Ferrous Applications II
<table>
<thead>
<tr>
<th>Application examples</th>
<th>Slide #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag liquidus temperature changing with an additional slag component</td>
<td>3</td>
</tr>
<tr>
<td>Dissolution mechanism of inclusions into molten slag</td>
<td>11</td>
</tr>
<tr>
<td>Non-metallic inclusion formation: oxide metallurgy</td>
<td>14</td>
</tr>
<tr>
<td>Inclusion control in Mn/Si killed steel</td>
<td>18</td>
</tr>
<tr>
<td>Reoxidation of steel - inclusion modification</td>
<td>27</td>
</tr>
<tr>
<td>Deoxidation diagram / Inclusion stability diagram</td>
<td>39</td>
</tr>
<tr>
<td>Inclusion in Al-killed Ti-bearing steel</td>
<td>45</td>
</tr>
<tr>
<td>Refractory dissolution in molten slag (RH degasser)</td>
<td>57</td>
</tr>
<tr>
<td>Ladle glaze formation</td>
<td>62</td>
</tr>
<tr>
<td>Thermal stability of refractory</td>
<td>65</td>
</tr>
<tr>
<td>Refractory / Liquid inclusion interaction</td>
<td>69</td>
</tr>
<tr>
<td>Refractory / Steel interaction</td>
<td>73</td>
</tr>
<tr>
<td>Desulfurization of hot metal and sulfide capacity calculation</td>
<td>79</td>
</tr>
<tr>
<td>Heat evolution during slag cooling and heating: Enthalpy diagram</td>
<td>132</td>
</tr>
<tr>
<td>New private compound database</td>
<td>140</td>
</tr>
<tr>
<td>Addition of ideal solution (private solution)</td>
<td>144</td>
</tr>
<tr>
<td>Addition of new component into slag (Henrian solution)</td>
<td>147</td>
</tr>
<tr>
<td>V$\text{$<em>{2}$O$</em>{3}$}$ addition to liquid slag (Henrian solution: optimization of parameter)</td>
<td>152</td>
</tr>
<tr>
<td>Zn galvanization: control of oxidation in annealing furnace</td>
<td>164</td>
</tr>
<tr>
<td>Zn galvanization: - remelting and oxidation of Zn galvanized steel</td>
<td></td>
</tr>
<tr>
<td>- interface reaction between liquid Zn and solid steel</td>
<td>179</td>
</tr>
<tr>
<td>- oxidation reaction of Zn coating</td>
<td></td>
</tr>
<tr>
<td>Carburization and de-carburization of steel</td>
<td>185</td>
</tr>
<tr>
<td>Viscosity of slags: Einstein-Roscoe equation for semi-liquid state</td>
<td>190</td>
</tr>
</tbody>
</table>
The effect of SiO$_2$/MgO and FeO and Al$_2$O$_3$ in slag on the liquidus temperature of the slag

Phase Diagram / Equilib
Phase diagram of $\text{SiO}_2$-$\text{MgO}$-$\text{Al}_2\text{O}_3$-$\text{FeO}$-$\text{Fe}$

Actually, the $\text{SiO}_2$/MgO ratio of laterite is almost the same as that of the slag produced.

The main system of the FToxid-SLAG phase is $\text{SiO}_2$-$\text{MgO}$-$\text{Al}_2\text{O}_3$-$\text{FeO}$.
Phase diagram of $\text{SiO}_2$-$\text{MgO}$-$\text{Al}_2\text{O}_3$-$\text{FeO}$-$\text{Fe}$

Select pure solid and liquid Fe for Fe-saturation condition.
Phase diagram of SiO₂-MgO-Al₂O₃-FeO-Fe
Phase diagram of \( \text{SiO}_2 - \text{MgO} - \text{Al}_2\text{O}_3 - \text{FeO} - \text{Fe} \)

Ternary phase diagram of \( \text{FeO} - \text{MgO} - \text{SiO}_2 \) at constant \( \text{Al}_2\text{O}_3 \) with Fe-saturation

Add small amount of Fe
Using ‘superimpose’ function, liquidus lines of the ternary system can be drawn.

Impossible to use ‘O’ option because the system always has Fe(s) or Fe(I) with slag, that is always more than 2 phases.
Phase diagram of SiO$_2$-MgO-Al$_2$O$_3$-FeO-Fe

With varying 0 to 8 wt% of Al$_2$O$_3$ at constant SiO$_2$/MgO=1 at Fe-saturation
Phase diagram of $\text{SiO}_2$-$\text{MgO}$-$\text{Al}_2\text{O}_3$-$\text{FeO}$-$\text{Fe}$

$\text{SiO}_2$-$1\text{MgO}/Z \text{ (g/g)} = 0$, $100\text{Al}_2\text{O}_3/Z \text{ (g/g)} = 0$, $100\text{Fe}/Z \text{ (g/g)} = 1$,
$Z=(\text{SiO}_2+\text{MgO}+\text{Al}_2\text{O}_3+\text{FeO}+\text{Fe})$, 1 atm

$100\text{FeO}/(\text{SiO}_2+\text{MgO}+\text{Al}_2\text{O}_3+\text{FeO}+\text{Fe}) \text{ (g/g)}$
Dissolution of Inclusions into Molten Slags

Phase diagram between slag and inclusions to understand the inclusion dissolution mechanism

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M21</th>
<th>M22</th>
<th>M23</th>
<th>M24</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Park, Jung and Lee: ISIJ Inter. No. 11, 2006
Dissolution of Inclusions into Molten Slags

\[(\text{CaO})_{0.525}(\text{SiO}_2)_{0.475}\]

Park, Jung and Lee: ISIJ Inter. No. 11, 2006
Dissolution of Inclusions into Molten Slags

Diagram showing the dissolution process of inclusions in molten slags. The diagram includes a ternary phase diagram with labels for different compositions: 

- \((\mathrm{CaO})_{0.58}(\mathrm{SiO}_2)_{0.42}\)
- \(\mathrm{Al}_2\mathrm{O}_3\)
- \(\mathrm{MgO}\)

The phase diagram illustrates various regions including:

- \(\text{L} + \mathrm{MgO}\)
- \(\text{L} + \mathrm{MgAl}_2\mathrm{O}_4\)
- \(\text{L} + \mathrm{MgO} + \mathrm{MgAl}_2\mathrm{O}_4\)

The diagram also includes a micrograph labeled M3, indicating a specific inclusion or reaction site.

Footnote: Park, Jung and Lee: ISIJ Inter. No. 11, 2006
Evolution of non-metallic inclusions: Formation of acicular ferrite

- Non-metallic inclusions: nucleation sites for acicular ferrite
- Acicular ferrite: enhances the strength of steel
Evolution of Non-metallic Inclusions

Morphologies of typical inclusions found in Fe-C-Mn-Si-O-S-Ti-Mg-Al-N

Concentration of additional alloying element

Fe-0.1C-0.0035S-1.45Mn-0.1Si-0.015Ti-0.0025O-0.03N+Mg
Evolution of Non-metallic Inclusions

Thermodynamic calculations
• Accurate prediction of inclusion phases
• Application to high strength steel design
Inclusion evolution with temperature: Mn/Si/Ti steel

- FToxid: oxide inclusions
- FTmisc: FeLiq, MnS solid (MS_c)
- FSStel: solid steel phases (fcc, bcc)

Select all phases (pure solids and solutions) with amount > 0

Ferrous Applications II 17
Application to Tire-Cord Steel (Mn/Si deoxidation)

- Undeformable inclusion should be removed
- Liquid phase is desirable at process temperature (~1200°C)

