FUNDAMENTALS OF EAF AND LADLE SLAGS
AND LADLE REFINING PRINCIPLES

By

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# TABLE OF CONTENTS

I) Introduction

II) Introduction to slag fundamentals
   a) What is slag?
   b) The functions of slag
   c) The building blocks of slag
   d) Slag calculation example
   e) Slag basicity and optical basicity
   f) The fluxing effect and the concepts of solidus and liquidus temperatures
   g) The slag balance
   h) Slag requirements and a simple slag classification

III) Foamy slag fundamentals and their practical application to electric furnace steelmaking
   a) Introduction
   b) Background on slag foaming
   c) A mass-balance approach to calculate the composition of EAF slag
   d) Utilizing the CaO-MgO-SiO₂-FeO system to determine MgO saturation levels
   e) Isothermal saturation diagrams
   f) Conclusions

IV) The impact of EAF practice on ladle refining
   a) The significance of the amount and composition of EAF carryover slag
   b) Steel deoxidation
   c) Slag deoxidation and slag/metal interactions

V) Ladle refining
   a) The significance of first making slag then making steel
   b) Slag volume and fluidity requirements for optimum LF refining
   c) Slag fluidity requirements for operations with a LF and those without a LF
   d) Stirring, heating and argon flow rates in the ladle

VI) Using phase diagrams to explain slag fundamentals and design slag recipes
   a) Utilizing the binary CaO-MgO system to explain binary diagrams
   b) Utilizing the ternary system CaO-MgO-SiO₂ system to explain ternary systems
   c) Slag requirements for refractory compatibility in the CaO-MgO-SiO₂ system
   d) The CaO-MgO-Al₂O₃ system
   e) The CaO-MgO-Al₂O₃-SiO₂ system
   f) Systems containing fluorspar

VII) Steel desulfurization
   a) Definition of terms
   b) The design of flux recipes to achieve specific steelmaking goals

VIII) References
1) INTRODUCTION

This course has been designed to provide a brief background on the theoretical principles of EAF and ladle slags, ladle refining, and slag conditioning. However, the principles are presented in such a manner that it can be applied in a practical fashion under actual steelmaking conditions. A complete and detailed course on slag fundamentals and steelmaking principles would probably require this whole week of lecturing rather than the 2 hours allocated.

One of the most exciting parts of this course is that it is based on the laws of nature, and if the engineer/operator understands the principles, they can be applied to optimize the steelmaking process.

In recent years, better refractory performance has been achieved by utilizing slag engineering principles. Slag foaming in the electric arc furnace (EAF) has not only lowered refractory and electrode consumption, but has also had a significant impact on improving thermal efficiency and decreasing melting time. Unfortunately, maintaining a predictable and consistent foamy slag for every heat has eluded many steelmakers for a long time. This paper will define the slag compositions required to obtain and control optimum foamy slag conditions in the Electric Furnace. In defining the optimal slags, consideration is given to the effects of scrap quality, carbon injection, slag basicity and MgO content.

Ladle refining is probably the most important part of steelmaking since it is here where the hot iron units from the furnace are changed into a salable high quality steel product.

Ladle refining implies the following:

- Deoxidation and alloying of the steel
- Temperature and composition homogenization
- Desulfurization or resulfurization of the steel
- Improved steel cleanliness; inclusion flotation and sulfide and oxide shape control

The goal of ladle refining is to deliver a ladle of homogeneous liquid steel to the caster (or ingot station) on time, at the right temperature, and meeting total chemical specifications.

Time: With the advent of sequence casting it is imperative that the heat arrive at the caster on time. Any delay can cause a disruption in the sequence and result in a bottleneck down the line - ultimately resulting in less heats being cast and a subsequent decrease in profitability.

Temperature: With ladle reheating furnaces, temperature can be controlled to within ± 5 °F of the target temperature.

Chemical Specifications: If the slag is well deoxidized, the carbon and alloy aims can be met within very tight tolerances.

The slag phase has a tremendous impact on the steelmaking goals listed above, and will be discussed in detail in this session. The truth of the old maxim “Take care of the slag and the steel will take care of itself”, will clearly be demonstrated in this course.
II) INTRODUCTION TO SLAG FUNDAMENTALS

a) What is slag?

**Dictionary Definition:**
"The dross or scoria of a metal" or "fused refuse separated from metal in smelting" - This definition applies to smelting operations and primary steelmaking operations (blast furnace or ferrochrome smelting). In the blast furnace slag originates from the gangue in the ore, ash in the coal, and the fluxes (lime, doloma, Al$_2$O$_3$) that were added to melt the gangue and coal ash so that the slag can be tapped from the blast furnace.

**Preferred Definition:**
Slags are ionic solutions consisting of molten metal oxides and fluorides that float on top of the steel (completely liquid or partially liquid). A partially liquid slag consists of a liquid fraction and a solid fraction. As the solid fraction of the slag increases the fluidity of the slag decreases and it changes from "creamy" to "fluffy", and eventually to "crusty" or solid.

**Why know more about slags?**

The drive in recent years by the iron and steelmaking industry to cut costs and still produce high quality steels has illuminated the importance of good slag practices in primary and secondary steelmaking processes.

There has been a gradual realization that the slag phase in steelmaking is not a necessary evil but a crucial part of modern steelmaking practices. Neither goal of producing high quality steel nor low costs can be realized by poor slag practices. The concept of "slag engineering" or "slag optimization" is becoming more common in many steelmaking works, as the need to implement these concepts are driven by more stringent steel quality requirements.

Despite the large volume of literature that has become available in recent years on slag-metal-refractory interactions, the *fundamentals* of slag engineering or optimization is still poorly understood and is still viewed by many as an art rather than a science.

This document will attempt to illustrate the fundamentals of slags and their impact on steel quality and refractory wear, in a practical and easy to understand manner.

b) The function of slag in Steelmaking:

1. Cover the arcs in the EAF and LF and protect the refractories from arc-flare
2. Improve the quality of the steel by absorbing deoxidation products (SiO$_2$, Al$_2$O$_3$) and inclusions (clean the steel)
3. Dephosphorize in the furnace and desulfurize in the ladle
4. Protect the metal from oxidation
5. Protect the metal from nitrogen and hydrogen absorption
6. Insulate the steel to minimize heat loss
7. Be fully compatible with the refractory lining
A "bad" slag will:

- Do nothing to improve the quality of the steel
- Be incompatible with the refractory container and dissolve it to satisfy its solution requirements.
- A "bad" ladle slag contain a large proportion of reducible oxides (FeO and MnO) that will react with the steel to cause Al, Si, and Mn fading

The viscosity (or fluidity) of the slag is also an important property. However, here there are somewhat conflicting requirements. A good slag for the metallurgical practice should have a high fluidity (low viscosity), whereas, a good slag in terms of refractory wear should have a low fluidity (high viscosity) to insure minimum penetration and reaction, and good coating formation. A compromise is therefore required, i.e., a slag that is still fluid enough to refine the metal but not to fluid to cause accelerated wear on the refractory, i.e., slags with a "creamy" consistency. A creamy slag has the consistency of latex paint.

c) Where does slag come and how is the slag formed - The building blocks of slag

The composition of a slag is usually expressed in terms of the component oxides (or flourides) on a weight percent basis. For example a slag could have the following composition:

<table>
<thead>
<tr>
<th>wt%</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>CaO</td>
</tr>
<tr>
<td>20</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>8</td>
<td>MgO</td>
</tr>
<tr>
<td>12</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>5</td>
<td>CaF$_2$</td>
</tr>
</tbody>
</table>

Where do these components come from?

CaO
- Lime (98 % CaO)
- Dolomite (≈58 % CaO & 39 % MgO)
- Ca-Aluminate (≈45% CaO & 53% Al$_2$O$_3$)
- Refractories (dolomite)

MgO
- Dolomite (≈58 % CaO & 39 % MgO)
- Magnesia (> 92% MgO)
- Refractories (Mag-C & Dolomite)

SiO$_2$
- Oxidation of the Si in the scrap (Si + O$_2$ = SiO$_2$)
- Steel deoxidation (2O + Si = SiO$_2$)
- Sand and dirt
- Refractories (High Alumina)
Al$_2$O$_3$ - Oxidation of the Al in the scrap ($2\text{Al} + 3/2\text{O}_2 = \text{Al}_2\text{O}_3$)
- Steel deoxidation ($3\text{O} + 2\text{Al} = \text{Al}_2\text{O}_3$)
- Ca-Aluminate ($\approx 45\% \text{CaO} & 53\% \text{Al}_2\text{O}_3$)
- Bauxite ($>80\% \text{Al}_2\text{O}_3$)
- Refractories (High Al$_2$O$_3$ sidewalls & bottoms)

FeO - Scrap ($2\text{Fe} + \text{O}_2 = 2\text{FeO}$)

MnO - Scrap ($2\text{Mn} + \text{O}_2 = 2\text{MnO}$)
- Steel deoxidation ($\text{O} + \text{Mn} \Rightarrow \text{MnO}$)

CaF$_2$ - Fluorspar ($\approx 90\% \text{CaF}_2$)

d) Slag calculation example

How to calculate a slag composition in a ladle using a mass-balance approach

Consider the following additions to a ladle:

<table>
<thead>
<tr>
<th></th>
<th>Amount</th>
<th>% CaO</th>
<th>% MgO</th>
<th>% Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime</td>
<td>700</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>500</td>
<td>60</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>Ca-Aluminate</td>
<td>500</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al (100%)</td>
<td>340</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Assumptions: No furnace slag was carried over into the ladle
The recovery of Al in the steel was 25%
(conversion factor for Al to Al$_2$O$_3$ is 1.89)

The mass-balance approach is used to calculate contributions of the various components.

**CaO Contributions**

- Lime: $700 \times 1 = 700$
- Dolomite: $500 \times 0.6 = 300$
- Ca-Aluminate: $500 \times 0.45 = 225$

**MgO Contributions**

- Dolomite: $500 \times 0.4 = 200$

**Al$_2$O$_3$ Contributions**

- Ca-Aluminate: $500 \times 0.55 = 275$
- Steel deoxidation: $340 \times 0.75 \times 1.89 = 485$

Total contributions: $760$
Total Slag Amount: $1225 + 200 + 760 = 2185$

- $\% \text{CaO} = \frac{1225}{2185} \times 100 = 56.1$
- $\% \text{MgO} = \frac{200}{2185} \times 100 = 9.1$
- $\% \text{Al}_2\text{O}_3 = \frac{760}{2185} \times 100 = 34.8$

e) Slag basicity and optical basicity

One of the formulations that had always eluded scientists and engineers was finding a universal compositional parameter that can be applied to slag in a fashion similar to which the pH formulation has been applied to aqueous solutions.

Slag component oxides can be classified as acidic, basic, or amphoteric (can act as an base or acid). However, the physical measurement of the basicity of an industrial slag is still not possible, even in these modern times. A number of formulations have been used to express the basicity of a slag. The most common approach is the use of a basicity index in which the basic oxides are placed on the numerator and the acid oxides on the denominator. Of these, by far the most commonly used is the $V$ ratio ($\%\text{CaO}/\%\text{SiO}_2$). While this is useful as a first approximation, in slags containing appreciable quantities of oxides other than $\text{CaO}$ and $\text{SiO}_2$ it is a very imperfect expression of basicity. Other formulations such as $\frac{\%\text{CaO} + \%\text{MgO}}{\%\text{SiO}_2}$ or $\frac{\%\text{CaO} + \%\text{MgO}}{\%\text{SiO}_2 + \%\text{Al}_2\text{O}_3}$, and many more, are also sometimes used. The first problem with these expressions is that they involve an arbitrary decision as to whether a component is basic or acidic and does not incorporate the differences in the relative basicities (acidities) of the different oxides. A second problem with these ratios is that the assessment of basicity becomes impossible in slags free of any recognized acid component. However, the following two basicity formulations are still commonly utilized to define oxidized slags (EAF or BOF) and reduced slags (ladle or AOD reduction slags), respectively:

**Basicity Index for oxidized slags ($B_3$)**

$$B_3 = \frac{\%\text{CaO}}{\%\text{SiO}_2 + \%\text{Al}_2\text{O}_3}$$

**Basicity Index for reduced slags ($B_5$)**

$$B_5 = \frac{\% \text{Total basic components}}{\% \text{Total acidic components}} = \frac{\%\text{CaO} + \%\text{MgO}}{\%\text{SiO}_2 + \%\text{Al}_2\text{O}_3 + \%\text{CaF}_2}$$

It is common to also add FeO and MnO to the acidic components in the $B_5$ ratio, provided that their sum (FeO + MnO) is less than 5%.

