaced by another
- Temperature 1600 C

Animation

- First Particle caused wall liquefaction
- Hence, minimum stage 1 duration time is 0 sec
Results – Stage 1

Particle composition

Results – Stage 2

Model Inputs:

– Initial nozzle wall composition is 90% CaO, 10% MgO
– Al₂O₃ concentration fixed at 100% on right domain boundary
– No area variation
– Initial nozzle/particle interface a X = 0
– No material removed
– Temperature 1600°C
Results - Stage 2

- Animation

Comparison with used nozzle measurements

Note that in reality some liquid will be removed by force of steel flow.
Estimation of CaO removal rate

3.1 mm of wear assuming all liquid is removed (worse case scenario)

The mass removed per unit area is therefore $3.1 \times 3.36 \times 10^{-6} = 1.04 \times 10^{-5} \text{ kg/mm}^2$
(Using an approximate wall density $= 3.36 \times 10^{-6} \text{ kg/mm}^3$)

Mass of CaO removed per unit area $= 1.04 \times 10^5 \times 0.9 = 9.4 \times 10^{-6} \text{ kg/mm}^2$

Removal rate of CaO
$= (9.4 \times 10^{-6} \text{ kg/mm}^2) / 190 \text{ mins}$

Removal rate of CaO $= 4.9 \times 10^{-8} \text{ kg/mm}^2 \text{ min}$

Max (upper limit) of CaO ppm in steel final product:
$= 9.3 \times 10^{-3} / 1780 \times 1 \times 10^6$

= 5.2 ppm
Estimation of inclusion limit

Can use liquefied inclusion region to estimate an inclusion limit/maximum that the nozzle can handle before clogging can occur:

- Liquefied inclusions region = 2.2 mm in 190 min (~ 3hrs) from previous figure

- Total mass of inclusions per unit area of nozzle as function of time:
  
  \[ \text{Total mass} = 7.92 \times 10^{-6} \text{ kg/mm}^2 \]  
  (for time = 190 mins)

  or,

\[ \text{Inclusion liquefaction rate} = 4.17 \times 10^{-8} \text{ kg/mm}^2 \text{ min} \]

Estimation of Inclusion limits

Assume an average inclusion particle diameter of 100 microns

Average inclusion mass = \[ \frac{4}{3} \pi (50 \times 10^{-3})^3 \times \text{(density of alumina)} \]  

\[ \approx 4 \times 10^{-6} \text{ kg/mm}^3 \]

Hence,

\[ \text{Inclusion limit} = \frac{\text{total mass of inclusions per unit area time}}{\text{Average inclusion mass}} \]

\[ = \frac{4.17 \times 10^{-8} \text{ kg/mm}^2 \text{ min}}{2.1 \times 10^{-9} \text{ kg}} \]

\[ \approx 20 \text{ inclusion/mm}^2 \text{ min} \]

With an SEN with a surface area = 1.88 \times 10^6 \text{ mm}^2

Inclusion limit = 3.8 million inclusions per min
Estimation of Inclusion limits

- Can express inclusion limit in terms of ppm:

  For the SEN dimensions as shown on the previous slide,

  \[
  \text{Inclusion limit} = 1.88 \times 10^5 \times 4.17 \times 10^{-8} \\
  = 7.84 \times 10^{-3} \text{ kg/min}
  \]

  \[
  \text{Steel flow rate} = 1780 \text{ kg/min} \quad \text{(as shown on slide 54)}
  \]

  \[
  \text{Inclusion limit (ppm)} = \frac{7.84 \times 10^{-3}}{1780} \times 10^6 \\
  = 4.40 \text{ ppm}
  \]

  (Note: This estimate is conservative, as model assumes a continuous \( \text{Al}_2\text{O}_3 \) source)

Interpreting Results

- Assume:
  - a steel flow rate of 1780 kg/min
  - Steel upstream inclusion content of 40 ppm
  - On average 10% of the inclusions come in contact with nozzle wall (4 ppm)
  - Casting time = 190 mins

- Nozzle walls can liquefy 4.4 ppm inclusions, so should not clog in this time
Summary

• 1-D Numerical model of ceramic ion diffusion developed for Al₂O₃ - CaO - MgO refractory systems
• Model tracks the inclusion particle interaction with a nozzle and simulates the stages of inclusion deposition and removal, wall liquefaction and inclusion entrainment and the insufficient liquefaction of inclusions leading to conventional clogging.
• The model provides a frame work for studying composition evolution and the behavior of nozzle/inclusion interactions
• Model results provide estimations of:
  – The removal rate of CaO from doloma nozzle wall
  – The lower limit on the amount of inclusion the nozzle can handle before clogging is likely.
  – The maximum wall erosion

Acknowledgments

• Continuous Casting Consortium Members (Nucor, Postech, LWB Refractories, Algoma, Corus, Labein, Mittal Riverdale, Baosteel, Steel Dynamics)
• Roy Maske (former student)
• Special thanks to Rob Nunnington and Donald Griffin of LWB Refractories for their help.