Fe-36%Ni Invar Steel

- 0.15~0.38mm diameter
- 150µm thickness

Mn/Si Deoxidation
MnO-Al$_2$O$_3$-SiO$_2$ Phase Diagram

Cristobalite: SiO$_2$
Tridymite: SiO$_2$
Rhodonite: Mn$_2$SiO$_3$
Spessartite: Mn$_3$Al$_2$Si$_3$O$_{12}$
Tephroite: Mn$_2$SiO$_4$
Manganoosite: MnO
Galaxite: MnAl$_2$O$_4$
Corundum: Al$_2$O$_3$
Mullite: Al$_6$Si$_2$O$_{13}$

Low liquidus temperature region
(1100°C ~ 1200°C)

Target inclusion composition

Inclusion composition with steel composition

Inclusion calculation in Mn/Si deoxidation

FactSage®
The compositions of Mn and Si are set based on the target Mn/Si ratio and Mn+Si content. Oxygen content should be controlled reasonably. If O is too high, Mn and Si will be largely changed from original target composition after reaction with oxygen.
Inclusion calculation in Mn/Si deoxidation

\[ \text{Mn} + \text{Si} + \text{Al} + \text{O} \rightarrow (\text{Mn, Si, Al}) \text{ oxide inclusion} \]

After deoxidation, \( \text{Mn} \approx 0.5 \) and \( \text{Si} \approx 0.5 \)

(Target steel composition: \( \text{Mn}/\text{Si} = 1 \) and \( \text{Mn} + \text{Si} = 1 \))

\( \rightarrow \) Extraction of slag composition
Inclusion calculation in Mn/Si deoxidation

Composition from Slag #1

\[ \text{A corner} = \frac{\text{wt}\%\text{SiO}_2}{100} \]
\[ \text{B corner} = \frac{(\text{wt}\%\text{MnO} + \text{Mn}_2\text{O}_3 + \text{FeO} + \text{Fe}_2\text{O}_3)}{100} \]
\[ \text{C corner} = \frac{\text{wt}\%\text{Al}_2\text{O}_3}{100} \]

Slag #1 (stable slag)

Slag #2 (metastable or same as #1 except in case of stable miscibility gap)
Inclusion calculation in Mn/Si deoxidation

Slag composition is slightly different from phase diagram because the actual slag contain Fe₂O and Mn₂O₃ as well.

According to calculations, mullite and Al₂O₃ form subsequently after slag.

Fe Liquid
[\%Mn] + [\%Si] = ~1.0

MnO - Al₂O₃ - SiO₂

T = 1600°C

Mn/Si = 7

1200°C liquidus

Ohta and Suito[34]
Kang and Lee [35]
Inclusion calculation in Mn/Si deoxidation

Soluble Al vs. inclusion composition

Ferrous Applications II  26
Re-oxidation and inclusion modification in the tundish – Ca-treated steel
Reoxidation and inclusion modification in the tundish

The target for Ca treatment
Reoxidation and inclusion modification in the tundish

At 1550°C

Fe+100ppm O
+?Mg
MgO based refractory

Al-killed steel
+ 600ppm Al
+? inclusion

Ca treatment: liquid slag
+ <50ppm Ca
+ ? Inclusion
+ ? Slag

Reoxidation: assuming mainly due to SiO₂-based slag
+ <100ppm SiO₂
+ ? Inclusion
+ ? Slag
Reoxidation and inclusion modification in the tundish

Al-killed steel

Fe+100ppm O

+?Mg

MgO-based refractory

Ferrous Applications II 30
Reoxidation and inclusion modification in the tundish

Only save liquid Fe as stream file for next step

MgO-based refractory
Reoxidation and inclusion modification in the tundish

Al-killed steel

+ 600ppm Al

+? inclusion
Reoxidation and inclusion modification in the tundish

Ferrous Applications II  33

Alumina inclusions cause nozzle clogging

Save all phases as a stream file for next step

Formation of spinel phase
Reoxidation and inclusion modification in the tundish

Ca treatment: liquid slag

+ <100ppm Ca
+ ? Inclusion
+ ? Slag
Reoxidation and inclusion modification in the tundish

100% [Ex4-1(b)] + <A> Ca

Diagram showing the composition of various compounds with labels such as Ca2Mg2Al2O46(s), CaMg2Al3O27(s), SLAGA#1, MeO_A#1, etc. The graph plots the concentration of these compounds against Alpha.
Reoxidation: assuming mainly due to SiO$_2$-based slag

+ <100ppm SiO$_2$
+ ? Inclusion
+ ? Slag

Reoxidation and inclusion modification in the tundish

![Chemical reaction simulation](image)
In this condition, SiO$_2$ is reduced by Al during the reoxidation (instead of Ca).
Reoxidation and inclusion modification in the tundish

Slag composition after Ca treatment (30 ppm Ca)

+ 1.2284E-02 gram  ASlag-liq#1
  (1.2284E-02 gram, 1.5945E-04 mol)
  (1550 C, 1 atm,  a=1.0000)
  (63.328 wt.% Al2O3
  + 33.369 wt.% CaO
  + 6.3444E-03 wt.% FeO
  + 3.9494E-05 wt.% Fe2O3
  + 3.2969 wt.% MgO

Reoxidation direction
Inclusion diagram: Fe-Al-O, Al deoxidation

(1): draw rectangular diagram
Inclusion diagram: Fe-Al-O, Al deoxidation


(3): change linear scale to log scale.

(3): change linear scale to log scale.


"After changing the axes to log scale, move all curves to +2 in linear scale"
Inclusion diagram: Fe-Al-O, Al deoxidation

Fe-liq + M2O3 (Corundum)

(4) Editing of title of x- and y-axis
Inclusion diagram: Fe-Al-Ti-O, Al/Ti deoxidation

Fe-liquid + M\textsubscript{2}O\textsubscript{3} (Corundum)

Fe-liquid + M\textsubscript{2}O\textsubscript{3} (Corundum)

Fe-liquid

M\textsubscript{2}O\textsubscript{3} (corundum) + Fe-liquid

\[\text{log wt\% Al} \quad \text{log wt\% O}\]

\[\text{log wt\% Al} \quad \text{log wt\% Ti}\]

Fe-Al-Ti-O, mass O/(Fe+Al+O+Ti) = 5E-6
Inclusion diagram: Fe-Al-Ti-O, Al/Ti deoxidation

1) Change oxygen content and calculate similar diagram
2) Superimpose all the diagrams together
3) Calculate the phase boundaries from Equilib (or simply connect boundaries in the calculated diagram)
Inclusions after Mn/Si deoxidation

Figure 11: Calculated inclusion stability diagrams in the Fe-Mn-Si-Al-O system at 1550°C for (a) mass% Mn = 0, (b) mass% Mn = 0.5, (c) mass% Mn = 1.0 and (d) mass% Mn = 1.5. Numbers adjacent to each line represent equilibrium oxygen contents (in ppm) in liquid steel [23].
Al-killed Ti-bearing steel
Al-killed Ti-bearing steel

Ferrous Applications II  46
“Recycle all streams”

- You don’t have to save the streams one by one. But the results will be used only one time because it is not saved under a special stream name.
- Convenient option when you want to do just one calculation.
Reoxidation of Al-killed Ti-bearing steel

Addition of oxygen to simulate reoxidation phenomena. Actual source of oxygen could be high-SiO$_2$ slag or refractories.
Reoxidation of Al-killed Ti-bearing steel

This calculation shows that a mixed inclusion of Al$_2$O$_3$(s) and liquid (Al$_2$O$_3$-TiO$_2$-Ti$_2$O$_3$) can be formed by the reoxidation of Al-killed Ti-bearing steel.