Recently, a more fundamental indicator of slag basicity, namely optical basicity, has been established. Using experimentally determined spectrographic information on a large number of glasses and Pauling's electronegativity data, the optical basicity for many components could be calculated. Table 1 shows optical basicity ($\Lambda$) values for the most common ladle slag components.
Table 1. Values of optical basicity ($\Lambda$) of slag components.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Optical Basicity ($\Lambda$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1.15</td>
</tr>
<tr>
<td>CaO</td>
<td>1.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.78</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>0.67</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.61</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.61</td>
</tr>
<tr>
<td>MnO</td>
<td>0.59</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.55</td>
</tr>
<tr>
<td>FeO</td>
<td>0.51</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.48</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The average optical basicity ($\Lambda$) for a slag of any composition can be calculated by means of the expression:

$$\Lambda = X_{Ao_x} \Lambda_{Ao_x} + X_{Bo_y} \Lambda_{Bo_y} + ...$$  \hspace{1cm} (1)

where,

$$X = \frac{\text{mole fraction of component} \times \text{number of oxygen atoms in oxide molecule}}{\Sigma \text{mole fraction of component} \times \text{number of oxygens in oxide molecule of all components}}$$  \hspace{1cm} (2)

Thus, in a CaO-Al$_2$O$_3$-SiO$_2$ slag for example:

$$X_{CaO} = \frac{N_{CaO}}{N_{CaO} + 3N_{Al_2O_3} + 2N_{SiO_2}}$$

$$X_{Al_2O_3} = \frac{3N_{Al_2O_3}}{N_{CaO} + 3N_{Al_2O_3} + 2N_{SiO_2}}$$

$$X_{SiO_2} = \frac{2N_{SiO_2}}{N_{CaO} + 3N_{Al_2O_3} + 2N_{SiO_2}}$$

The optical basicity concept has been used with great success in correlation with sulfide and phosphorous capacities, as will be illustrated later.

While the optical basicity is currently the best compositional parameter available that can be used to describe the composition (basicity) of a slag, it does not say anything about the physical properties of a slag. For example, consider the following "slag" composition:

- % CaO 62
- % MgO 8
- % SiO$_2$ 30
The optical basicity of this slag can be calculated as $\Lambda = 0.756$, which could be considered sufficiently basic to ensure good sulfur removal and minimum refractory wear. However, the calculation of this number is meaningless because the slag listed above is completely solid at steelmaking temperatures, and it will only start to melt at 1790°C and will be fully molten at 1950°C.

The application of the optical basicity concept to steelmaking slags is only useful if the slags are completely melted.

From the above illustration it is clear that significantly more information, such as solidus and liquidus phase relations and viscosity data, are required in order to completely evaluate slags that would be suitable in, for example, the ladle furnace.

f) The fluxing effect and the concepts of solidus and liquidus temperatures

Slags typically consist of the following oxide components: SiO$_2$, CaO, MgO, Al$_2$O$_3$, FeO, MnO and Cr$_2$O$_3$. The pure individual component oxides melt at very high temperatures as shown in Table 2. Pure elements or oxides will melt at a specific temperature (Table 2). For example, pure MgO will go from all solid at 2799°C to all liquid above 2800°C. In this case the solidus temperature (where the material starts to melt) = liquidus temperature (where the material is fully molten).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting point (°C)</th>
<th>Melting point (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>1720</td>
<td>3128</td>
</tr>
<tr>
<td>CaO</td>
<td>2600</td>
<td>4712</td>
</tr>
<tr>
<td>MgO</td>
<td>2800</td>
<td>5072</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2030</td>
<td>3686</td>
</tr>
<tr>
<td>FeO</td>
<td>1370</td>
<td>2498</td>
</tr>
<tr>
<td>MnO</td>
<td>1850</td>
<td>3362</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>2260</td>
<td>4100</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>1420</td>
<td>2588</td>
</tr>
</tbody>
</table>

Slags typically consist of a solution (mixture) of more than one oxide. For example, a pure CaO "slag" will be completely solid at steelmaking temperatures and will only form a liquid slag at temperatures above 2600°C (4712°F).

What is fluxing: When we add pure B to pure A and the addition of B to A results in a lowering of the melting point of A we can say that B is fluxing A. Take salt for example: Salt is a flux for ice – we add salt on ice (or snow) to lower the melting point of the ice. Ice is also a flux for salt – ice will lower the melting point of salt. The resultant liquid (or slush) that forms when we add salt to ice, or ice to salt, is a solution (mixture of salt and water). The same principle applies to steelmaking – for example a solution of SiO$_2$, MgO, and CaO is called a slag.
It can be inferred that the extent of fluxing will be dependent on the amount of flux added. Adding only a few grains of salt to a large chunk of ice will result in only a small amount of liquid (solution) formation and a remaining large chunk of ice. It is important to note that the moment we have a solution or mixture then the solidus temperature ≠ liquidus temperature.

The solidus temperature is defined as the temperature where the first drop of liquid will start to form and the liquidus temperature is the temperature where the mixture is completely molten.

From the above discussion it clear that extensive "fluxing" between the component oxides had to occur at steelmaking temperatures in order to form liquid slags. The extent of fluxing between the various oxides is usually shown graphically on phase diagrams. A phase diagram is really a plot showing the fluxing effect of one oxide on another as a function of temperature and composition. For example from the phase diagram of the components CaO and SiO$_2$ it can be determined exactly how much SiO$_2$ must be added to CaO to have a completely liquid slag (solution) at $1600^\circ$C ($2912^\circ$F).

g) The slag balance

The approach that will be used to demonstrate slag principles is very simple. The slag components are divided into two groups as follows:

<table>
<thead>
<tr>
<th>Refractory Oxides</th>
<th>Fluxing Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>MgO</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>CaF$_2$</td>
</tr>
<tr>
<td></td>
<td>Iron oxide</td>
</tr>
</tbody>
</table>

The individual components CaO ($2600^\circ$C) and MgO ($2800^\circ$C) are very refractory, but even when these components are combined, minimal fluxing occurs between them and a liquid phase will only form above $2300^\circ$C ($4712^\circ$F). It is therefore common to find that dolomite, (~58% CaO and ~39% MgO) as a refractory material in the steel industry.

The addition of other fluxes (component oxides or fluorides) to CaO and MgO is therefore required to form a liquid slag at steelmaking temperatures.

In very simple terms slag engineering can be defined as the balance between the refractory oxides (CaO and MgO) and the fluxing oxides (SiO$_2$, Al$_2$O$_3$, CaF$_2$, and iron oxide). This balance is typically expressed as a basicity ratio:

$$B_s = \frac{\text{Refractory Oxides}}{\text{Fluxing Oxides}} = \frac{%\text{CaO} + %\text{MgO}}{%\text{SiO}_2 + %\text{Al}_2\text{O}_3 + %\text{CaF}_2 + \text{FeO}}$$

The following simple set of figures give a graphical view of the balance between the refractory oxides and the fluxing oxides.
A balanced slag ("creamy") -
Ideal for refractory protection and metallurgical requirements

Refractory Oxides
(CaO & MgO)

Fluxing Oxides
(SiO₂, Al₂O₃, CaF₂)

The addition of too much CaO and MgO -
Slag too stiff or solid - little metallurgical benefit. Little or no refractory protection

Refractory Oxides

Fluxing Oxides

The addition of too little CaO and MgO -
Slag too fluid - little metallurgical benefit, very aggressive toward refractory
As a general guideline a **minimum** B₅ basicity ratio of 1.5 is required (60% refractory oxides and 40% fluxing oxides) to obtain a reasonable ladle slag. However, while a B₅ ratio of 1.5 might be adequate for silicate slags, it will be too low for slags containing considerable amounts of Al₂O₃ and CaF₂. The solubility of CaO in the slag increases as the Al₂O₃ contents of the slag increases. In order to maintain a slag with a "creamy" consistency, greater amounts of lime must therefore be added. The B₅ basicity ratio for an aluminate slag (~ 25% Al₂O₃) is around 1.8. When the slag contains considerable amounts of fluorspar, the required B₅ basicity ratio could be around 2.0 since fluorspar will increase the solubility of CaO **and** MgO in the slag.

From the above discussions it became clear that SiO₂, Al₂O₃, and CaF₂ are the three main fluxing components in ladle refining operations. The fluxing potential of these components are not equal!. SiO₂ is the "weakest" flux to bring CaO into solution, whereas CaF₂ is the most potent flux to bring CaO into solution. One important point to note; if compared on a two component basis; CaO-SiO₂ , CaO-Al₂O₃, or CaO-CaF₂, there is not much difference in the amount of CaO the different fluxes can dissolve at a specific temperature. However, when the fluxes are combined (SiO₂ + Al₂O₃ or SiO₂ + CaF₂), the solubility of CaO in the slag increases dramatically.

h) What are slag requirements?

To improve the quality of the steel!
To be compatible with the refractories!

These are not opposing goals! Since a basic slag practice is utilized for most grades of steel, the best slag for steelmaking quality will also be the best slag for refractory compatibility. These optimum slags have a "creamy" consistency and are normally **just** saturated with respect to CaO, or MgO, or both. Slags can be classified as follows:

**Slag Classification:**

**Crusty** - Too much CaO (and/or MgO)

**Fluffy** - CaO/MgO saturated, Ok for refractories but not optimum for desulfurization

**Creamy** - Just CaO/MgO saturated, Good for steelmaking and refractories (Ideal)

**Watery** - Too liquid, aggressive to the refractories

The following simplified phase diagram of the CaO-Al₂O₃ system can be used to classify the consistency (viscosity) of slags:
In this discussion on slag fundamentals only the major slag components (CaO, MgO, SiO₂, Al₂O₃, CaF₂, and FeO) will be considered. There are many other minor components such as Cr₂O₃, MnO, TiO₂, and P₂O₅, which have also an impact on the phase relations of slags. The discussion of these components falls outside the realm of this paper on slag fundamentals. Fortunately, the levels of these components are not very high (< 5%) in typical steelmaking slags. Furthermore, the effect of some of these components on the phase relations is so similar that they can be considered equivalent. A good example is FeO and MnO that behaves almost identically in slags. The only difference is that slags involving FeO will be much lower melting than slags involving MnO.
III) EAF Slags and Slag Foaming Fundamentals

1. Introduction

The two major requirements for EAF slags are:

1. Compatibility with the refractories
   - **MgO saturation** - most slaglines consist of magnesia-carbon refractories

2. Good foaming properties
   - Foam at the right time and long enough

A typical EAF slag composition is the following:

<table>
<thead>
<tr>
<th>% CaO</th>
<th>% MgO</th>
<th>% SiO₂</th>
<th>% Al₂O₃</th>
<th>% FeO</th>
<th>% MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>9</td>
<td>15</td>
<td>5</td>
<td>32</td>
<td>5</td>
</tr>
</tbody>
</table>

| Refractory Oxides | Fluxing Oxides |

The following basicity ratio is used to define EAF slags:

\[ B_3 = \frac{\% \text{CaO}}{\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3} \]

In this discussion on EAF slags, it was assumed that MnO is approximately equivalent to FeO in strength and would act as a fluxing oxide. The phase relations in the equivalent ternary systems are very similar, since these two components have similar molecular weights and ionic radii. For the balance of this paper FeO and MnO will be considered equivalent so that "FeO" will represent the sum of FeO and MnO, i.e. FeO = FeO + MnO.

