The Role of Transient Slags in Steelmaking, Part I

Slag samples are typically collected at the end of the steelmaking process, and the slag compositions are then often used as a reference for process control and refractory compatibility. While these samples are important and essential, they don’t reflect the transient slags that were responsible for the refining reactions such as dephosphorization, desulfurization and inclusion absorption during the process. This two-part paper will focus on the role of these transient slags and how they can be engineered to benefit the basic oxygen furnace, electric arc furnace and ladle refining processes. This paper will also provide some insights on the physical-chemical aspects of slags in steelmaking.

The old maxim “Take care of the slag and the steel will take care of itself” is now even more important as new and complex grades of steel are being produced. The advances in automation and level 2 systems in meltnshops allow for the control and tracking of material additions and timing in these processes. When combined with in-line mass and energy balance tools, slag control is more precise than ever before.

An understanding of slag fundamentals, their evolution and design during the process is an essential requirement for today’s steelmaking industry. The transient slags that form during the steelmaking process, which essentially control the slag/metal and slag/refractory interactions, are as important as the final slag compositions. This paper will focus on these transient slags and how they could be optimized to achieve the final target slags, which are typically the focus of steelmakers.

Phase diagrams of oxide systems have been the prominent tools used to demystify slags and design flux recipes. These diagrams are fairly complicated and can be intimidating to most novice users. Most steelmaking operations are conducted at around 1,600°C (2,912°F) so that the diagrams can be greatly simplified if the phase relations are examined in isothermal sections at this temperature. However, due to the 2D nature of the phase diagrams, detailed understanding of slags was limited to binary and simple ternary and quaternary systems. Fortunately, recent advances in the slag databases in thermodynamic software such as FactSage allow for the comprehensive evaluation and analysis of complex multi-component slag systems, which will be demonstrated in this paper.

It is also important to recognize that the phase diagrams and the thermodynamic software represent equilibrium conditions, which are not always achieved in steelmaking. The “rate” of slag formation in the steelmaking operation is therefore very dependent on the “path of slag making” and choices of raw materials used to obtain a final slag composition. The first part of the paper will provide some insights on the physical-chemical aspects of slags, while the second part, to be published separately, will focus on examples of transient slags in different steelmaking processes (basic oxygen furnace (BOF), electric arc furnace (EAF) and refining processes).

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Physical and Chemical Aspects of Slags

The Concept of Bulk Slag Composition Versus Liquid Slag Composition — Most slag samples taken from steelmaking vessels and analyzed on x-ray fluorescence (XRF) slag analyzers represent the bulk composition of the slag and are typically a mixture of solid and liquid phases. Dipping a cold steel rod in a fairly liquid slag will capture a slag sample that is representative of the bulk slag composition. However, dipping a steel rod in a slag that appears “crusty” will result in mostly liquid slag sticking to the rod and most likely be more representative of the liquid portion of the slag and not the composition of the bulk slag. Therefore, special care should be taken when collecting slag samples that don’t have a very high fluidity. In such cases, a cup sample taken away from the stir eye in ladle will be more representative of the bulk slag in the ladle.

The concept of bulk slag and liquid slag composition can be explained by the simple 1,600°C (2,912°F) isothermal section of the CaO-MgO-SiO₂ system in Fig. 1. A schematic of the slag phases is represented in Fig. 2, and the corresponding slag compositions are listed in Table 1. Slag A in Fig. 1 is the bulk composition of the slag that contains some solid phases and has a “creamy” consistency (red dot). Slag B in Fig. 1 represents the liquid composition of the bulk slag (black dot). The bulk slag (slag A) consists of about 80% liquid phase (slag B) and 20% Ca₂SiO₄. An XRF chemical composition of a rod sample of slag A will likely be closer to composition B than composition A.