→ Nozzle clogging.

$100\% [\text{Rc}_\text{Fe-liq}] + 100\% [\text{Rc}_\text{M2O3(Corundum)}] + <\text{A} > \text{O}_2$

C:\Slag-Steel-Inclusions\Equi0.res 25Sep12

Alpha
gram
0.00 0.01 0.02 0.03 0.04 0.05
0.00
0.05
0.10
0.15
0.20

+ 0.12253 gram ASlag-liq#1
(0.12253 gram, 1.1558E-03 mol)
(1600 C, 1 atm, a=1.0000)
(33.379 wt.% Al2O3
+ 0.17724 wt.% SiO2
+ 0.83830 wt.% FeO
+ 1.1051E-03 wt.% Fe2O3
+ 1.9943 wt.% MnO
+ 40.135 wt.% Ti2O3
+ 23.475 wt.% TiO2
+ 1.0928E-03 wt.% Mn2O3

→ Nozzle clogging.
TiN formation in Al-killed and Ti-bearing steel

Original steel composition at 1600°C: high N and high Ti → may form TiN

Ferrous Applications II  50
During the solidification, a large amount of TiN can be formed.
Nozzle Clogging in Ti-bearing Al-killed steel

- Kawashima et al., CAMP-ISIJ (1991)
  - Liquid Al-Ti-O (reoxidization) attached to Al$_2$O$_3$ inclusions
  
  Significant difference in nozzle clogging of Ti-bearing steel from that of Ti-free steel is the existence of Al-Ti-O inclusions covering Al$_2$O$_3$ core oxides. Reoxidation in tundish (high-SiO$_2$ slags) causes the nozzle clogging.
Inclusions generated by reoxidation process

RH process after Ti addition (POSCO)
*Doo et al. (2007)*

![Images of inclusions](Image)

Ti/Al of outer layer = 1.0~1.5

Reoxidation in Tundish
(high SiO2 slags)
*Park et al. (2004)*

Reoxidation in Tundish
*Basu et al. (2004)*
Inclusion causing nozzle clogging in Al-killed Ti-bearing steel

1) Drawing the phase diagram of the Al₂O₃-Ti₂O₃-TiO₂ system.
2) Drawing the same diagram with fixed PO₂ and superimposing them.
Calculated inclusion composition in Fe-Al-Ti-O liquid at 1600°C

1) Drawing the phase diagram of the Al₂O₃-Ti₂O₃-TiO₂ system.
2) Calculating equilibrium inclusion (Al₂O₃-Ti₂O₃-TiO₂) composition in liquid Fe containing small amounts of O with certain fixed amounts of Ti. Then, plotting the inclusion compositions on the phase diagram.

Similar to Mn/Si deoxidation calculations
Newly calculated inclusion diagram of Fe-Al-Ti-O system

Existence of Liquid $\text{Al}_2\text{O}_3$-$\text{Ti}_2\text{O}_3$-$\text{TiO}_2$ phase at 1600°C

Al deoxidation + Ti addition

Reoxidation (Nozzle Clogging)

$[\text{wt ppm O}] = 4.5$ ppm

T = 1600°C

Liquid

[log [wt% Al]]

[log [wt% Ti]]

[wt ppm O]
RH Vessel Refractory

**RH OB**
- *High amount of oxygen blowing*
- *Increase of ferro-alloy (Al, Si, Mn, etc) addition*

→ *More severe local corrosion of RH vessel refractory*

![Flow pattern in RH CFD model](image)

- Normal corrosion
- Abnormally severe corrosion
Quite enough thermodynamic database (gas, molten steel, slag, refractory, etc…)

Write kinetic process using Macro:
input/output to Excel spreadsheet

Predicted slag composition in RH vessel from RH process simulation

Experimental and calculation conditions

Table 1: Composition of the synthetic slags (wt%).

<table>
<thead>
<tr>
<th>Slag</th>
<th>Symbol</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle slag</td>
<td>L</td>
<td>5.3</td>
<td>27.7</td>
<td>10.7</td>
<td>56.3</td>
<td>0.0</td>
</tr>
<tr>
<td>FeO-rich slag 1</td>
<td>F1</td>
<td>4.2</td>
<td>22.2</td>
<td>8.6</td>
<td>45.0</td>
<td>20.0</td>
</tr>
<tr>
<td>FeO-rich slag 2</td>
<td>F2</td>
<td>3.2</td>
<td>16.6</td>
<td>6.4</td>
<td>33.8</td>
<td>40.0</td>
</tr>
<tr>
<td>CaO-Al₂O₃ slag 1</td>
<td>C1</td>
<td>0.0</td>
<td>45.0</td>
<td>0.0</td>
<td>55.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CaO-Al₂O₃ slag 2</td>
<td>C2</td>
<td>0.0</td>
<td>60.0</td>
<td>0.0</td>
<td>40.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2: Overall composition and apparent porosity of the investigated refractories.

<table>
<thead>
<tr>
<th>Refractory</th>
<th>Overall composition (wt%)</th>
<th>Apparent porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgO</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>Magnesia-chromite</td>
<td>55.8</td>
<td>22.9</td>
</tr>
<tr>
<td>Magnesia-carbon</td>
<td>90.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Refractory finger tests at 1600°C
Thermodynamic Calculations: Refractories – Slag Interactions
Ladle glaze formation

Dipping time: 120 sec

<table>
<thead>
<tr>
<th>Slag composition (wt.%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>54.06</td>
<td>10.47</td>
<td>26.24</td>
<td>9.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refractory composition (wt.%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.35</td>
<td>0.76</td>
<td>88.06</td>
<td>8.35</td>
</tr>
</tbody>
</table>

As received

Dipped for 120 sec
Glaze (Reaction product of slag and refractory)

Glaze area: glass + spinel

Glaze composition (glass)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35.8</td>
<td>6.6</td>
<td>51.1</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Original refractory  ⇐  Ladle slag  ⇒

Phase distribution (wt%)

Spinel islands

Ca₂Al₁₂O₁₉
Ca₂Al₄O₇
Al₂O₃

Slag composition (wt %)

CaO  SiO₂  Al₂O₃  MgO
35.8  6.6  51.1  6.5
Equilibrium stability calculations with temperature: refractories

Equilibrium stability of 20MgO-78Al₂O₃-2CaO refractories
Equilibrium stability calculations with temperature: refractories

The refractory is mechanically unstable above 1600°C:
- considerable volume change due to the significant change in phase distribution
The refractory cannot be used above 1690°C:
- significant amount of liquid phase formation
### Thermal Stability Test of Refractories

<table>
<thead>
<tr>
<th>wt%</th>
<th>REF-1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>88</td>
<td>60</td>
<td>11</td>
<td>4</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>9</td>
<td>38</td>
<td>58</td>
<td>61</td>
<td>89</td>
<td>75</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>2</td>
<td>2</td>
<td>0.9</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>20</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>8.8</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>1.6</td>
<td>0.4</td>
<td>0.5</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}$</td>
<td>7</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Al}$</td>
<td>2</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Phase distribution graphs](image-url)
Depending on the refractory compositions, the refractory components can vary drastically.

- Formation of liquid
  - Stability of refractory ↓
- Change in MgO/Spinel fraction
  - Mechanical wear resistance
  - Volume change
Refractory – Liquid Inclusion Interactions

Stopper Head

SEN Collar

Inner side/mouth of SEN

Stopper (Al\textsubscript{2}O\textsubscript{3}-C)

Corroded area

SEN (submerged entry nozzle)

Inner side of SEN

Fig. 2. Calculated inclusions formed in high oxygen steel (Fe–0.08C–1.2Mn–0.35–0.01Si–O–minor P, B, etc. in wt%) during continuous casting process. (a) and (b): amount and composition of liquid inclusion varied with total oxygen content in steel at 1550°C, (c) and (d) amount and composition of liquid inclusion in molten steel containing 200 wt ppm oxygen varied with temperature.