Part of the section on EAF slags and slag foaming was extracted from the paper entitled "Foamy slag fundamentals" which was presented at the 1998 EAF conference in New Orleans.
III) Foamy Slag Fundamentals and their Practical Application to Electric Furnace Steelmaking

a) Introduction

The process of slag foaming can be simply stated as: Reactions that generate gas bubbles are required along with the proper slag to sustain these bubbles. The goal of this paper is to define the conditions required to obtain and control optimum foamy slags in the electric furnace (finding the proper slag). Readily available technical information and published phase diagrams have been utilized to present slag foaming principles in a practical and easy to understand fashion.

b) Background on slag foaming in the EAF

Slag Viscosity and Surface Tension

Previous research has shown that foaming characteristics improve with decreasing surface tension and increasing viscosity of the slag. However, it was also shown that the presence of suspended second phase particles in the slag had a much greater impact on foaming than surface tension and slag viscosity. In laymen’s terms, the slags that achieve the best foaming properties have a consistency (fluidity) that falls between "creamy" and "fluffy", with "watery" and "crusty" on the extreme ends of the spectrum. This means that these "optimum" slags are not completely liquid ("watery") but are saturated with respect to CaO ($\text{Ca}_2\text{SiO}_4$) and/or MgO (Magnesia - wustite solid solution). These second phase particles serve as gas nucleation sites, which lead to a high amount of favorable small gas bubbles in the foaming slag.

The term effective viscosity was defined to relate the amount of second phase particles in the slag and viscosity as follows:

$$\eta_e = \eta (1 - 1.35 \Theta)^{-5/2}$$  

where

$\eta_e$ - effective viscosity of the slag  
$\eta$ - viscosity of the molten slag  
$\Theta$ - fraction of precipitated solid phases

Figure 2 shows the relationship between the foaming index ($\Sigma$) and the relative effective viscosity. As the relative effective viscosity is increased, the residence time of the gas bubbles in the slag is prolonged, extending the stability and subsequently the life of the foam. However, as indicated in Figure 2, there is a maximum amount of second-phase particles that is beneficial for foam stability (optimum slag). Once this point is exceeded the slag becomes too "crusty" (oversaturated) and the foaming index decreases.

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* The foaming index ($\Sigma$) is a parameter that relates the gas flow rate, foam height, and the foam life.
Gas Generation

In the previous section, the importance of slag properties on foaming behavior was discussed. The second essential factor for foaming is gas generation (bubbles) and the sustaining of these gas bubbles in the slag. The predominant species in the gas phase is CO, with smaller amounts of CO₂ present.

The CO₂ is usually formed from the calcination of residual carbonate in the lime or dolomite that is added to the furnace. Since the calcination reaction is endothermic, unburned limestone or dolomitic stone is rarely used as a bulk add in the furnace. However, towards the end of the heat, small additions of raw stone can be beneficial as will be discussed later in this paper.

The CO is generally produced according to the following two chemical reactions:

\[
C \text{ (in the bath or injection)} + \frac{1}{2} O_2 \text{ (g)} = CO \text{ (g)} \hspace{2cm} (2)
\]

and

\[
FeO + C = Fe + CO \text{ (g)} \hspace{2cm} (3)
\]

The CO generated at the liquid bath level is generally more conducive to good slag foaming than CO formed in the slag itself. This is because the CO coming from the bath consists of small bubbles that are almost uniformly distributed.

Figure 2. The Relationship between the Foaming Index and Effective Viscosity.
The injection of oxygen alone (without carbon) gives poor slag foaming despite good gas presence. This is due to the temperature increase and the FeO generated from the following exothermic reactions, which dramatically decreases the viscosity of the slag:

\[
\begin{align*}
C + \frac{1}{2} O_2 (g) &= CO \\
Fe + \frac{1}{2} O_2 (g) &= FeO
\end{align*}
\]

(2) (4)

From the above, it is clear that controlling the FeO content of the slag is a key factor to predictable foaming behavior. FeO is the major fluxing component in the slag and strongly influences the effective viscosity and hence the foaming properties of the slag. The amount of FeO that will form is essentially a race (competition) between the rate of FeO generated due to oxygen injection (reaction (4)), and the rate of FeO reduced by the injected carbon (reaction (3)).

If the injected oxygen is balanced by a sufficient amount of carbon injection, and the slag is foaming well, the FeO content in the slag will stay fairly constant. However, if the fluidity of the slag increases due to either an increase in temperature or FeO content, a decrease in the foaming height could result. In this case, the effectiveness of FeO reduction by carbon is diminished because the retention time of the carbon (CO) in the slag is decreased. This is a typical phenomenon in many shops. As the fluidity of the slag increases, such that the foam height significantly drops, it is very difficult for the slag to foam again, even if the rate of carbon injection is significantly increased.

c) A mass-balance approach to calculating the composition of the EAF slag

Understanding and control of the parameters affecting the efficiency of the EAF process empowers the steelmaker to make the essential decisions for optimization. A mass-balance approach, using simple spreadsheets, is a fundamental tool that can be employed to evaluate the critical operational (and cost) parameters in the EAF.

A mass-balance calculation can be used to approximate the slag composition in the EAF from typical heat data: metal and slag heel in the furnace, scrap composition, fluxes, and the extent of blow and carbon injection. With the use of historical slag analyses, the assumptions and "boundary conditions" of the mass balance can be adjusted to give a fairly reliable prediction of the EAF slag composition. This will enable the steelmaker to adjust his flux addition and carbon and oxygen injection for optimum energy consumption, good foaming practice, and minimum refractory wear.

In setting up the mass-balance, it is important to consider all contributions to the furnace slag:

- Residual slag in the furnace
- The Si and Al content of the scrap
- The amount of dirt (sand) coming in with the scrap
- The SiO₂ and Al₂O₃ from the DRI and pig iron
- The extent to which the scrap is rusted (increases the FeO content in the slag)
- The compositions of all the oxides (lime and dolomite) added to the furnace
- The size of the scrap (fine scrap tends to oxidize more readily than large pieces of scrap)
- The amount of ash in the coal and the chemistry of the ash (normally SiO₂ and Al₂O₃)
- The amount of slag that is lost during the foaming process
A mass-balance approach is essentially an attempt to balance the added refractory oxides (lime and dolomite) with the fluxing oxides (SiO₂, Al₂O₃, FeO and MnO) that are generated from the scrap. Slagmaking in the EAF is very dynamic in that the slag composition is changing throughout the heat. The extent the composition of the slag will change is dependent on the type of EAF operation. There are essentially three types of EAF operations:

a) Conventional – Scrap and fluxes (lime and dolomite) are charged by bucket into the furnace. In some cases the lime is pneumatically injected into the furnace.

b) Conventional/DRI – A large part of the iron units is added as DRI. The DRI and fluxes are continuously fed through the roof of the furnace.

c) Consteel – Scrap and flux is continuously fed into the furnace via conveyor belt.

**Conventional EAF Steelmaking**

In conventional EAF steelmaking operations, the ability to add material through the roof of the furnace is not available, thereby necessitating that all material is added in scrap buckets. The lime and dolomite are normally added with the scrap, resulting in an initial slag that is "crusty". The oxidation of the Si and Al in the scrap is normally insufficient to fully flux the added refractory oxides. When all of the scrap is melted, the basicity of the slag is fairly constant, and is fixed by the amount of lime added and the amount of Si and Al that was present in the scrap. It is obviously very important to have a good idea of the Si and Al levels of the scrap, as these can dramatically affect the basicity ratio of the slag.

As oxygen is injected into the bath, the steel is decarburized, but FeO (the principal flux) is formed. The slag fluidity changes accordingly from crusty to fluffy and the slag starts to foam. The amount of FeO that is generated will obviously depend on the amount of oxygen and carbon injected. It is important to inject good quality coal/coke, i.e. low ash and volatile content. Coal ash consists primarily of fluxing oxides (SiO₂, Al₂O₃ and alkalis) so that the injection of coal with a high ash content could gradually decrease the basicity of the slag. This could adversely affect the foaming properties of the slag.

Optimizing and controlling the slag in Conventional EAF operations is the most difficult, since the opportunity to add fluxes to the furnace is limited to additions with the scrap. A good knowledge of the quality of the scrap is therefore required, i.e., the Si and Al levels, the rustiness, and the size distribution. Unfortunately, this information is rarely available. If the amount of lime and dolomite is not adjusted for scrap quality, then the foaming behavior of the furnace slags will be erratic and difficult to control. Some slags could be too basic and foam too late where other slags could be too acidic and foam too early. Essentially, control of the slag in conventional EAF operations can be compared to trying to hit a moving target. The only chance to adjust the slag chemistry in this type of operation is by carbon injection or injection of limited amounts of magnesia or dolomitic stone. This practice will only serve as a "band-aid" approach in order to prolong the foaminess in the furnace. The merits of these injections will be discussed later in the paper.

**Conventional/DRI and Consteel Steelmaking processes**

In these processes, an auxiliary flux feeding system is normally available. This greatly enhances the ability to control the slag in the furnace so that a more consistent slag foaming is generally observed. Another very important benefit of this type of process is that the chemistry of the feed
materials is better known, resulting in a more accurate mass-balance calculation. For example, when the composition or metallization of the DRI changes slightly, an adjustment can immediately be made to maintain an optimum practice. The biggest benefit of the auxiliary feeding system is that during the heat, the amount of material that is fed into the furnace can be adjusted to maintain consistent foaminess.

A mass-balance approach is an indispensable tool to calculate the composition of the slag. Even more important is the knowledge of what slag composition to aim for and what factors will negatively affect slag foaminess. The next part of the paper will address these issues.

d). Utilizing the CaO-MgO-SiO$_2$-FeO system to determine MgO saturation levels.

The CaO-MgO-SiO$_2$-FeO system and the limiting ternary systems CaO-MgO-SiO$_2$ and CaO-MgO-FeO were used to determine the points of dual saturation with respect to CaO and MgO (Ca$_2$SiO$_4$ and (Fe,Mg)O). The effect of Al$_2$O$_3$ on the solubility of CaO and MgO was determined relative to these reference systems.

The MgO content at dual saturation is shown graphically in Figure 3 as a function of slag basicity ($B_2 = \%\text{CaO}/\%\text{SiO}_2$) at 1600°C (2912°F). This figure shows that the saturation limit of MgO decreases as the basicity of the slag increases. The data in Figure 3 is therefore very important as it defines the minimum amount of MgO required in the slag to be compatible with basic refractories, for a specific basicity ratio.

![Figure 3. The solubility of MgO for slags that are dual saturated with respect to CaO and MgO at 1600°C (2912°F).](image-url)
For slags with a basicity ratio \((B_2) > 3.5\), the solubility limit levels off to about 6 to 5.5% MgO where it remains constant into the CaO-MgO-FeO system \((B_2 = \infty)\). The MgO solubility at dual saturation in this system is about 5.5% at 1600°C (2912°F).

Another important feature of this diagram is the significant increase in MgO solubility (with decreasing basicity) for slags with basicity levels less than 2.0. In some cases, the initial slag that is formed in the EAF might have a low basicity, resulting in a higher MgO solubility. The addition of dolomite with the first scrap bucket will provide the necessary MgO units for saturation, minimizing refractory wear on the bottom and lower banks of the furnace.