The addition of more lime (CaO) to slag A will move the bulk slag composition further away from the liquidus boundary toward the CaO apex of the diagram. This will certainly make the bulk slag composition more basic but will further increase solid Ca₂SiO₄ formation in the bulk slag and decrease the amount of liquid slag, whose composition will essentially stay the same at point B in Fig. 1. In steelmaking operations, it is the liquid slag fraction of the bulk slag that is responsible for any refining reactions. Hence for desulfurization, the slogan “thin to win” is sometimes used to emphasize that a highly fluid basic slag is essential for effective desulfurization (slag B in this case).

Slag Viscosity: Theoretical Versus Effective Viscosity — In many steelmaking processes, it is advantageous for the bulk slag to contain a certain amount of saturation or “second phase” particles as it increases

Table 1

| Slag Compositions at 1,600°C That Show the Difference Between Liquid and Bulk Composition |
|---------------------------------|--------|--------|--------|----------|--------|----------|----------|
|                                | % SiO₂ | % CaO  | % MgO  | C/S ratio | % Liquid | Viscosity (poise) | Effective viscosity |
| Bulk slag (Slag A)             | 40.7   | 53.2   | 6.1    | 1.31      | 80.4    | —         | 1.86      |
| Liquid slag (Slag B)           | 42.0   | 51.8   | 6.8    | 1.23      | 100     | 1.07      | 1.07      |

Figure 1

 Isothermal section at 1,600°C (2,912°F) of the CaO-MgO-SiO₂ system. Slag A represents the bulk slag composition and Slag B represents the liquid portion of the slag.

Figure 2

Schematic of the phases in the bulk slag.
the effective viscosity of the slag that could enhance foaming in the EAF and will also indicate to the ladle refining operator that the ladle slag is compatible with the refractories when it has a “creamy” consistency (contain some second-phase Ca$_2$SiO$_4$ particles), such as slag A in Table 1. The effective viscosity of the slag was determined as follows: The compositions and the amounts of the phases in the bulk slag were determined with the Equilib module in FactSage 7.3 and the con3 database (FactSage consortium database). The viscosity of the liquid phase was determined with the Viscosity module in FactSage 7.3. The phase amounts of simple slags can be determined from the phase diagrams (in this example) but for more complex slags, FactSage is an indispensable tool to calculate the amounts and composition of the phases. The effective viscosity of the bulk slag was determined from the information above and the modified Einstein-Roscoe equation:

$$\text{Effective Viscosity}_{\text{solid + liquid mixture}} = \frac{\text{Viscosity}_{\text{liquid}} \times (1 - \text{solid fraction})^{-2.5}}{1}$$

The 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. As an approximation, the solid fraction (weight fraction) is used for this equation.

### Important Differences Between Silicate and Aluminate Refining Slags

It is standard practice in ladle refining operations to add lime to liquid slags until the viscosity changes to a creamy consistency, i.e., a slag that is just lime-saturated. However, silicate slags are much more sensitive to rapid changes in viscosity when too much lime is added compared to aluminate slags. This is due to the unique phase relations in the CaO-MgO-SiO$_2$ and CaO-MgO-Al$_2$O$_3$ base systems and differences between the length of the liquid to solid levers in the two systems (lever rule). Consider the impact of adding 100 kg of lime to 1,000 kg of 100% liquid slag on the liquidus boundary at 1,600°C (2,912°F). Table 2 and Fig. 3a show that for silicate slags, the impact on viscosity is significant because of the short liquid to solid lever, whereas for aluminate slag (Fig. 3b), the impact is considerably less. The B3