Refractory – Liquid Inclusion Interactions

Please see the details in the ISIJ paper
Table 1. Chemical compositions of the refractories investigated in the present study.

<table>
<thead>
<tr>
<th>wt%</th>
<th>Al₂O₃–C</th>
<th>Al₂O₃–AlN–C</th>
<th>Spinel–L–C</th>
<th>Spinel–H–C</th>
<th>ZrO₂–C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>95</td>
<td>54</td>
<td>70</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td></td>
<td></td>
<td></td>
<td>85*</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>15</td>
<td>4</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>SiC</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>AlN</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>etc.</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*CaO stabilized ZrO₂.

Please see the details in the ISIJ paper.
Refractory – Liquid Inclusion Interactions

Relative stability of the refractories against liquid MnO-SiO$_2$ type inclusions

Please see the details in the ISIJ paper

Fig. 10. Thermodynamic stability of the refractory components against liquid inclusion (MnO–SiO$_2$) at 1550°C. The arrows (gray arrow represents high degree of reduction, and empty arrow represents low degree of reduction) in phase diagrams represent the possible amount of dissolution of each refractory component.
Refractory-Steel Interaction

\[ 95 \text{ Fe} + 4 \text{ Mn} + \text{ Si} + <100-100A> \text{ MgO} + \]

\[ \text{C:\Slag-Steel-Inclusions\Equi0.res 24Sep12} \]

\[ \leftrightarrow \text{Change in the amount of phases} \]

\( <A> \text{ Al}_2\text{O}_3 + <1-A> \text{ Al}_2\text{O}_3 \)

Change in steel composition \( \rightarrow \)
High Mn-Fe melt storage for TWIP steel production

Melt / refractory reactions simulation

85%Mn-15%Fe melt

1g Mn-Fe melt + 1g refractory (MgO - Cr\(_2\)O\(_3\))

(MgO-MnO)

Steel

Cr\(_2\)O\(_3\) ⇔ MgCr\(_2\)O\(_4\) ⇔ MgO

FactSage™

Ferrous Applications II  75
High Mn-Fe melt storage for TWIP steel production

1g Mn-Fe melt + 1g refractory (MgO-Al₂O₃)

MgO

MnO

Al₂O₃ ↔ MgAl₂O₄ ↔ MgO

Spinel

Steel

MgAl₂O₄
MnAl₂O₄
Al₈O₁₂

MgO

Mn

Fe

Al
Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C

MgO-Al₂O₃ type: Very stable refractory
Refractory for TWIP steel: Fe-20%Mn-1.5%Al-0.6%C

T = 1500°C

MgO-Cr₂O₃ type: less stable
→ Cr pickup
→ Al loss
Desulphurization

Desulphurization of hot metal in the De-S station,
Desulphurization of steel during ladle treatment
and calculating sulphide capacity

More examples can be found in:
http://in-ho-group.mcgill.ca/publicfiles.php#
Desulphurization of Hot Metal

- The hot metal tapped out of the blast furnace typically contains 0.04-0.07% S.
- To reduce the amount of sulphur in the hot metal between the blast furnace and the oxygen converter, desulphurization is usually performed at a De-S station such as KR using flux (CaO, CaC$_2$, Mg, …)
- In secondary steelmaking (recently in LF unit), de-S can occur between slag (CaO-rich) and steel due to strong agitation.
Desulphurization of Hot Metal

The following reactions have been proposed to reduce the sulphur content in hot metal:

\[
\begin{align*}
\text{Mg(s)} + \text{S} & \rightarrow \text{MgS(s)} \\
\text{CaC}_2 + \text{S} & \rightarrow \text{CaS(s)} + 2\text{C} \\
\text{CaO} + \text{S} + \text{C} & \rightarrow \text{CaS(s)} + \text{CO(g)} \\
\text{Mg} + \text{CaO} + \text{S} & \rightarrow \text{CaS(s)} + \text{MgO(s)} \\
\text{CaO} + 2\text{Al} + \text{S} + 3\text{O} & \rightarrow (\text{CaO} \cdot \text{Al}_2\text{O}_3) (\text{S}) \\
(\text{CaO} \cdot \text{Al}_2\text{O}_3)(\text{s}) + \text{S} & \rightarrow (\text{CaO} \cdot \text{Al}_2\text{O}_3)(\text{S})
\end{align*}
\]

In the following pages, it will be shown how FactSage could be used to calculate the efficiency of each desulphurizing agent.

It will then be shown how the exact amount of desulphurizing agent can be selected to achieve the desired sulphur content.
Desulphurization of Hot Metal using Mg

1. Double-click on units...

2. ... to select the desired units

3. Enter the hot metal composition and put <A> for the desulphurizing agent amount

4. Click on “Data Search”...

5. ... and select the FTmisc database

6. Click “Next”
Desulphurization of Hot Metal using Mg

1. Right-click on “pure solids”

2. The selection contains data from both FTmisc and FactPS. Some of the data are overlapping (highlighted in red as “Duplicates”)

3. We need to select each phase only once, so we will have to “suppress duplicates”
Desulphurization of Hot Metal using Mg

1. Left-click on “suppress duplicates”

2. Then enter the database names in the order they should be prioritized. Here, FTmisc was given priority over FactPS

3. Press “OK”

4. Press “apply” – Now the number of solids selected should be inferior to that selected in the beginning.
Desulphurization of Hot Metal using Mg

1. Left-click to select the liquid steel solution phase

2. If you don’t see the available solution phase, click “show all”

3. Enter the desired equilibrium temperature.

4. We will vary the amount of desulphurizing agent from 0 to 1 g in steps of 0.01 g

5. Press “Calculate”
Desulphurization of Hot Metal using Mg

Now we want to see how the amount of sulphur in the hot metal decreases with the addition of magnesium.

1. Press “Output” → “Plot” → “Plot Results…”

2. Press “Axes”

3. This window will pop-up
Desulphurization of Hot Metal using Mg

1. Press “Y-variable”
2. Select “weight %” in “log10(Y)” scale
3. Select the maximum, minimum and incremental value for the graph
4. In the same way, select alpha as the X-variable
Now we can see that the axes have been selected. We just need to choose sulphur as the species.

1. Press “Select” species

2. Select S(FeLQ) – sulphur in the liquid steel solution.

3. Press “OK”
1. Now we can see that both the axes and the species have been selected.

2. The “Plot” button is now activated. Click it!
1. It can be seen that after the addition of 0.1g Mg, the desulphurization is not so effective.

2. If our target was 0.001% S, we can read off the graph that this sulphur level will be achieved after adding approximately 0.05g Mg.

3. However, there is a better way.
Desulphurization of Hot Metal using Mg: Composition target

1. Right-click on the Ftmisc-FeLQ selection

2. Click on "composition target"

3. This window will pop-up
Desulphurization of Hot Metal using Mg: Composition target

1. Select “element composition”
2. Choose element S
3. Enter the desired value (here – 0.001%)
4. Press “OK”
1. Now “C” indicates that we have selected a composition target for this calculation.