**The effects of Al\(_2\)O\(_3\), TiO\(_2\), VO\(_2\) and MnO on the solubility of MgO in the slag**

The effects of Al\(_2\)O\(_3\), TiO\(_2\), and VO\(_2\) on the solubility of MgO have been evaluated in prior research where it was found that replacing SiO\(_2\) with Al\(_2\)O\(_3\), TiO\(_2\) and VO\(_2\), decreased the solubility of MgO\(^8\). The decrease was somewhat greater for VO\(_2\) and TiO\(_2\) than for Al\(_2\)O\(_3\).

The majority of EAF slags consists primarily of the components CaO, MgO, SiO\(_2\), Al\(_2\)O\(_3\), MnO, and FeO. The sum of the remaining components in the slag (TiO\(_2\), VO\(_2\), and Cr\(_2\)O\(_3\)) generally totals less than 2% (excluding stainless steel EAF slags). Therefore, in this paper the effects of TiO\(_2\), VO\(_2\) and Cr\(_2\)O\(_3\) on the solubility of MgO were considered small enough to be ignored.

In this paper, the effect of Al\(_2\)O\(_3\) on the solubility of MgO was incorporated as follows:

1) The B\(_3\) basicity ratio was used instead of the simple B\(_2\) ratio to express slag basicity.
2) The MgO solubility using the data from Figure 3 was calculated as a function of the B\(_3\) ratio.
3) The decrease in MgO solubility as Al\(_2\)O\(_3\) replaces SiO\(_2\) is incorporated by a correction factor. This is demonstrated by considering the two MgO-Saturated slags in Table 3:

<table>
<thead>
<tr>
<th></th>
<th>Slag A</th>
<th>Slag B</th>
</tr>
</thead>
<tbody>
<tr>
<td>% MgO</td>
<td>9.3</td>
<td>8.3</td>
</tr>
<tr>
<td>% CaO</td>
<td>43.1</td>
<td>43.2</td>
</tr>
<tr>
<td>% SiO(_2)</td>
<td>21.5</td>
<td>11.5</td>
</tr>
<tr>
<td>% Al(_2)O(_3)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>% FeO</td>
<td>26.1</td>
<td>27.0</td>
</tr>
<tr>
<td>(B_2) (\frac{CaO}{SiO_2})</td>
<td>2.0</td>
<td>3.8</td>
</tr>
<tr>
<td>(B_3) (\frac{CaO}{(SiO_2+Al_2O_3)})</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>
In Slag B, 10% of the SiO₂ was replaced by an equivalent amount of Al₂O₃. This resulted in a decrease in the solubility of MgO from 9.3 (Slag A) to 8.3% (Slag B). If the simple B₂ ratio rather than the B₃ ratio had been used to determine the MgO solubility from Figure 3, a significant underestimation of the solubility of MgO would have resulted. The effect of Al₂O₃ on the solubility of MgO using the B₃ ratio and the correction factor can be calculated as follows:

\[
\% \text{ MgO}_{\text{sat}} = \% \text{ MgO}_{\text{ref}} (\text{B₃ ratio}) - \text{Al₂O₃ correction factor}
\]

where

\[
\% \text{ MgO}_{\text{ref}} = \text{Obtained from Figure 3.}
\]

\[
\text{Al₂O₃ correction factor} = 0.615 \times \left( \frac{\% \text{Al₂O₃}}{(\% \text{SiO₂} + \% \text{Al₂O₃})} \right) \times (\% \text{MgO}_{\text{ref}} - 6)
\]

So that for Slag B,

\[
\% \text{ MgO}_{\text{sat}} = 9.3 - [0.615 \times \left( \frac{10}{21.5} \right) \times (9.3 - 6)]
\]

\[
= 8.3
\]

In this paper, it was assumed that MnO is approximately equivalent to FeO in strength and would act as a fluxing oxide. The phase relations in the equivalent ternary systems are very similar, since these two components have similar molecular weights and ionic radii. For the balance of this paper FeO and MnO will be considered equivalent so that "FeO" will represent the sum of FeO and MnO, i.e. FeO = FeO + MnO.

### The effect of temperature on the solubility of MgO

From the various ternary diagrams of the quaternary CaO-MgO-Al₂O₃-SiO₂ system, the effect of temperature on the solubility of MgO has been approximated. In the CaO-MgO-FeO system, the MgO solubility is the least temperature sensitive and the dependence is about 1.75 % MgO per 100 °C (using 1600°C as midpoint temperature). However, in the other systems, the MgO solubility change per 100° is approximately 2 - 3% MgO. In this paper, a temperature dependence of 1.75 % MgO per 100° was used as follows:

\[
\% \text{ MgO}_{T} = \% \text{ MgO}_{\text{ref}} + (0.0175 \times (T-1600))
\]

Where,

\[
\% \text{ MgO}_{T} = \% \text{ MgO at temperature T in °C}
\]

\[
\% \text{ MgO}_{\text{ref}} = \% \text{ MgO at 1600°C from Figure 3}
\]

e) Isothermal Solubility Diagrams (ISD)

### Generation and features of Isothermal Solubility Diagrams at constant basicity

The data on the solubility of MgO as a function of slag basicity in Figure 3 is very important as it defines the minimum amount of MgO required in the slag for refractory compatibility. However, in its current format, it is difficult to relate the data in this figure to foaming properties in the
EAF. It was mentioned previously that FeO is the major fluxing component in the slag and has a distinct impact on foaming properties. The effect of FeO on the solubility of MgO is not shown in Figure 3 although it is possible to back-calculate the amount of FeO that would be present in a slag at any basicity ratio. In most conventional EAF operations, the basicity of the slag remains fairly constant throughout the heat and is determined by the Si and Al levels in the scrap and the amount of refractory oxides added with the scrap. For this reason, the phase relations at constant basicity would be of great interest as they probably best represent the slag conditions throughout the heat.

The solubility data from Figure 3 and the CaO-MgO-SiO2-FeO system were used to construct maps of the phase relations as a function of MgO and FeO content at a constant basicity and temperature. The "maps" of these phase relations are called Isothermal Solubility Diagrams (ISD). Figure 4 is the ISD for slags with a basicity (B3) of 1.5 and shows the stability regions of the various phases at 1600°C (2912°F) and for slags with 0% Al2O3.

![Figure 4. Isothermal Solubility Diagram (ISD) for a basicity (B3) of 1.5. (Where C2S = Ca2SiO4, MW = Magnesio-wustite, and L = Liquid)](image)

Point (a) on this diagram is the point of dual saturation with respect to MgO (MW) and CaO (C2S) on the liquidus surface, and has been determined from Figure 3. The liquidus lines (saturation curves) originate from point (a) and are defined as (a)-(b) and (a)-(c) for MgO and CaO saturation respectively. The saturation curves and the phase stability lines were generated from the CaO-MgO-SiO2-FeO system and its lower-order ternaries. The dashed line tracing the liquidus region, is an inferred line for slags with peak foaming characteristics, i.e. optimum effective viscosity due to the presence of second phase particles (Point [G] in Figure 2).
Figure 4 is characterized by a fairly large all-liquid area. Slags that fall in this area will have poor foaming properties due to the low viscosity of the slag and the lack of second phase particles ($\Theta = 0$). The position of the liquidus curves is very important as they show the maximum amount of FeO that can be tolerated before the slag will be fully liquid. Also clearly shown in this diagram is the relationship between the FeO level and the amount of liquid in the slag. As the FeO level increases, so too does the liquid fraction, clearly demonstrating the fluxing effect of FeO. Another important feature displayed in this diagram is the decrease in MgO solubility (on the MgO saturation curve $[a] - [b]$) with increasing FeO content for slags that are not saturated with CaO.

Consider slag X in Figure 4 and the path the composition of slag X will take as the FeO content increases. At position X, the slag consists of C$_2$S, MW and liquid and is probably too crusty to foam very well at this stage. As the FeO content of the slag increases (due to the injection of oxygen), the MgO content of the slag is diluted and the slag follows the path X to X'. As the composition of the slag moves from X to X', the fluidity of the slag changes from "crusty" to "fluffy" and the foaming properties of the slag improve. However, as the composition of the slag continues to move towards the liquidus boundary (point X, to X'), the effective viscosity of the slag decreases as the amount of liquid in the slag increases. This results in a decrease in foaming. At point X the slag is fully liquid and remains liquid as the FeO content increases to point X'.

The initial slag composition (X) is MgO saturated but as the FeO content increases, the slag becomes unsaturated with respect to MgO making it aggressive to the furnace refractories.

Consider slag Y in Figure 4 and the path of the liquid composition as the FeO content of the slag increases. The initial FeO content of slag Y is identical to slag X, yielding the same crustiness and poor foaming properties. As the FeO content of the slag increases and the liquid composition follows the path Y to Y', the foaming characteristics of the slag improve. However, as the slag composition moves from Y, to Y', the good foaming properties of the slag are maintained due to the presence of second phase MW particles. This is in contrast to slags X and X1, which are fully liquid at this FeO level. Not only is slag Y fully compatible with the refractories over the entire composition interval (MgO saturated), but the foaming properties are much less sensitive to FeO content. The foaming "window" for slag Y is significantly larger (8 – 20% FeO) than for slag X (8 – 17% FeO). Also, since slag Y has the ability to foam over a larger composition range, the injection of carbon to reduce FeO could be more effective in this slag, than in slag X.

Consider slag Z in Figure 4. The initial MgO content of this slag is too high resulting in a slag that will have poor foaming properties and remain fairly crusty, even if its FeO content is increased significantly.

The ISD presented in Figure 4 clearly demonstrates the effects of FeO and MgO on the phase relations and hence the foaming properties of slags. Not only is the MgO content of the slag important in terms of refractory compatibility, but it is also very important for foaming properties. The ISD also shows the difference between research on foaming and actual steelmaking conditions. In the former, solid particles are added to a liquid slag, gradually
increasing the effective viscosity of the slag, whereas in real steelmaking conditions the reverse is true. In steelmaking, the slag is initially crusty because of the addition of refractory oxides with the charge, and then gradually becomes more liquid as the fluxes (SiO₂, Al₂O₃ and FeO) are generated by the oxygen blow.

The generation of Isothermal Stability Diagrams at other slag basicities

The same principles that were used to develop the example ISD at a basicity of 1.5 (Figure 4), can be used to generate ISD’s for other basicities. Figures 5 to 7 represent the 1600°C (2912°F) Isothermal Stability Diagrams at basicities of 2.0, 2.5 and 3.0, respectively.

![Figure 5](image1.png)

Figure 5. Isothermal Solubility Diagram (ISD) for a basicity (B₃) of 2.0.

![Figure 6](image2.png)

Figure 6. Isothermal Solubility Diagram (ISD) for a basicity (B₃) of 2.5
Figure 7. Isothermal Solubility Diagram (ISD) for a basicity (B₃) of 3.0.

The most significant features of these Isothermal Stability Diagrams (ISD's) are the following:

a) The shrinking of the all-liquid area as the basicity of the slag increases.
b) The subsequently higher levels of FeO that are required to reach the liquidus boundary.
c) The decrease in MgO solubility as the basicity of the slag increases.
d) The smaller effect of FeO on the MgO saturation curve as the basicity of the slag increases.  
   (Note slope of the MgO saturation line [a]-[b] in Figures 4 to 7.)
e) The effect of MgO content on the CaO saturation curve

These Isothermal Stability Diagrams show the importance of the initial MgO content of the slag.  
If the initial MgO level is too low, the window of effective foaming (as a function of FeO  
content) is small.  Conversely, if the initial MgO content is too high, the slag could be too crusty  
and potentially not achieve optimum foaming conditions.  From the diagrams it can be concluded  
that the "ideal" aim MgO content for foaming and refractory compatibility is about 1 – 1.5 %  
higher than the MgO value at dual saturation.