### Table 2

**The Effect of CaO Addition on the Phase Relations in Silicate and Aluminate Slags**

<table>
<thead>
<tr>
<th>Slag Type</th>
<th>%SiO$_2$</th>
<th>%Al$_2$O$_3$</th>
<th>%CaO</th>
<th>%MgO</th>
<th>B3 = C/(S + A)</th>
<th>% Liquid</th>
<th>Viscosity (poise)</th>
<th>Effective Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicate Slag:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial 100% liquid slag</td>
<td>41.40</td>
<td>—</td>
<td>49.80</td>
<td>8.80</td>
<td>1.21</td>
<td>100</td>
<td>1.04</td>
<td>1.04</td>
</tr>
<tr>
<td>Bulk slag (+100 kg CaO)</td>
<td>37.60</td>
<td>—</td>
<td>54.40</td>
<td>8.00</td>
<td>1.45</td>
<td>46.30</td>
<td>—</td>
<td>6.74</td>
</tr>
<tr>
<td>Liquid slag composition</td>
<td>40.20</td>
<td>—</td>
<td>47.40</td>
<td>12.40</td>
<td>1.18</td>
<td>—</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td><strong>Aluminate slag:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial 100% liquid slag</td>
<td>—</td>
<td>42.00</td>
<td>54.00</td>
<td>4.00</td>
<td>1.29</td>
<td>100</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>Bulk slag (+100 kg CaO)</td>
<td>—</td>
<td>38.20</td>
<td>58.20</td>
<td>3.50</td>
<td>1.52</td>
<td>90.70</td>
<td>—</td>
<td>1.26</td>
</tr>
<tr>
<td>Liquid slag composition</td>
<td>—</td>
<td>42.00</td>
<td>54.00</td>
<td>4.00</td>
<td>1.29</td>
<td>—</td>
<td>0.95</td>
<td>0.95</td>
</tr>
</tbody>
</table>

### Figure 3

Solid to liquid levers in the systems CaO-MgO-SiO$_2$ (a) and CaO-MgO-Al$_2$O$_3$ (b) at 1,600°C (2,912°F).
ratio \( \frac{C}{(S + A)} \) is typically used for slags that contain appreciable amounts of SiO\(_2\) and/or Al\(_2\)O\(_3\).

The addition of 100 kg of lime to the silicate slag results in a significant amount of Ca\(_2\)SiO\(_4\) formation (the CaO-saturation phase) so that the amount of liquid in the bulk slag decreases to 46%. The effective viscosity of the slag changes from 1.04 poise to 6.74 poise, resulting in a crusty slag. The liquid portion of the bulk slag has a low viscosity (0.98 poise) but the amount of liquid slag is very low. In contrast the addition of 100 kg of lime to the aluminate slag only results in about 9% solid phases (CaO) and a creamy slag is the result. There is only a fairly small change in the effective viscosity of the bulk slag from 0.95 to 1.26 poise.

The Dissolution of Lime and Dolime in Steelmaking Slags — CaO and MgO are the major components of basic refractories and therefore are also the major components of compatible slags in contact with these refractories. Lime and dolime are typically added to the furnace, the converter and ladle slags to saturate the slags with these components and minimize refractory erosion. Basic slags (high in CaO) are also beneficial to dephosphorize in the furnace and desulfurize in the ladle.

A key requirement of the CaO and MgO added to the slag for steel quality improvements and/or refractory compatibility is the rapid dissolution of the CaO and MgO to ensure the components are available to protect the refractories or react with the steel. The following factors are important when considering dissolution rates:

1. The size of the material added. Too coarse sizing will delay complete dissolution, but too fine sizing could result in excessive losses as dust or increase the possibility of hydration.
2. The method and timing of the additions. Adding the material too early before fluxing components are available to dissolve the lime will result in crusty slags (see BOF and EAF discussion in Part II). Adding the material in bulk in a vessel could result in “islands” of unreacted material floating in the slag for a considerable period of time. It is normally recommended to add the material gradually if possible or add it in the form of a blend of pre-mixed CaO and MgO with some fluxes, to ensure rapid dissolution and slag formation.
3. The type of material (lime, magnesia, dolime or lime/dolime mixtures). If equilibrium is assumed in the steelmaking process, then the type of material added is not important. However, in many cases, equilibrium is not achieved and therefore a material that dissolves in the slag faster could have a distinct advantage over another material.
4. The type of fluxing or acidic components that are added to these materials to form a liquid slag. The base components in the materials are very high melting, CaO at 2,572°C (4,662°F) and MgO at 2,852°C (5,166°F), so that extensive fluxing (or fluidizing) of these basic components must therefore occur by acidic components to form liquid slags at steelmaking temperatures.