2. We must leave the <A> field blank, because <A> is what we want to calculate.

3. Press “Calculate”. Note that only one calculation will be performed.
Desulphurization of Hot Metal using Mg: Composition target

1. The $<A>$ value for reducing sulphur content to 0.001% is 0.0494g.

2. The mass fraction of S is exactly what we want it to be.
Desulphurization of Hot Metal using CaC$_2$

In the same manner, we can calculate the desulphurization ability of CaC$_2$

$$\text{CaC}_2 + S \rightarrow \text{CaS(s)} + 2\text{C}$$

We will keep the same hot metal composition, the only thing we will change is the desulphurizing agent.

This example can be found in EquiCase2-2.dat
Desulphurization of Hot Metal using CaC$_2$

The same conditions are selected
After addition of 0.14g of CaC$_2$, the amount of S in the hot metal becomes so small that the reaction does not proceed and CaC$_2$ is precipitated as a solid phase.
This can also be seen on the graph – after \( <A> = 0.14 \), the sulphur level remains constant.

1. In order to compare this graph with the graph for Mg desulphurization, we should save this figure.

2. But first, to differentiate this curve from the others, we will change the labels.
It can now readily be seen that Mg and CaO+Mg are the most effective hot metal desulphurizing agents.
It is also convenient to compare the amounts obtained using “Composition Target”
We will now apply the same calculations for the desulphurization of steel in the ladle.

The starting steel contains 0.01% S and it needs to be reduced down to 0.001% S.

We will also assume that a slag is present in the ladle. It consists of 40% CaO, 40% Al₂O₃, 10% MgO and 10% SiO₂. The ratio of slag to metal is 1/10.
Desulphurization of Steel using Slag

1. Enter the metal and slag composition

2. In “Data Search” select FTmisc and FToxid

This example can be found in EquiCase2-7.dat
Desulphurization of Steel using Slag

1. Enter the <A> and temperature

2. Select liquid steel and SlagA as the solutions

3. Note that the slag phase is selected with possible immiscibility

4. Press “Calculate”
Results show a slag phase and a metal phase.

Solid periclase (MgO) appears as $<A>$ is increased.

We can plot the results in the same way as was done for the hot metal desulphurization in the previous slides.
A constant decrease in metal sulphur content is observed.
Another useful way to visualize these results, is the sulphur partition coefficient:

$$L_s = \frac{[S_{\text{in slag}}]}{[S_{\text{in metal}}]}$$

1. Press “Output” → “Save or Print” → “Save or Print As…”

2. Select “Open Text Spreadsheet”

3. Press “Spreadsheet Setup”
Desulphurization of Steel using Slag

1. Select “Alpha” as the property column
2. Select “wt%” as the Species properties
3. Select the desired species
Desulphurization of Steel using Slag

1. Select sulphur from liquid steel and all elements from the slag

2. Press “OK”
Desulphurization of Steel using Slag

1. Press “OK” on this window and the next one
Desulphurization of Steel using Slag

1. A spreadsheet with the composition of slag and metal at each \( \alpha \) value will appear.

2. It is convenient to copy the whole table and paste it into Excel.
1. All unnecessary columns were deleted keeping only the sulphur content in the steel and the slag.

2. The last column was used to calculate the sulphur partition coefficient $L_s$.

3. Plotting Alpha against $\log(L_s)$
A good way of comparing the ability of a slag to absorb sulphur is the sulphide capacity calculated in the following manner:

\[ C_S = (S_{\text{in slag}}) \times \left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2} \]

In the following slides, the sulphide capacity of four different slags will be calculated.
Calculating Slag Sulphide Capacity

1. Enter the amount and species for the first slag

2. Select FactPS and FToxid databases
Calculating Slag Sulphide Capacity

1. Select gas and SlagA as possible products

2. We will calculate the sulphide capacity at three temperatures: 1580, 1600 and 1620°C

3. Press “Calculate”
Calculating Slag Sulphide Capacity

It is now possible to calculate the sulphide capacity using these results.

In the next slides, two ways of calculating sulphide capacity will be demonstrated.
The first way is to use Excel

1. Save the results in a spreadsheet

2. Press “Spreadsheet setup”
Calculating Slag Sulphide Capacity

1. Set T(C) as the system property

2. We need wt%S and the activity of O_2 and S_2 in the gas, so select “wt%” and “a” as the species properties.

3. Select the species
Calculating Slag Sulphide Capacity

1. Select \( \text{O}_2(\text{g}) \), \( \text{S}_2(\text{g}) \) and all Elements in SlagA

2. Press “OK” on all three screens
Calculating Slag Sulphide Capacity

1. All the needed results (and even more) appear in the spreadsheet.

2. Copy the results in Excel and delete the unnecessary columns

3. Calculate the sulphide capacity in a separate column.

4. Plot log(Cs) versus temperature
Another way to plot the sulphide capacity is to use the function builder tool coupled with Fact-XML.

1. Press “Edit/Create functions” under the Fact-Function-Builder Menu.
1. We need to select \( \text{wt}\%S \) as one variable

2. Select “Amount/Composition” under “Variable selection”

3. Select “\( \text{wt}\% \)”

4. Right-click on \( S(\text{total}) \) in slag and add it to variables list
1. The amount of S now appears in the variables list.

2. Right-click on the variable and rename it “wtS”

3. Partial pressure and activity of a gas is the same thing, so we need to select activity of $O_2$ and $S_2$ in the gas as the two other variables.
Calculating Slag Sulphide Capacity

1. Select “Activity” under “Variable Selection”

2. Right-click on O₂ and S₂ and add them to the variable list

3. Rename the variables to aO₂ and aS₂ accordingly
Calculating Slag Sulphide Capacity

1. Enter the function for log(Cs)

2. Press “preview results”

3. Note that the results are the same as for the Excel calculation
Calculating Slag Sulphide Capacity

1. Save the function as "Sulphide_Capacity"

2. Close the window
Calculating Slag Sulphide Capacity

1. Go back to the “Results” window, and select the “Sulphide_Capacity” function group

2. Check “Always calculate function groups”

3. Click “Refresh Results …”
1. A separate “Functions” tab will appear with the results of the calculations.

2. Each tab will have information on the function along with the calculated equilibrium.
Calculating Slag Sulphide Capacity

1. In order to plot the sulphide capacity as a function of temperature, press the XML button.

2. Then select “Graph” → “Setup”.

3. Import the “Sulphide_Capacity” function.
Calculating Slag Sulphide Capacity

1. Select “Functions” as the Y-Axis
2. Select “Temperature” as the X-axis
3. Adjust the min and max values, the step, etc.
4. Press “Draw”
Calculating Slag Sulphide Capacity

The figure is then obtained.
Calculating Slag Sulphide Capacity

Repeating the same procedure for the other slag compositions, it is possible to compare the sulphide capacities of the different slags.