The diagrams also show that there are an infinite number of slag composition possibilities that  
can yield good foaming properties.  This is supported by EAF slag practices throughout the  
industry where slag basicities can vary from less than 1.5 to more than 3.0 with FeO levels from  
10 to 50%, while achieving good slag foaming behavior.  Figure 8 graphically depicts the  
effective foaminess as a function of slag basicity and FeO content.  Note the decrease in MgO  
solubility as the slag basicity increases.
Figure 8. Inferred Effective foaminess as a function of basicity and FeO content (time)

In the examples presented earlier (Figures 4 to 8), the Al₂O₃ content of the slag was 0%. Replacing SiO₂ with Al₂O₃ will not change the basicity of the slag since the B₃ ratio is used but it will decrease the solubility of MgO which will shift the position of the dual saturation point ([a]) in these diagrams. Increasing temperature will increase the MgO and CaO solubility of the slag, but decrease the FeO content at dual saturation and shift the CaO-saturation liquidus curves accordingly.

The effect of Temperature on Slag Foaming

It was mentioned earlier that a typical phenomenon in EAF steelmaking is that the foaminess in furnace tends to diminish towards the end of the heat. The Isothermal Stability Diagrams clearly show that an increase in the FeO content of the slag increases the amount of liquid present, adversely impacting the effective viscosity and hence foaming properties. This fluxing effect of FeO can be somewhat curtailed by targeting a MgO content slightly above the MgO saturation curve. However, the slope of the liquid composition path is such that the slag will eventually move through the MgO saturation field into the all liquid field (see line X – X’ in Figure 4).

A very important factor that has not been addressed yet is the effect of temperature on the phase relations and hence the effective viscosity of the slag. In all of the examples presented, a temperature of 1600°C (2912°F) was used. This temperature is typical for steelmaking and most experimental data is available at this temperature. Under steelmaking conditions, the temperature in the furnace gradually increases towards the end of the heat so that tap temperatures are typically around 1700°C (3050°F). This increase in temperature could dramatically affect the foaming properties of the slag. A slag that had good foaming properties at 1600°C might foam very poorly at 1700°C since the slag could be completely liquid.
The effect of temperature on phase relations and the corresponding shift of the liquidus curves is demonstrated in Figure 9. The increase in fluidity with increasing temperature results in a decrease in the amount of second phase particles in the slag. The increased fluidity might also diminish the reduction reaction of the injected carbon, resulting in an increase in the FeO content of the slag. This "one-two" punch is normally too much for the slag to absorb, and foaming in the furnace dramatically drops off.

In shops where an auxiliary feeding system (roof or pneumatic injection) is available, adjustments to the slag composition (by the addition of refractory oxides) throughout the heat is possible. It is especially useful to add lime or dolomite to the furnace to restore foaming conditions when the foaming in the furnace starts to deteriorate due to increased temperature and/or FeO levels. The addition of the refractory oxides at this point will increase the basicity of the slag and "shrink" the all-liquid area, thus offsetting the temperature effect.

Figure 9. Isothermal Stability Diagrams at 1600 and 1700°C for a $B_3 = 2.0$

The merits of injecting Magnesia or raw dolomitic stone into the furnace

Most conventional steelmaking operations do not have the luxury of auxiliary feeding systems and have to rely on the injection of refractory oxides through the slag door. These injections are typically "band-aid" additions in order to prolong the foaming in the furnace. Figure 10 shows the potential benefit of injecting MgO fines in the slag toward the end of the heat to maintain foamy conditions. Consider slag K in this diagram. As the composition of slag K moves from K toward K_2 the fluidity of the slag increases as the FeO content of the slag increases. Initially the foaming properties of the slag increases from point K to K_1 but then decreases from K_1 to K_2 as the slag becomes too liquid to foam adequately. The injection of MgO fines into the slag at point
K₁ will change the slope of the liquid path and the composition of the slag will now follow the path K₁ to K₃, thereby maintaining the presence of second phase particles and sustaining the foamy conditions.

![Figure 10. Isothermal Stability Diagrams showing the effect of MgO injection on the path of the liquid composition](image-url)

The effectiveness of the MgO injection is dependent on the initial MgO levels in the slag. For example, consider slag T in Figure 10 where the initial MgO content is too low. The injection of MgO fines into slag T will probably only show a small improvement on foaming due to localized chilling of the slag, but the chemical effect as shown for slag K, will be absent.

The injection of dolomitic stone into the furnace towards the end of the heat has the capability of prolonging the foaming conditions in a similar fashion as MgO. Consider the possible benefits of using dolomitic stone:

a) Dolomitic stone is significantly cheaper than magnesia fines
b) Dolomitic stone is more readily available than magnesia fines
c) The calcination reaction of the stone is endothermic and will "chill" the slag locally, thereby increasing the effective viscosity of the slag

\[
(Ca,Mg)(CO_3)_2 + \text{heat} = [CaO+MgO] + 2\ CO_2(g)
\]

d) The calcination reaction releases CO₂ gas bubbles into the slag. As 50% of the weight of the stone is attributable to CO₂, significant amounts of gas bubbles can be generated.
e) The CaO and MgO released into the slag locally increases the basicity, increasing the amount of second phase particles and hence foaming properties. However, for the chemical effect of dolomitic stone to be equivalent to MgO, double the amount has to be added due to the weight loss of CO₂.

f). Conclusions

Over the past several years, new processes have evolved in the steelmaking industry, often in an effort to improve steel quality and lower total costs. One area where steelmakers have invested significant resources is in slag foaming in the EAF. Although their efforts have been consistent, some steelmakers have met with less than consistent results in achieving and maintaining a good foamy slag practice.

This paper has attempted to provide a comprehensive, yet practical explanation of the mechanics of slag foaming in the EAF. And throughout the paper, both the requirements and methods of achieving and maintaining a good foamy slag practice has been discussed in great detail. In effect, an attempt has been made to prove that a good foamy slag practice is based on science, rather than luck.

One of the best ways to maximize the effectiveness of a process is to provide some general training and knowledge of the process in conjunction with tools for monitoring the process. The tools need to be efficient (in terms of time), effective and of course user friendly. This criterion has been incorporated in the development of the foamy slag model. By employing a mass balance approach, and graphically displaying the results on an ISD, steelmakers can not only monitor their existing slag practice, but can also design foamy slags to better suit their operations.
IV. THE IMPACT OF EAF PRACTICE ON LADLE REFINING

a) The significance of the amount and composition of EAF carryover slag into the ladle

EAF slag carryover: Friend or Foe?

The extent to which oxidized carryover slag from the EAF can be tolerated in the ladle depends largely on the type and quality of steel produced. For example, for some grades of steel, such as rebar, the slag in the ladle plays a limited metallurgical role because of the fairly high P and S specifications of the steel. Here the carryover slag has an advantage as it provides the necessary slag volume required for arc-flare protection. A major benefit of utilizing and optimizing furnace carryover slag is that the carryover slag is already hot, and mostly liquid, so that it can act as a fluxing precursor, enhancing the dissolution kinetics of other flux additions. A suitable amount of lime is usually added to “neutralize” the slag to improve refractory compatibility. One of the primary concerns regarding slag carryover is the reversion of phosphorous for steel grades with very low P specifications. In these cases the carryover slag is either minimized during tap or removed after tap and a complete “synthetic” slag mixture is used.

For most Al-killed steel grades, carryover slag from the EAF has to be minimized. Carryover slag contains significant amounts of FeO, MnO, SiO₂, and P₂O₅, which will be reduced back to the steel by the dissolved Al in the steel during stirring operations. The FeO and MnO are particularly responsible for Al fade and inclusion formation, whereas the reversion of Si and P may be detrimental for some grades of steel. Most AK-steel producers use some kind of method to eliminate or minimize the carryover of furnace slag into the ladle.

However, for the majority of steel grades, a certain amount of slag carryover can be tolerated, and can even be beneficial, provided that it is controlled and conditioned by the addition of suitable fluxes and deoxidation agents. The composition of the EAF slag will have a major impact on the type of slag formed in the ladle, i.e., the carryover of a "balanced" EAF slag could result in a good slag in the ladle. This is demonstrated in the following mass-balance example which calculates the composition of slags that will be generated in the ladle when no fluxes are added during tap.

| 1000 pounds of carryover slag |
| 300 pounds of FeSi (75% recovery) |
| 500 pounds of SiMn (95% recovery) |

Table 4 shows the changes in ladle slag composition as the EAF slag is deoxidized using either Al shot or FeSi or CaC₂ pellets. For the sake of simplicity, it was assumed that complete slag reduction was achieved during the slag deoxidation process.

From Table 4 an estimated slag composition is obtained. Utilizing a mass balance approach the necessary additions of lime, dolomite, fluorspar, and/or Ca-aluminate for optimum metallurgical and refractory slags, can be calculated and incorporated in the flux mix.

The control of the carryover amount of EAF slag and deoxidation of the slag is essential!
Table 4. Changes in ladle slag composition using various slag deoxidation agents.
(Units in pounds)

<table>
<thead>
<tr>
<th>Mass-balance Application</th>
<th>Carryover slag % MgO</th>
<th>Deoxidized slag using Al</th>
<th>Deoxidized slag using FeSi</th>
<th>Deoxidized slag using CaC₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8</td>
<td>8.3</td>
<td>8.4</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>44.6</td>
<td>45.2</td>
<td>52.9</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>15</td>
<td>5.3</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>32.1</td>
<td>41.2</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>49.8</td>
<td>51.7</td>
<td>72.8</td>
</tr>
</tbody>
</table>

The amounts of CaO and MgO required for refractory protection, calculated using a slag model at 1600°C (2912°F). †This slag is already CaO and MgO saturated.

The following example highlights the different flux requirements when the carryover slag in ladle is skimmed and when the carryover slag is deoxidized with aluminum.

Table 5. Carryover slag composition and ladle target slag

<table>
<thead>
<tr>
<th>Composition</th>
<th>Carryover slag from EAF % MgO</th>
<th>Target slag in the ladle % MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>% MgO</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>% CaO</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>% Al₂O₃</td>
<td>4</td>
<td>17-19</td>
</tr>
<tr>
<td>% SiO₂</td>
<td>23</td>
<td>18-20</td>
</tr>
<tr>
<td>% MnO</td>
<td>6</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>% FeO</td>
<td>25</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

Table 6. Calculated Al and flux additions when the slag is skimmed or reduced

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Slag skimmed</th>
<th>Slag reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of initial slag carryover (lb.)</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Amount of slag skimmed (lb.)</td>
<td>1800</td>
<td>0</td>
</tr>
<tr>
<td>Amount of Al added (lb.)</td>
<td>0</td>
<td>209</td>
</tr>
<tr>
<td>Amount CaO required (lb.)</td>
<td>1210</td>
<td>550</td>
</tr>
<tr>
<td>Amount MgO required (lb.)</td>
<td>230</td>
<td>100</td>
</tr>
<tr>
<td>Amount SiO₂ required (lb.)</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Amount Al₂O₃ required (lb.)</td>
<td>460</td>
<td></td>
</tr>
<tr>
<td>Total fluxes added (lb.)</td>
<td>2300</td>
<td>650</td>
</tr>
<tr>
<td>Total final slag weight (lb.)</td>
<td>2480</td>
<td>2440</td>
</tr>
</tbody>
</table>
b) Steel deoxidation

For Al-killed steel:  \[ 2[\text{Al}] + 3[\text{O}] = (\text{Al}_2\text{O}_3) \]  

\[
\begin{align*}
\{54 + 48 & = 102\} & \text{where } [\text{ ]} & \text{denote in the metal} \\
& & \text{and } () & \text{in the slag}
\end{align*}
\]