The simple binary phase diagrams and ternary isothermal sections are useful tools to evaluate the reactions between CaO and MgO and various fluxing components. It is beyond the scope of this paper to show these diagrams, but the results from these diagrams will be discussed in detail in the following section. These diagrams essentially show when CaO and MgO are the primary saturation phases in contact with a fluxing component, the rapid liquid formation is achieved but when an intermediate high-temperature phase forms (>1,600°C, 2,912°F), the dissolution of CaO and MgO in the slag is delayed.

Fluxing a Slag

Silica (SiO\(_2\)) as a Flux for CaO and MgO: The phase diagrams of the binary systems CaO-SiO\(_2\) and MgO-SiO\(_2\) show that both CaO and MgO will react with SiO\(_2\) to form high-melting intermediate compounds Ca\(_2\)SiO\(_4\) (2,130°C, 3,870°F) and Mg\(_2\)SiO\(_4\) (1,910°C, 3,470°F) which limits the solubility of the pure components in a silicate slag. When SiO\(_2\) reacts with CaO the following reactions occur: CaO and SiO\(_2\) first reacts to form the intermediate phase Ca\(_2\)SiO\(_4\), then the Ca\(_2\)SiO\(_4\) reacts with SiO\(_2\) to form CaSiO\(_3\), which then gradually melts. Ca\(_2\)SiO\(_4\) is a refractory phase that could form a coating around CaO grains and hence delay the dissolution of CaO into the slag (Fig. 4).

The behavior of pure MgO is similar to CaO due to the formation of the high-melting Mg\(_2\)SiO\(_4\)
intermediate phase. However, when a combination of CaO and MgO is used, such as dolime (58% CaO and 39% MgO), the reaction with SiO₂ will result in low-melting Ca, Mg-silicate phases that are liquid at steelmaking temperatures. This enhances the dissolution of both the CaO and MgO into the slag, so that in practice dolime will dissolve much faster than lime in silicate slags. Operational experience has also shown that lime that contains some MgO (up to 15% MgO) in some cases is better for desulfurization than regular lime (>94% CaO), because liquid slag with all the CaO in solution is formed faster.

**CaF₂ as a Flux for CaO and MgO** — Fluorspar is typically added to silicate slags to increase the kinetics of lime dissolution by breaking down the Ca₃SiO₄ barrier around the lime grains and to increase the solubility of CaO for better desulfurization. The 1,600°C (2,912°F) isothermal section for the CaO-CaF₂-SiO₂ system is shown in Fig. 5. Noteworthy in this diagram is the low solubility of CaO in binary CaO-CaF₂ slags (25% CaO – point A) but as the SiO₂ content of the slag increases, CaO solubility increases up to 58% CaO (point B). This is a very important consideration when designing fluorspar containing flux mixes, i.e., a flux mixture that contain some SiO₂ in the mixture will form more liquid and at lower temperatures than a pure lime/spar blend. This diagram also shows that the maximum amount of CaF₂ needed for the highest CaO-solubility slag is <15% CaF₂ (point B).

Two major misconceptions in the steel industry regarding fluorspar are:

- Fluorspar is bad for refractories.
- Fluorspar will desulfurize the steel.
Fluorspar is a fluxing component, similar to SiO₂, Al₂O₃ and FeO, and any liquid slag that is not saturated with the refractory component can result in refractory wear. If CaF₂ is added in a blend or with other components during early slag making, its effect on refractory wear is benign. However, when added in concentrated form to fluidize a stiff slag, it could lead to local refractory erosion. The effect of CaF₂ on slag is best illustrated by plotting the compositions of the dual-saturated slags (CaO and MgO) as a function of CaF₂ content, as shown in Figs. 6 and 7. For comparison, the dual-saturated slags as a function Al₂O₃ content are also shown on these diagrams. A significant decrease in the solubility of MgO (Fig. 6) is observed when CaF₂ or Al₂O₃ replaces SiO₂ as the fluxing component. CaF₂-based slags are actually more “forgiving” to MgO-based refractories because MgO solubility decreases faster for CaF₂-containing slags than Al₂O₃-containing slags. The actual percentages of CaF₂ and Al₂O₃ in the slag are also listed in the figures.