![Graph showing the comparison of sulphide capacities at different temperatures for different slag compositions. The graph plots log(Cs) against temperature in °C. The different lines represent BOF Low-P Hot Metal, BOF High-P Hot Metal, LF Al-Killed Steel, and LF Si-killed Steel. The temperatures range from 1580°C to 1620°C.]
Slag cooling and heating  
(Enthalpy diagram)

• When slag forms from pure oxides, a certain amount of heat (enthalpy) is needed.
• When slag is cooled down, a certain amount of heat should be extracted.
• FactSage Phase diagram: Enthalpy diagram
Heat required to form and increase temperature of slag

Pure FeO(s) is not in the FToxid compound database
(Strictly speaking, FeO is a non-stoichiometric compound so it is in the FToxid MeO solution)

FactSage can use two variables, <A> and <B>
<A> can actually be varied but <B> should be constant

Initial condition

ΔH = H_{final} − H_{initial}
So initial conditions(phase, T, P) should be defined
Heat required to form slag and increase the temperature of slag

\[ \Delta H = H_{\text{final}} - H_{\text{initial}} \]

This is the heat we add to increase the temperature up to 1600°C. That is, \( \Delta H = H_{\text{slag at 1600°C}} - H_{\text{initial oxides at 25°C}} \)

This is the enthalpy of the final products at 1600°C
Heat required to form slag and increase the temperature of slag

\[
\text{MgO} + (1-A-B) \text{FeO} + B \text{SiO}_2
\]
Enthalpy diagram: phase change with $\Delta H$
\[ \text{Enthalpy diagram: phase change with } \Delta H \]

- Only X-Y type diagram allowed.
- Y axis should be Enthalpy (H−H_{T_{\text{min}}}).
- \( H_{\text{initial}} (H_{T_{\text{min}}}) \) is the enthalpy of products stable at \( T_{\text{min}} \). For example, \( Fe_2SiO_4 \) (fayalite_olivine) and \( SiO_2 \) are stable at 0\% MgO and 30\% SiO_2 rather than FeO and SiO_2.
If we increase the temperature of the mixture of (monoxide + olivine) at 20 wt % MgO and 30 wt % SiO₂ from 25 °C to 1625 °C, liquid slag is formed and the amount of heat required for this is about 2250 J/g.

If we heat the mixture of (monoxide + olivine) at 30 wt % MgO and 30 wt % SiO₂ from 25 °C by adding 1500 J/g, the mixture becomes a mixture of (liquid slag + olivine) at about 1425 °C.
Enthalpy diagram: phase change with $\Delta H$

\[
\text{MgO - FeO - SiO}_2
\]

\[
\text{SiO}_2/(\text{MgO}+\text{FeO}+\text{SiO}_2) \ (g/g) = 0.4, \ 1 \ \text{atm}
\]

\[
\begin{array}{c}
\text{H} - \text{H}_2\text{O} (\text{J/g}) \\
0 \ 0.1 \ 0.2 \ 0.3 \ 0.4 \ 0.5 \\
0 \ 500 \ 1000 \ 1500 \ 2000 \ 2500 \ 3000
\end{array}
\]

\[
\begin{array}{c}
\text{MgO/(MgO+FeO+SiO}_2) \ (g/g) \\
0 \ 0.1 \ 0.2 \ 0.3 \ 0.4 \ 0.5
\end{array}
\]
Application: Addition of new compounds and solutions (user defined) in calculations

\[ \text{MnCr}_2\text{O}_4-\text{MnAl}_2\text{O}_4 \] ideal solid solution

- New stainless steel production: high Mn stainless steel 400 grade. High MnO formation in AOD / VOD refining process
- \( \text{MnCr}_2\text{O}_4-\text{MnAl}_2\text{O}_4 \) inclusion formation in Mn- and Cr-containing steels

Fig. 1. Computed phase diagram of the \( \text{CaOSiO}_2\text{CrO}_x\)–5 mass.\%MgO–10 mass.\%MnO system at 1973 K under the oxygen partial pressure, \( p_{\text{O}_2} = 10^{-11} \) atm.
Creating user compound database: \( \text{MnCr}_2\text{O}_4 \) from MnO and Cr\(_2\)O\(_3\)

1. Type the compounds

2. Select “mixer”

3. Add the MnO and Cr\(_2\)O\(_3\) from known database

4. Select your own database (INHOBASE) and copy the result
\[ G^\circ(\text{cubic-MnCr}_2\text{O}_4) = G^\circ(\text{MnO}) + G^\circ(\text{Cr}_2\text{O}_3) + \Delta H^f - T\Delta S^f \]
\[ \Delta H^f = -51 \text{ kJ/mol}, \quad \Delta S = 0 \text{ J/mol-K} \]
Creating user compound database: \( \text{MgCr}_2\text{O}_4 \) from \( \Delta H_{298} \), \( S_{298} \) and \( C_p \)

Add \( \Delta H_{298} \), \( S_{298} \) and \( C_p \)
Ideal solution between compounds

Database selection

Priority of database
Ideal solution between compounds

MnCr$_2$O$_4$-MgCr$_2$O$_4$ ideal sol’n: (Mg,Mn)Cr$_2$O$_4$

→ Both MnCr$_2$O$_4$ and MgCr$_2$O$_4$ are selected as ideal solution #1 with no activity coefficients entered (ideal)
Ideal solution between compounds

O₂ - CaO - SiO₂ - Cr₂O₃ - MnO - MgO
1700°C, p(O₂) = 10⁻¹¹ atm, MnO/Z (g/g) = 0.1, MgO/Z (g/g) = 0.05, Z=(CaO+SiO₂+Cr₂O₃)

SiO₂

Liquid + Ideal #1

Ideal solution of MgCr₂O₄-MnCr₂O₄
Application: Addition of a new component in slag

$V_2O_3$ into molten slag for V distribution calculations
(Henriant solution)
New component in slag: Henrian activity coefficient

V$_2$O$_3$ containing slag // Liquid Fe-Al steel

→ All V goes to liquid Fe  ??
(because no V oxide in slag yet)
New component in slag: Henrian activity coefficient

Setting activity coefficient of $V_2O_3$ in slag
New component in slag: Henrian activity coefficient
New component in slag: Henrian activity coefficient

V in FeLq = 0.577 wt%

V2O3 in slag = 0.134 wt%

The distribution of V between slag and metal can be varied depending on the activity coefficient.
(evaluated from experimental data)
Vanadium partition coefficient in Steel/Slag melts based on literature data (BOF condition)

FINAL REPORT for MIME572

• By Jonathan Spring
• Undergraduate student
  McGill University

More details can be found in:
http://in-ho-group.mcgill.ca/publicfiles.php#
V distribution coefficient between steel and slag

Background

- Partition coefficients used to quantify solute concentrations in steel/slag
- Partition coefficient, $L_v = (\text{wt}\% \, V) / [\text{wt}\% \, V]$
- No known expression to predict vanadium distribution coefficient

Henry’s Law

- We are dealing with dilute solutions
  - $(V_2O_3) \sim 3 \, \text{wt}\%$
  - $2 \, V + 3 \, O = V_2O_3$
  - $K_{eq} = A_{V_2O_3} / (A_V^2 A_O^3)$
  - Activity $= \Upsilon_{V_2O_3} x_{V_2O_3}$
  - $\log_{10}(\Upsilon_{V_2O_3}) = A/T + B$
Literature Search

- Found ~ 20 articles with data on vanadium partition coefficients in slag/steel melts
- 3 of those contained tables of raw data with slag compositions (Zhang, Shin and Inoue) and 2 were performed at similar temperatures (Shin and Inoue). These 2 were used initially.
- Shin’s article dealt with slag containing Al$_2$O$_3$. His experiments were performed without proper control of the oxygen partial pressure and the partition coefficients for V he found were drastically different than in Inoue’s article. His results are therefore unreliable. Furthermore, the initial V partition coefficient model had trouble fitting Shin’s data. It was decided after my presentation to redo the model using only Inoue’s data.
- Total data points: 63
V distribution coefficient between steel and slag