Atomic weights: \( \text{Al} = 27, \text{O} = 16, \text{Al}_2\text{O}_3 = 102, \)

If the dissolved oxygen in the steel from the furnace was 1000 ppm (0.1%) then the amount of Al required to deoxidize 50 tons of steel (100000 lb.) to 10 ppm would be the following:

\[
\text{Al required} = \frac{\Delta[\text{O}]}{1000000} \times 1.125 \times M_w
\]

where \( \Delta[\text{O}] = (\text{O ppm in furnace} - \text{O ppm in ladle}), M_w = \text{Metal Weight (lb.)}, \) and \( 1.125 = \frac{54}{48} \)

\[
\text{Al required (1000 to 10 ppm O)} = \frac{990}{1000000} \times 1.125 \times 100000 = 111.4 \text{ lb.}
\]

The amount of Al required to achieve an Al spec of 0.2% = \( M_w \times (\text{Al spec}) \)

\[
= 100000 \times (0.002) = 200 \text{ lb.}
\]

Combining the two equations and incorporating the efficiency (Eff) gives:

\[
\text{The total Al required} = \frac{M_w \left( \frac{\Delta[\text{O}]}{1000000} \times 1.125 + \text{Al Spec} \right)}{\text{Eff}}
\]

\[
\text{The total Al required (70 % Eff)} = \frac{100000 \left( \frac{990}{1000000} \times 1.125 + 0.002 \right)}{0.7}
\]

\[
= 445 \text{ lb.}
\]

The amount of \( \text{Al}_2\text{O}_3 \) released to slag will be:

\[
\text{Al}_2\text{O}_3 \text{ to slag} = (\text{Total Al added} - (M_w \times \text{Al spec})) \times 1.89
\]

\[
= (445 - (100000 \times 0.002)) \times 1.89
\]

\[
= 463 \text{ lb.}
\]

* Dissolved oxygen is different from total oxygen; total oxygen includes that associated with inclusions.
Exercise:

Metal Weight: 140 tons

Aim Al in Steel: 0.35%

Aim Oxygen in steel: 6 ppm

Efficiency: 65%

1) Calculate the amount of Al required to deoxidize the steel and achieve the Al aim chemistry.

2) Calculate the amount of Al\(_2\)O\(_3\) reporting to the slag

For Si-killed steel:

\[
[\text{Si}] + 2[\text{O}] = (\text{SiO}_2) \quad \text{--------------------------------------------- (2)}
\]

\[
\{28 \quad + \quad 32 \quad = \quad 60\}
\]

Atomic weights: Si = 28, O = 16, SiO\(_2\) = 60,

\[
\text{FeSi required} = \frac{\Delta[\text{O}]}{1000000} \times \frac{0.875}{\% \text{ Si in FeSi}} \times M_w
\]

The amount FeSi required for specifications:

\[
= \frac{M_w \times (\text{Si spec})}{\% \text{ Si in FeSi}}
\]

The total FeSi required

\[
= \frac{M_w}{\% \text{ Si in FeSi}} \times \left( \frac{\Delta[\text{O}]}{1000000} \times 0.875 \right) + \text{Si Spec} \times \frac{\% \text{ O}}{\% \text{ Si in FeSi}}
\]

The amount of SiO\(_2\) released to slag will be:

\[
\text{SiO}_2 \text{ to slag} = [(\text{Total FeSi added} \times \% \text{ Si in FeSi}) - (M_w \times \text{Si spec})] \times 2.13
\]

The thermodynamic relationship between the oxygen in the steel and the Al and/or Si in the steel can be represented by the following equations at 1600°C (2912°F) [6]:

\[
(\text{Al}_2\text{O}_3) = 2[\text{Al}] + 3[\text{O}] \quad K = \frac{a_{\text{Al}^2} \times a_{\text{O}^3}}{a_{\text{Al}_2\text{O}_3}} , \quad K^* = \left(\frac{[\% \text{Al}]^2 \times [\% \text{O}]^3}{a_{\text{Al}_2\text{O}_3}}\right) = 4.3 \times 10^{-14}
\]

and

\[
(\text{SiO}_2) = [\text{Si}] + 2[\text{O}] \quad K = \frac{a_{\text{Si}} \times a_{\text{O}^2}}{a_{\text{SiO}_2}} , \quad K^* = \left(\frac{[\% \text{Si}] \times [\% \text{O}]^2}{a_{\text{SiO}_2}}\right) = 2.2 \times 10^{-5}
\]

K* - Activities are chosen such that a\(_M\) \equiv %M and a\(_O\) \equiv %O when %M \rightarrow 0

The equilibrium oxygen content for a Fe-Si alloy with 0.2% Si that is in contact with a silica saturated slag (a\(_{\text{SiO}_2} = 1\)), can be calculated as follows:
\[(\% \text{Si})^* (\% \text{O})^2 = 2.2 \times 10^{-5}\]

\[(\% \text{O})^2 = \left(\frac{2.2 \times 10^{-5}}{0.2}\right); \quad \% \text{O} = 0.0105 \text{ or } 105 \text{ ppm}\]

However, if the slag in contact with steel is not silica saturated and has an \(a_{\text{SiO}_2}\) much less than 1, then the equilibrium oxygen content of the steel will be much less.

The equilibrium oxygen content of a 0.2\% Si steel in equilibrium with a slag with \(a_{\text{SiO}_2} = 0.25\), is 0.0024 or 24 ppm.

In reality, typical steels contain many other elements such as carbon and Mn which have a significant influence on the equilibrium dissolved oxygen. The calculations of the equilibrium oxygen content of these steels are more complex and fall outside the scope of this course. However, the implication of the simple example shown above is very important. For certain grades of Si-killed steel (especially high-C steel) where the Si-O equilibrium dominate, the \(a_{\text{SiO}_2}\) of the slag should not be too low as it could result in a too low oxygen content in the steel and hence make it vulnerable to clogging problems. The use of Ca-aluminate fluxes or very high CaF\(_2\) additions should be carefully evaluated in these special cases. The following two diagrams show the effect of slag composition on the \(a_{\text{SiO}_2}\).

![Diagram](image.png)

Figure 11. Activity of SiO\(_2\) in the systems CaO-MgO-SiO\(_2\) and Al\(_2\)O\(_3\)-CaO-SiO\(_2\) at 2912 °F.
c) Slag deoxidation and slag/metal interactions

**Stability of the oxides**

During melting of the steel in the EAF the following oxides are released into the slag: Al₂O₃, SiO₂, Cr₂O₃, MnO and FeO. Normally, lime and doloma additions are made with the scrap charge during the heat to form a liquid slag in the furnace. During tap some of the furnace slag is carried over into the ladle and will react with alloys that were added during (or after) tap. The following diagram is the key to understanding the interactions between the components in the steel and the components in the slag.

![Stability Diagram](image)

*Figure 12. Stability diagram for the various oxides*

This diagram shows the **thermodynamic stability** of the various oxides (in equilibrium with their respective metals). The lower the line for the oxide on the diagram the more stable it is. The word stable can be defined as the difficulty to remove the oxygen from the oxide. For example at 1000°C, CaO is the most stable oxide, then MgO, followed by Al₂O₃ etc. It is very difficult to remove the oxygen from CaO according to the reaction:

\[
\text{CaO} \rightarrow \text{Ca} + \frac{1}{2} \text{O}_2
\]
In contrast, according to the diagram, Cu$_2$O is the least stable oxide - it is very easy to remove the oxygen from the oxide to form Cu metal. It is common to see Cu tubing but never pure Ca tubing. Pure Ca will spontaneously react with air to form the oxide at room temperature (a very explosive reaction). Ca is usually combined with some other metal (that is less stable) to form a metallic compound; CaC$_2$ or Ca-silicide (Calsil wire).

From the slope of the curves it is also clear that these oxides become less stable with increasing temperature.

In terms of oxidation-reduction reactions the following very important information can be obtained from this diagram: The metal of any oxide can only reduce the oxides that are above it on the diagram. For example Si metal (find the line for the Si/SiO$_2$ equilibrium on the diagram) can only reduce the oxides MnO, Cr$_2$O$_3$, FeO, NiO, and Cu$_2$O to their respective metallic states:

$$\text{Si} + 2 \text{FeO} \rightarrow 2 \text{Fe} + \text{SiO}_2$$

Si metal can’t reduce the oxides that are below it on the diagram: TiO$_2$, Al$_2$O$_3$, MgO, or CaO.

To summarize this point: Ca metal can reduce any oxide above it on the diagram. Al metal can reduce SiO$_2$ to Si in the steel but can never reduce CaO to Ca metal.

This diagram also shows why scrap with residual elements (Cu and Ni) is such a problem. The oxides NiO and Cu$_2$O are less stable than Fe so that in a EAF or BOF all the Fe in the steel must first be oxidized to FeO before the Cu or Ni will be removed.

In an EAF practice where oxygen is blown into the steel it is clear the Al in the steel will be oxidized first to Al$_2$O$_3$, which will report to the slag, then Ti and Si, then the Mn, followed by the Cr and the C. Finally the Fe will start to burn and report to the slag as FeO. The “open” heat that is tapped from the furnace will therefore only contain Fe, C, Ni, Cu with almost no Si and low concentrations of Mn.

[Important: These curves on the diagram are for the pure metal/oxide equilibrium. In steel, the C or Mn are usually in diluted concentrations (minor components) so that the C/CO or Mn/MnO equilibrium curves can be moved up for various diluted levels.]

This diagram also clearly show why the amount of EAF slag carryover should be minimized for Al-killed steel or steel grades with high Ti levels. All the oxides in the slag above the Al$_2$O$_3$ line (on the diagram) could be reduced from the slag into the steel by the dissolved Al in the steel (a white slag is the trademark of AK-steel). If the carryover slag is not minimized or removed it can lead to circumstances where the grade has to be changed or the heat scrapped due to Mn and Si reversions from the slag to the steel.

The Al in the steel could react with the SiO$_2$ in the slag according to the following reaction:

$$\text{Al (in steel)} + \text{SiO}_2 \text{ (in slag)} \rightarrow \text{Al}_2\text{O}_3 \text{(report to slag)} + \text{Si} \text{(report to steel)}$$
The Al in the steel that reacted with the SiO₂ in the slag is now present in the steel as Al₂O₃. If this Al₂O₃ is not absorbed by the slag during rinsing with Argon it will stay in the steel, which will make the steel dirty, or even worse, clog the nozzle or SEN at the caster.

**Slag deoxidition**

In order to minimize or eliminate most of the reactions discussed above, most shops have resorted to conditioning the slag in the ladle by adding a suitable reductant (deoxidizer) to reduce the reducible oxides (FeO, MnO, Cr₂O₃) in the slag. Typical slag deoxidizers are the following:

- Al shot
- FeSi fines
- CaC₂
- SiC

For low-C steel, Al shot or FeSi fines are usually used for deoxidizing the slag, whereas, for high C-steel, CaC₂ or SiC are used. One of the benefits (or limitations) of using carbon-containing materials (CaC₂ and SiC), is that CO₂ gas is generated. If excessive amounts of furnace slag is carried over so that large amounts of CaC₂ or SiC are required, significant amounts of gas can be released which can result in excessive foaming of the slags in the ladle. In such cases a mixture of slag deoxidizers can be used. Slight foaming of the slag, however, can be beneficial for ladle furnace operations as it will help to cover the arc and temporarily provide necessary slag volume when a insufficient amount of slag is present in the ladle.