Fluorspar as a component is not a strong desulfurizing agent but its impact on lime solubility justifies its use in slags to enhance desulfurization. Fig. 7 shows the CaO-solubility of dual saturated slags comparing the effect of CaF₂ and Al₂O₃. This figure shows that CaF₂ is a much more effective component to dissolve CaO than Al₂O₃ at levels <15% of the component.

**Al₂O₃ as a Flux for CaO and MgO:**
The reaction of MgO and Al₂O₃ results in a very stable high-melting spinel phase (MgAl₂O₄) with a melting point of 2,135°C (3,875°F) and no liquid phase is formed at steelmaking temperatures. In contrast, the reaction of CaO and Al₂O₃ shows extensive fluxing at steelmaking temperatures with CaO as the saturation phase so that Al₂O₃ is an excellent flux for lime. The reason why CaO does not react with Al₂O₃ to form a spinel phase is that the Ca²⁺ cation is too large (1.14 Å) to fit into the spinel structure. Other divalent cations such as Mg²⁺ (0.86 Å), and Fe²⁺ (0.92 Å) are small enough to fit in the spinel structure and they all form intermediate phases with the spinel structure in those systems.

**FeO as a Flux for CaO and MgO:**
MgO and FeO form a complete solid solution over the whole composition range so that FeO is a very poor flux for MgO as it will be absorbed into the monoxide structure. Iron oxide (FeO or Fe₂O₃) is an excellent flux for CaO as low-temperature eutectics are formed (1,100–1,200°C, 2,012–2,192°F) between the two components and CaO is the saturation phase in these slags. The solubility of CaO in iron oxide is high, about 50% CaO for FeO and about 55% CaO for Fe₂O₃, at 1,600°C (2,912°F). The formation of very low-melting liquids in these systems and the large solubility of CaO show why doloma refractories are very vulnerable to slags with high iron oxide levels. In fired doloma refractories, the bounding phase is typically CaO.

The “No Man’s Land” Region for Refining Slags — Most refining slags (ladle, argon oxygen decarburization and vacuum oxygen decarburization) consist of the components CaO, MgO, SiO₂ and Al₂O₃ so that the isothermal and isoplethal sections of the phase diagrams of these components are good references to engineer good steelmaking slags. When the slags are essential silicate-based for a Si-killed operation or aluminate-based for an Al-killed operation, the phase relations are straightforward. However, when Si and Al dual-deoxidation practices are applied or a combination of SiO₂ and Al₂O₃-containing fluxes are used, the resultant slags can generate some challenges. Consider, for example, the 1,600°C isothermal
sections of the CaO-Al₂O₃-SiO₂ and CaO-Al₂O₃-SiO₂-5%MgO systems in Fig. 8.

A prominent feature in these two diagrams is the large stability area of Ca₂SiO₄ (red line) that limits the solubility of CaO in these systems. As the Al₂O₃ levels in the slag increase, there is a sudden and rapid increase in CaO solubility. This large change in CaO solubility over a minor slag composition change is called a “no man’s land.” The data from the diagrams are plotted in Fig. 9 and clearly show the rapid increase in CaO solubility as a function of the %Al₂O₃/%SiO₂ of the slag.

When designing slag recipes or considering combined Si and Al deoxidation of the steel, special care must be taken to design slags that are either to the left or right of this area of rapid CaO solubility increase. Significant changes in slag fluidity and viscosity could be experienced from heat to heat due to process variability, if the slag composition falls in or around the no man’s land area.

Part II of this paper will apply the principles illuminated in Part I to the transient slags generated during refining processes in the BOF, EAF and ladle operations.