- 1550 °C: 15 data points
- 1600 °C: 28 data points
- 1650 °C: 18 data points
- Slag
  - $x\ SiO_2$
  - $x\ CaO$
  - $x\ FeO$
  - $x\ Fe_2O_3$
  - $x\ MgO$
- $L_v$ for each data point
<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(CaO)</th>
<th>(SiO$_2$)</th>
<th>(FeO)</th>
<th>(Fe$_2$O$_3$)</th>
<th>(MgO)</th>
<th>(V)</th>
<th>Lv</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650</td>
<td>27</td>
<td>28</td>
<td>21</td>
<td>2</td>
<td>19</td>
<td>1</td>
<td>410.1</td>
</tr>
<tr>
<td>1650</td>
<td>19</td>
<td>22</td>
<td>36</td>
<td>4</td>
<td>16</td>
<td>1</td>
<td>751.4</td>
</tr>
<tr>
<td>1650</td>
<td>29</td>
<td>15</td>
<td>36</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>1087.6</td>
</tr>
<tr>
<td>1650</td>
<td>8</td>
<td>13</td>
<td>52</td>
<td>4</td>
<td>22</td>
<td>1</td>
<td>850.6</td>
</tr>
<tr>
<td>1650</td>
<td>25</td>
<td>7</td>
<td>47</td>
<td>11</td>
<td>8</td>
<td>2</td>
<td>1510.0</td>
</tr>
<tr>
<td>1650</td>
<td>17</td>
<td>3</td>
<td>58</td>
<td>12</td>
<td>7</td>
<td>2</td>
<td>1439.3</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>4</td>
<td>71</td>
<td>6</td>
<td>16</td>
<td>1</td>
<td>1142.9</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>15</td>
<td>50</td>
<td>3</td>
<td>29</td>
<td>1</td>
<td>705.9</td>
</tr>
<tr>
<td>1650</td>
<td>19</td>
<td>28</td>
<td>29</td>
<td>2</td>
<td>20</td>
<td>1</td>
<td>522.1</td>
</tr>
<tr>
<td>1650</td>
<td>28</td>
<td>22</td>
<td>30</td>
<td>4</td>
<td>13</td>
<td>1</td>
<td>761.7</td>
</tr>
<tr>
<td>1650</td>
<td>37</td>
<td>14</td>
<td>31</td>
<td>8</td>
<td>8</td>
<td>2</td>
<td>1174.2</td>
</tr>
<tr>
<td>1650</td>
<td>21</td>
<td>13</td>
<td>46</td>
<td>6</td>
<td>11</td>
<td>2</td>
<td>937.9</td>
</tr>
<tr>
<td>1650</td>
<td>31</td>
<td>7</td>
<td>40</td>
<td>13</td>
<td>7</td>
<td>2</td>
<td>1495.1</td>
</tr>
<tr>
<td>1650</td>
<td>0</td>
<td>1</td>
<td>82</td>
<td>6</td>
<td>8</td>
<td>2</td>
<td>1006.2</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>7</td>
<td>71</td>
<td>5</td>
<td>14</td>
<td>1</td>
<td>900.7</td>
</tr>
</tbody>
</table>

The amount of V in the slag was not considered. The same fixed amount of V was used for all equilibrium calculations and the subsequent calculation of Lv.

V distribution coefficient between steel and slag

- Databases: FToxid, Ftmisc (FeLQ), FactPS
- Equilibrium
  - $x \text{SiO}_2$
  - $x \text{CaO}$
  - $x \text{FeO}$
  - $x \text{Fe}_2\text{O}_3$
  - $x \text{MgO}$
  - 300 g Fe
  - 2 g V

3:1 metal to slag ratio
• Assume V in slag exists as $V_2O_3$

Solid $V_2O_3$ was considered because solid $V_2O_3$ is stable at these temperatures.
V distribution coefficient between steel and slag

- Change “A” value, “B” assumed to be 0

![Henrian activity coefficient window]

For ideal behaviour $A = 0$, $B = 0$, $P = 1$. Click on [Help] for an explanation of $P$. Click on [Cancel] to remove this species from the ideal solution.
- Calculate equilibrium
- Calculate $L_v$
- Compare to measured $L_v$
- Go back and try new $<A>$ value
- Trial and error
- More negative $<A>$ value creates a smaller $L_v$

$L_v = \left( \frac{\text{Wt}\% \text{ V}}{\text{Wt}\% \text{ V}} \right) = 68.6$
### V distribution coefficient between steel and slag

#### <A> Value to Activity Coefficient

\[ \log_{10}(Y_{V_{2}O_{3}}) = \frac{A}{T} + B \]

\[ \log_{10}(Y_{V_{2}O_{3}}) = -\frac{1025}{1923} \]

\[ Y_{V_{2}O_{3}} = 10^{\frac{-1025}{1923}} \]

\[ Y_{V_{2}O_{3}} = 0.293 \]

A more negative <A> value indicates a smaller activity coefficient.

<table>
<thead>
<tr>
<th>T (C)</th>
<th>(CaO)</th>
<th>(SiO₂)</th>
<th>(FeO)</th>
<th>(Fe₂O₃)</th>
<th>(MgO)</th>
<th>(V)</th>
<th>Lᵦ</th>
<th>A</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650</td>
<td>27</td>
<td>28</td>
<td>21</td>
<td>2</td>
<td>19</td>
<td>1</td>
<td>410.1</td>
<td>-1025</td>
<td>0.29</td>
</tr>
<tr>
<td>1650</td>
<td>19</td>
<td>22</td>
<td>36</td>
<td>4</td>
<td>16</td>
<td>1</td>
<td>751.4</td>
<td>-1200</td>
<td>0.24</td>
</tr>
<tr>
<td>1650</td>
<td>29</td>
<td>15</td>
<td>36</td>
<td>6</td>
<td>10</td>
<td>1</td>
<td>1087.6</td>
<td>-2175</td>
<td>0.07</td>
</tr>
<tr>
<td>1650</td>
<td>8</td>
<td>13</td>
<td>52</td>
<td>4</td>
<td>22</td>
<td>1</td>
<td>850.6</td>
<td>-1100</td>
<td>0.27</td>
</tr>
<tr>
<td>1650</td>
<td>25</td>
<td>7</td>
<td>47</td>
<td>11</td>
<td>8</td>
<td>2</td>
<td>1510.0</td>
<td>-2750</td>
<td>0.04</td>
</tr>
<tr>
<td>1650</td>
<td>17</td>
<td>3</td>
<td>58</td>
<td>12</td>
<td>7</td>
<td>2</td>
<td>1439.3</td>
<td>-2300</td>
<td>0.06</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>4</td>
<td>71</td>
<td>6</td>
<td>16</td>
<td>1</td>
<td>1142.9</td>
<td>-1300</td>
<td>0.21</td>
</tr>
<tr>
<td>1650</td>
<td>1</td>
<td>15</td>
<td>50</td>
<td>3</td>
<td>29</td>
<td>1</td>
<td>705.9</td>
<td>-750</td>
<td>0.41</td>
</tr>
<tr>
<td>1650</td>
<td>19</td>
<td>28</td>
<td>29</td>
<td>2</td>
<td>20</td>
<td>1</td>
<td>522.1</td>
<td>-1000</td>
<td>0.30</td>
</tr>
<tr>
<td>1650</td>
<td>28</td>
<td>22</td>
<td>30</td>
<td>4</td>
<td>13</td>
<td>1</td>
<td>761.7</td>
<td>-1475</td>
<td>0.17</td>
</tr>
</tbody>
</table>
V distribution coefficient between steel and slag

- The regression using slag basicity, $A = a\frac{CaO}{SiO_2} + b\frac{MgO}{SiO_2} + c(FeO + Fe_2O_3)$, was discarded because the fit was not as good as for the regression using each slag component.
- The regression using each slag component was poor nonetheless. Another regression, using all slag components and the slag temperature, was introduced.
- Option #1
  $A = aCaO + bSiO_2 + c(FeO + Fe_2O_3) + dMgO$
- Option #2 (Option #1 including temperature)
  $A = aT(K) + bCaO + cSiO_2 + d(FeO + Fe_2O_3) + eMgO$
- Option #3 (Option #2 including Constant)
  $A = aT(K) + bCaO + cSiO_2 + d(FeO + Fe_2O_3) + eMgO + \text{Constant}$
Regression #3 is best