**Slag color**

The color of the slag is an excellent indicator for the amount of reducible oxides in the slag. Consider the following:

<table>
<thead>
<tr>
<th>Component Oxide</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>White</td>
</tr>
<tr>
<td>MgO</td>
<td>White</td>
</tr>
<tr>
<td>SiO₂</td>
<td>White</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>White</td>
</tr>
<tr>
<td>CaF₂</td>
<td>White</td>
</tr>
<tr>
<td>FeO</td>
<td>Black</td>
</tr>
<tr>
<td>MnO</td>
<td>Green</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>Dark Green</td>
</tr>
</tbody>
</table>
EAF slags are usually black (high in FeO) and ladle slags range from dark brown (FeO and MnO) to white. The term “white slag practice” is commonly used when SBQ grades or Al-killed grades are made. By default, for these types of steels, the slags in contact with these grades will eventually become white, as the Si and Al in the steel will deoxidize the slag. It is obvious that conditioning the slag with a suitable deoxidizer is a prerequisite for these grades in order to minimize alloy fading.

It is common to find a range of slag samples with different colors displayed in bottles in the LFS. Coupled with this is a table relating slag color, slag volume and the amount of deoxidizer required. For example, consider the following example table for high-C steel:

<table>
<thead>
<tr>
<th>Slag Amount</th>
<th>Black</th>
<th>Brown</th>
<th>Green</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2 inches</td>
<td>20 CaC₂</td>
<td>15 CaC₂</td>
<td>10 CaC₂</td>
</tr>
<tr>
<td>2-4 inches</td>
<td>40 CaC₂</td>
<td>30 CaC₂</td>
<td>20 CaC₂</td>
</tr>
<tr>
<td>4-6 inches</td>
<td>40 CaC₂ + 20 Al</td>
<td>40 CaC₂ + 10 Al</td>
<td>30 CaC₂</td>
</tr>
</tbody>
</table>

The slag samples and different tables for different grades of steel, serve as a guide for the operators to optimize the ladle refining process.
**V) LADLE REFINING**

a) The significance of first making slag then making steel

Earlier it was mentioned that the goal of ladle refining is to deliver a ladle of homogeneous liquid steel to the caster (or ingot station) on time, at the right temperature, and meeting total chemical specifications. This is only possible if the slag is conditioned and optimized first. The following shows the sequence of events and the benefits that can be realized for operations where the slag is not skimmed off before ladle refining starts:

<table>
<thead>
<tr>
<th>Event</th>
<th>Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add suitable fluxes for good fluidity and slag volume during tap</td>
<td>Reactions in a liquid slag is always faster than in a crusty or solid slag</td>
</tr>
<tr>
<td>Add suitable slag deoxidizers during tap (or after tap) so that $\Sigma (FeO + MnO) &lt; 3$</td>
<td>Better alloy recoveries (yields) and less fading of the steel</td>
</tr>
<tr>
<td>Further deoxidizing of the ladle slag might be required for certain grades of steel so that $\Sigma (FeO + MnO) &lt; 1$</td>
<td>Stable and consistent steel chemistries</td>
</tr>
</tbody>
</table>
| A liquid (creamy) deoxidized slag 5 minutes after ladle refining started | Improved desulfurization  
- Crusty slags do not desulfurize very well  
- Black or brown slags do not desulfurize | |
| Add lime to maintain a creamy slag in the ladle. As the slag heats up it will become more liquid | Improved refractory life  
- Very fluid(watery) slags is an indication that these slags are not saturated with the refractory oxides and will therefore tend to dissolve them from the refractories. |
b) Slag volume and fluidity requirements for optimum LF refining

The efficiency of heating in a ladle furnace is a function of stirring and slag depth at a given voltage setting. Typically the arcs of 2” to 3” should be buried in slag which is slightly deeper. The slag weight can be calculated using a general equation that incorporates the size and shape of the ladle as follows:

\[
\text{Slag Weight} = [(\pi r^2 + 2rL) \times d] \times \rho_{\text{slag}}
\]

where:
\[
\pi = 3.14
\]
\[
r = \text{Radius of inside of lining (ft.)}
\]
\[
L = \text{length of ladle flat side (0 if round)}
\]
\[
d = \text{slag depth (required)}
\]
\[
\rho_{\text{slag}} = \text{slag density*}
\]

*A typical slag density value for gas-free ladle slags is 150 lb./ft\(^3\). Heavy metal oxides (FeO, MnO) increases the density value. A 10% heavy metal content changes the density by about 12 lb./ft\(^3\) so that a typical furnace slag will have a density of around 180 lb./ft\(^3\).

It was mentioned earlier that carbon-containing slag deoxidizers could be used in the ladle to "artificially" increase the slag volume due to CO\(_2\) gas evolution. This is a very important consideration when using the equation above to calculate the slag weight to achieve a certain slag thickness. For foamy ladle slags a slag density value of between 120 - 140 lb./ft\(^3\) should then be used in the calculation (the foamier the slag the lower the density value).

**Example:**

ABC Steel has a round ladle with an inside shell diameter of 12ft. and a capacity of approximately 160 tons of steel. The ladle is lined with a 3 inch hi alumina safety lining, 1 inch of high alumina backfill, 6 inch mag-carbon slagline and a 5 inch dolomite barrel.

How many pounds of slag would be needed to achieve a slag depth of 4 inches?
c) Slag fluidity requirements for operations with a ladle furnace (LF) and those without a LF

Operations with a LF

- All the fluxing oxides should be added to ladle as soon as possible, preferably during tap.

- The amounts of lime, dolomite and fluxing oxides should be sufficient to cover the arc in the ladle furnace (3 to 4”)

- Mixtures of pure components can be used (lime + bauxite or lime + fluorspar + silica sand). The slag will be superheated by the arc and the heat will spend enough time at the LF station for all the components to go into solution.

- The slags should be fluid, but not watery - slags with a "creamy" consistency.

- The "creaminess" of the slag should be maintained throughout the heat by adding lime to slag if it becomes too watery.

Operations without a LF

- All the slag components should be added to ladle during tap.

- Pre-fused materials (Ca-Aluminate) or (70/15/15) lime/spar/sand mixtures should be used. The mixtures should melt immediately and go into solution very fast after a few minutes of vigorous stirring.

- Since no external source of heat is available to heat the slag but the steel, the aim chemistry of the slag should be chosen so that it will be fully liquid at around 2850°F.

- Since the tapping temperatures are usually higher for these operations, the slag initially should be very liquid but then become creamy as the steel cools down to teeming temperatures

d) Stirring, heating and argon flow rates in the ladle

Stirring and argon flow rates

Gas stirring can aggravate refractory erosion. Too little stirring will lead to superheating of the slag and surface layers of the steel, low heating efficiency, and also increased refractory erosion. Excessive stirring causes metal splashing, short-circuiting, carbon pickup, electrode "seeking" and low heating efficiency. Short-circuiting and electrode seeking can destabilize the arc, causing arc flare and refractory damage. Higher stir rates are typically used to open the eye for alloy adds and desulfurization. Better thermal efficiency and inclusion flotation are usually realized at lower stir rates.
Heating and arc control

The electrode arcs must be electrically balanced and proper aligned to prevent excessive arc impingement on the ladle walls. The temperatures of carbon arc plasmas are over 6000°F and well melt quickly through any type of refractory lining. If the arcs are imbalanced electrically or are physically misaligned, this can cause the arc flare to overheat a small section of the ladle slag line leading to early failure of the slagline. Serious damage can also occur if the arc length is too long and the arc is not covered by the slag layer in the ladle. The maximum heating rate that is typically used is 5-7°F/min.
VI) USING PHASE DIAGRAMS TO EXPLAIN SLAG FUNDAMENTALS AND DESIGN SLAG RECIPES

a) Utilizing the system CaO-MgO to explain binary phase diagrams.

From melting points of pure MgO (2800°C) and CaO (2600°C) it is clear that the individual components will never form a liquid slag at steelmaking temperatures. Could MgO and CaO be combined to form a liquid slag at steelmaking temperature?

The following figure is simplified phase diagram (ignoring solid solution) of the CaO-MgO system.

![Figure 13. Simplified phase diagram of the CaO-MgO system](image)

Before we start it is important to define a few terms first:

In this diagram the composition of the two components (CaO & MgO) is presented on the abscissa (X-axis) and the temperature on the ordinate (Y-axis). The diagram consists of four areas: All Liquid area, All solid area (Lime + Periclase), and two solid + liquid areas (Lime + Liquid and Periclase + Liquid). The melting points of pure CaO and pure MgO is shown by points [l] and [p], respectively. The addition of MgO to CaO causes the melting point of CaO to be lowered from point [l] on the diagram (2570°C) to point [f] on the diagram (2300°C). This curved line [l]-[f] is called the liquidus line (or liquidus curve). The liquidus temperature is...
the temperature above which no crystals can exist. It is the locus of temperatures at which crystals first begin to appear on cooling the slag under equilibrium conditions. In a similar fashion, the addition of CaO to MgO causes the melting point of MgO to be lowered from point [p] on the diagram (2800°C) to point [f]. This curved line [p]-[f] is also a liquidus line. The horizontal line [g]-[h] is very important and is called the solidus line (2300°C). Below this line no liquid exists, and any mixture of CaO and MgO will be completely solid.

In order to demonstrate the fluxing of effect on this diagram, consider a mixture X containing 60% MgO and 40% CaO (dashed line on the diagram).

At 2600°C (point (a))

At 2600°C, a 60% MgO - 40% CaO (mixture X) is completely liquid (- point (a) falls in the liquid area of the diagram).

Between ≈2540°C (b) and 2300°C

When the fully liquid mixture X is cooled from 2600°C (a) it will intersect the periclase + liquid liquidus curve at ≈2540°C (b). At this temperature periclase crystals start to precipitate from the liquid. This temperature (≈ 2540°C (b)) is therefore the liquidus temperature for mixture X. It is clear from the diagram that there are an infinite number of liquidus temperatures for mixtures to the left and right of mixture X; the liquidus temperature is dependent on the composition of the mixture.

As mixture X is cooled below 2540°C, periclase crystals continue to precipitate from the liquid and the liquid composition follows the path b → f. At 2300°C (f) all the remaining liquid crystallizes to from lime + periclase so that, at temperatures below 2300°C, mixture X will be completely solid. The solidus temperature for mixture X is therefore 2300°C.

At 2350°C (c)

At 2350°C, mixture X consist of periclase + liquid; point (c) falls in the liquid + periclase area. The composition of the liquid at point (d) and the composition of the periclase is at point (e). The periclase at point (e) is not pure but contains a small of amount CaO in solid solution. The amounts of liquid and periclase can easily be determined with the use of the lever rule:

\[ \% \text{ Liquid} = \frac{c\rightarrow e}{d\rightarrow e} \times 100 = 61 \]
\[ \% \text{ Periclase} = \frac{d\rightarrow c}{d\rightarrow e} \times 100 = 39 \]

Although extensive fluxing between CaO and MgO occur (Figure 13), forming a slag containing only these two components is not possible at steelmaking temperatures. The phase diagram of the CaO-MgO system, however, shows why dolomite (mixture of CaO and MgO) is successfully used as a refractory material (very high solidus temperature).

The addition of other fluxes (component oxides or flourides) to CaO and MgO is therefore required to form a liquid slag at steelmaking temperatures.
b) Utilizing the CaO-MgO-SiO$_2$ phase diagram to explain ternary systems

In order to evaluate the fluxing effect of SiO$_2$ on CaO and MgO together, an equilateral triangle with the three components on the corners of the triangle is usually drawn. A map of the phase relations as a function of temperature and composition for any mixture inside this triangle, under equilibrium conditions, is plotted in the phase diagram as shown in Figure 14.

![Figure 14. Phase diagram for the CaO-MgO-SiO$_2$ system](image)

This diagram is fairly complicated and can be intimidating to most novice users. The question now arises how can this diagram be used as a tool for the steelmaker. Most steelmaking operations are conducted around 1600°C (2912°F) so that this diagram can be greatly simplified if the phase relations is examined only at this temperature. Figure 15 is a simplified version of Figure 14 (isothermal section at 1600°C) and is easier to understand.
As indicated in the legend, this diagram contains three distinct areas, which, for the sake of simplicity have been labeled as follows:

- **Sea area (all liquid)**
- **Land area (all solid)**
- **Swamp area (liquid + solid)** Note the abbreviations used for the solid phases.