- Slope of measured vs predicted \(<A>\) and measured vs predicted \(L_v\) is closest to 1
- Smaller residuals
- Residuals are randomly distributed

\[
A = -7 \times \text{Temperature (K)} - 51 \times \text{wt\% CaO} + 133 \times \text{wt\% SiO}_2 + 31 \times (\text{wt\% FeO} + \text{wt\% Fe}_2\text{O}_3) - 37 \times \text{wt\% MgO} + 10,100
\]

Need to test against more data!
Zn Galvanizing process

Reduction furnace: selective oxidation
Galva-annealing: Zn melting and oxidation
Oxygen partial pressure control using dew-point control

- **Ice**($H_2O(s)$), $T= -30^\circ C$
- **Dew point**
- **N$_2$-5%H$_2$

- **Annealing** $T= 800^\circ C$
- **H$_2 + \frac{1}{2}O_2 = H_2O**
- **PO$_2 = ?$ Oxidation ?**

- **Cold worked at 300 ^\circ C**
- **Hot Dip galvanizing**
We should select real gas to obtain accurate Gibbs energy and volume fraction of gas at low temperature and high pressure.
We will heat this gas at 800°C using a stream file.
Creating stream file

\[ \text{N}_2-\text{H}_2 \text{ gas with } -30^\circ\text{C dew point} \]
N₂-H₂ gas with -30°C dew point → 800°C
Dew points – PO₂/T Relationship

95%N₂, 5%H₂

Dew Point = 0°C
-10°C -20°C -30°C -40°C -50°C

-15 -14 -13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5

log pO₂, bar

Temperature °C

90%N₂, 10%H₂

Dew Point 0°C
-10°C -20°C -30°C -40°C -50°C

-15 -14 -13 -12 -11 -10 -9 -8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5

log pO₂, bar

Temperature °C
Phase diagram $PO_2 - T$: Oxidation of Fe-1%Mn-1%Si
$O_2$ - Fe - Mn - Si

mass $Mn/(Fe+Mn+Si) = 0.01$, mass $Si/(Fe+Mn+Si) = 0.01$

Ferrous Applications II 172
EX17-3. Primary oxide formation diagram

Drawing of the diagram:
1) Collect all blue/red/green lines at different PO2 and superimpose them in one diagram.
2) The boundary of each colored line (different phase) is the phase boundary of the primary oxide phases in the diagram.
Fe-Mn-Si at $PO_2=10^{-28}$ atm, $T=800^\circ$C
Boundaries for oxide phases

Fe - Mn - Si - O$_2$

$p(O_2) = 10^{-25}$ atm, 800°C, 1 atm

Ferrous Applications II  175
Primary and Secondary Oxidation

SiO₂ formation

Mn = 0.5
Si = 1.5

SiO₂ depletion in metal

SiO₂ + MnSiO₃ formation

Mn = 0.5
Si = 1.0

Ferrous Applications II  177
Oxidation phase diagram of Fe-0.002%C-Mn-Si steel at 800°C
Remelting and oxidation of Zn galvanized steel

1. L/S Interfacial reaction
2. Oxidation reaction

By controlling the partial pressure, different layer oxides can be calculated. But the partial pressure does not decrease linearly with depth of oxide layer. So this type of calculation shows quantitative oxidation behavior.
FTlite database contains reasonable Zn bath data for Zn-galvanizing. So, this is chosen instead of FSStel.
Interface reaction between liquid Zn and steel

Reaction products: Zn-rich Liquid

Reaction products: BCC + FCC

Original steel: Fe-1%Mn-0.5%Cr

We need this liquid Zn for the oxidation reaction
→ Save it as a stream
Oxidation of liquid Zn

(1) Setting oxygen partial pressure: activity or log activity can be fixed

(2) Remove duplicate compounds
Give a priority in database
Typically “FToxid > any metallic database > FactPS”
Oxidation of liquid Zn
Oxidation of liquid Zn

It is hard to predict the thickness of each layer.
Carburization and Decarburization of Steel

CO / CO₂ is variable
Carburization and Decarburization of Steel
Carburization and Decarburization of Steel

99.62 Fe + 0.08 C + 0.2 Mn + 0.1 Si + (<1-A>)mol CO + (<A>)mol CO₂

An amount of carbon in FCC phase (Fe)
Composition Target: “How to calculate optimum amount of CO₂ to reduce C in steel to a targeted composition”
Carburization and Decarburization: Composition target

$$99.62 \text{ Fe} + 0.08 \text{ C} + 0.2 \text{ Mn} + 0.1 \text{ Si} + <1-A>\text{mol CO} + <A>\text{mol CO}_2$$
**Einstein-Roscoe Equation** (one of the most well-accepted equation of viscosity for solid+liquid mixtures)

Viscosity \( (\text{solid+liquid mixture}) \approx \text{Viscosity}_{(\text{liquid})} \cdot (1 - \text{solid fraction})^{-2.5} \)

Original Einstein-Roscoe equation used ‘volume fraction of solid’ instead of ‘solid fraction’ and a correction term for morphology, but all these values are not very well-known for general solids. We can simply use the solid fraction (wt fraction) for this equation as an approximation. This value can be calculated using the “Equilib” module at a given system composition and temperature (Step-1).

Viscosity of liquid slag can be calculated from “Viscosity” module from slag composition calculated from “Equilib” (Step-2)
Viscosity calculations “Step-1”: Composition of liquid slag
Viscosity calculations “Step-2”: Viscosity of liquid slag

“Melts” database is for liquid slag

Composition of liquid slag from Equilib

Take these results for next step
Viscosity calculations “Step-3”: Liquid + Solid mixture

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% SiO₂ (SLAGA#1)</td>
<td>Wt% CaO (SLAGA#1)</td>
<td>Wt% MgO (SLAGA#1)</td>
<td>g x id-SLAGA#1</td>
<td>amount of solids</td>
<td>viscosity of liquid</td>
<td>solid + liquid</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>2.366</td>
<td>2.366</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>2.503</td>
<td>2.503</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>2.649</td>
<td>2.649</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>2.805</td>
<td>2.605</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>2.972</td>
<td>2.972</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>3.152</td>
<td>3.152</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>3.345</td>
<td>3.345</td>
</tr>
<tr>
<td>35</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>0</td>
<td>3.535</td>
<td>3.535</td>
</tr>
<tr>
<td>35.264514</td>
<td>39.930352</td>
<td>10.254331</td>
<td>93.496742</td>
<td>5.503258</td>
<td>3.744</td>
<td>4.423997</td>
</tr>
<tr>
<td>35.858294</td>
<td>39.633643</td>
<td>11.03572</td>
<td>73.503694</td>
<td>26.493606</td>
<td>3.897</td>
<td>8.412355</td>
</tr>
<tr>
<td>38.252378</td>
<td>38.793831</td>
<td>12.32313</td>
<td>46.07094</td>
<td>53.52906</td>
<td>4.042</td>
<td>28.05619</td>
</tr>
</tbody>
</table>

- **Step-1**: Amount of slag
- **Step-2**: Einstein-Roscoe Eq.
- **Step-3**: Amount of solids (100 - amount of liquid)
Thanks to FactSage Steelmaking Consortium Members

Developments of
- Thermodynamic database
- Process simulation model

Training for FactSage and Process simulation