Consider slag X

Slag X has the following composition:

- % SiO₂ 50
- % CaO 35
- % MgO 15

Slag X falls within the Sea area of the diagram (Figure 15) and is therefore completely liquid at 1600°C (2912°F).
Consider slag Y
Slag Y has the following composition:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% SiO₂</td>
<td>20</td>
</tr>
<tr>
<td>% CaO</td>
<td>70</td>
</tr>
<tr>
<td>% MgO</td>
<td>10</td>
</tr>
</tbody>
</table>

Slag Y falls in the "land area" of the diagram, indicating that this slag will be completely solid at 1600°C. It is clear from the Figure 15 that any slag that falls within the "land area" of the diagram will be completely solid.

Consider slag Z
Slag Z has the following composition:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% SiO₂</td>
<td>80</td>
</tr>
<tr>
<td>% CaO</td>
<td>10</td>
</tr>
<tr>
<td>% MgO</td>
<td>10</td>
</tr>
</tbody>
</table>

Slag Z falls in the SiO₂ + liquid "swamp area" of the diagram, indicating that this slag will consist of SiO₂ and liquid. This area of interest has been enlarged and is shown in Figure 16.

![Figure 16. Enlarged view of the SiO₂ + liquid area.](image)

For any mixture that falls in the SiO₂ + liquid "swamp" area, the composition of the silica is always at the silica apex (pure silica) and the composition of the corresponding liquid will be somewhere on the silica liquidus curve (n to p). The exact composition of the liquid is determined by drawing a line from the silica apex of the diagram (S) through the composition of the slag until it intersects the silica liquidus curve (n-p). For mixture Z the point of intersection is at (L). The composition of the liquid (L) can be read directly from the diagram. (%SiO₂ = 67.4, %CaO = 16.3, %MgO = 16.3).

The relative amounts of liquid and silica can easily be calculated using the lever rule:

\[ \% \text{ Liquid} = \frac{Z \rightarrow S}{L \rightarrow S} \times 100 = 61.2 \quad \% \text{ Silica} = \frac{Z \rightarrow L}{L \rightarrow S} \times 100 = 38.8 \]
It is clear that if the composition of the slag is close to the silica apex then the amount of silica in the slag will be large and the amount of liquid will be small, conversely, if the composition of the slag is closer the silica liquidus curve the amount of liquid will increase.

Consider slag K

Slag k has the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35</td>
</tr>
<tr>
<td>CaO</td>
<td>50</td>
</tr>
<tr>
<td>MgO</td>
<td>15</td>
</tr>
</tbody>
</table>

Slag K falls in a "swamp" area that consists of liquid + Ca₂SiO₄ (C₂S) + MgO (M). Because there are three phases (2 solids + a liquid) present, the compositions of all the phases are fixed so that this swamp area is defined by the triangle C₂S - liquid - M. Figure 17 is an enlarged drawing of this triangle.

![Figure 17. Enlarged view of the C₂S + liquid + M "swamp" area.](image)

Very Important: the composition of the liquid is fixed at point L (%SiO₂ = 38, %CaO = 45, %MgO = 17) which means that for any slag that falls within this triangle the composition of the liquid portion of the slags stays constant but the relative amounts of the phases will change. The relative amounts of the phases present in slag K can easily be calculated by drawing lines from the apex's of the triangle through the slag composition point K until the triangle sides are intersected.

\[
\text{% Liquid} = \frac{K \rightarrow L'}{L \rightarrow L'} \times 100 \quad \text{% Ca₂SiO₄} = \frac{K \rightarrow C₂S'}{C₂S \rightarrow C₂S'} \times 100 \quad \text{% MgO} = \frac{K \rightarrow M'}{M \rightarrow M'} \times 100
\]

% Liquid = 56.4, % Ca₂SiO₄ = 38.4, % MgO = 5.2.

* From the phase rule the degrees of freedom (f) = 0 so that the compositions of the phases are fixed
c) Slag requirements for refractory compatibility in the CaO-MgO-SiO$_2$ system

The fundamental slag requirement for refractory compatibility is saturation of the slag with the components of the refractory material. For example, for a Magnesia-C refractory, MgO saturation is a required, whereas, for a dolomite refractory, CaO saturation is required. There are many other factors that influence refractory wear such as; quality and type of the material, carbon levels, preheat practices, carbon burnout, thermal discipline etc.

Most Si-killed steel slags contain MgO, CaO and SiO$_2$ as the major components so that the CaO-MgO-SiO$_2$ phase diagram can be used as an approximation to evaluate these slags. Consider the slag (X) at 1600°C (2912 °F):

\[
\begin{array}{c|c|c|c}
\% SiO_2 & 50 \\
\% CaO & 35 \\
\% MgO & 15 \\
\end{array}
\]

The same simplified phase diagram discussed in Figure 15 can be used to evaluate this slag. In the evaluation of the slag, two types of slag-line refractories will be considered: a Magnesia refractory and a doloma (dolomite) refractory. Equilibrium conditions will be assumed in the analysis. The slag (X) falls in the "sea" area of the phase diagram (Figure 18) and is therefore fully liquid at 1600°C (2912°F).

**Slag requirements for Magnesia-Carbon slag lines (Figure 18)**

This slag (slag X) will dissolve MgO from the refractory in order to be magnesia saturated and its composition will move from X to X’ (Figure 18). The composition of the slag at X’ is:

\[
\begin{array}{c|c|c|c}
\% SiO_2 & 41 \\
\% CaO & 29 \\
\% MgO & 30 \\
\end{array}
\]

1000 lb. of slag with composition X could dissolve 220 lb. of MgO from a magnesia slag line to be MgO saturated at 1600°C. Fortunately, this extent of refractory dissolution does not often happen in practice, as the slags are not usually this bad and equilibrium conditions are not attained. However, with extensive stirring and long holding times, the equilibrium value could be approached.

Slags that are MgO saturated are indicated by the wide solid line in Figure 18 stretching from O to P to Q. This line shows that there is no "magic" MgO aim value, but that the solubility of MgO in the slag is a function of slag composition. This compositional dependence is shown in Figure 19, which is a plot of the solubility of MgO (for slags O to P) as a function of slag basicity (expressed as the %CaO/%SiO$_2$). A tremendous increase in the solubility of MgO is seen as the basicity of the slag decreases. Important to note is that the MgO saturation value is at a minimum when the slag is also CaO saturated (point O). This is a very important point because if the slag is just CaO saturated, but not MgO saturated, the driving force to dissolve MgO from the brick will be the lowest so that the rate of dissolution of MgO in the brick will be slow.
Figure 18. Reaction of slag X with a magnesia refractory at 1600°C (2912°F)

Figure 19. MgO saturation requirements of CaO-MgO-SiO₂ slags at 1600°C (2912°F)
Slag requirements for Doloma (dolomite) refractories

Once again the simple system CaO-MgO-SiO₂ (Figure 20) will be used to demonstrate slag reactions with dolomite slag lines. Consider slag X again. Since dolomite (doloma) refractories consist of CaO and MgO, slag x will dissolve MgO and CaO from the refractory in order to satisfy its solution requirements. The composition of slag X will move to X" if equilibrium is attained. The composition of the slag at X" is:

% SiO₂ 39
% CaO  40
% MgO  21

1000 lb. of a slag with composition X could dissolve 280 lb. of dolomite (CaO + MgO) from the refractory to be MgO-saturated. However, the slag is still not CaO saturated at this point and will continue to react with the CaO component in the dolomite lining. The liquid composition follows the path X" → O, where at (O) it is now also lime saturated. The final slag composition is at X''' and consist of ≈ 6% periclase and 94% liquid. 1000 lb. of slag with composition X could dissolve 390 lb. of dolomite refractory to be CaO and MgO saturated at 1600°C (2912°F).

1600°C (2912°F) Isothermal Section

Figure 20. Reaction of slag X with a dolomite refractory at 1600°C

In most dolomite refractories the MgO component is embedded in a continuous matrix of CaO. Because only the CaO component is normally "exposed" to slag, the key requirement for dolomite refractories is CaO-saturation. The area of CaO saturation is indicated by the thicker line. When using dolomite refractories in slag line areas or in stainless steel vessels, slags with low MgO levels can be utilized. For some steelmaking grades, slags with a low MgO content are required to minimize the possibility of Mg pickup in the steel during ladle furnace refining.
d) The CaO-MgO-Al2O3 system

The 1600°C (2912°F) isothermal section of the CaO-MgO-Al2O3 system is shown in the next figure.

![1600°C Isothermal Section](image)

Figure 21. The isothermal section of the CaO-MgO-Al2O3 system at 1600°C (2912°F)

This figure has the following important features:

The all-liquid (sea area) in this diagram is significantly smaller than that of the CaO-MgO-SiO2 system. The reason for this is the presence of the very stable spinel phase (MgAl2O4) which is imposing its stability on the liquidus phase relations in this system.

The solubility of CaO is higher in this system than the CaO-MgO-SiO2 system indicating that Al2O3 is a better flux for CaO than SiO2. The following table shows the composition of slags in the two systems that are dual saturated (both CaO and MgO)
Table 7. Dual Saturated slags in the CaO-MgO-SiO₂ and CaO-MgO-Al₂O₃ systems at 1600°C

<table>
<thead>
<tr>
<th></th>
<th>CaO-MgO-SiO₂</th>
<th>CaO-MgO-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>44.5</td>
<td>53</td>
</tr>
<tr>
<td>% MgO</td>
<td>17.5</td>
<td>10</td>
</tr>
<tr>
<td>% SiO₂</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>% Al₂O₃</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>

Figure 21 also shows why it could be difficult to "read" aluminate slag in a ladle. Consider for example slag (a) that would appear "creamy" in the ladle but would be "glassy" on a rod sample. When lime is added to slag (a) the slag composition will follow the path from (a) to (b) without any visible effect on the fluidity (viscosity) of the slag in the ladle. If successive rod samples are taken between points (a) and (b) the quenched slag sample will change from a glass to a mixture of glass and crystals, and finally at point (b) it will be all crystals. If more lime is added beyond point (b) the slag consistency will change from "creamy" to fluffy as the saturation level of CaO is exceeded.

The solubility of MgO is much lower in the CaO-MgO-Al₂O₃ system and is much less sensitive to the basicity ratio of the slag (CaO/(SiO₂+Al₂O₃)). This has a significant implication on the potential refractory wear of magnesia-based refractories. A silicate slag that has a basicity ratio (CaO/SiO₂) of 1.0 could dissolve 21.7 % MgO at 1600°C, whereas an aluminate slag with a basicity ratio (CaO/Al₂O₃) of 1.0 could only dissolve 12.2 % MgO. The effect of basicity on MgO solubility for the two systems is graphically shown in the next figure.

![Graph showing MgO solubility in CaO-MgO-SiO₂ and CaO-MgO-Al₂O₃ systems at 1600°C](image)

Figure 22. The solubility of MgO in slags of the systems CaO-MgO-SiO₂ and CaO-MgO-Al₂O₃ at 1600°C (2912°F)
This figure clearly shows that magnesia-based slaglines would be much more vulnerable to "watery" (acidic) silicate slags than the equivalent aluminate slags.

e) The CaO-MgO-Al₂O₃-SiO₂ system

While the phase diagrams of the CaO-MgO-SiO₂ and CaO-MgO-Al₂O₃ systems are useful to demonstrate slag fundamentals, their direct application to steelmaking slags are limited. Most steelmaking slags contain both SiO₂ and Al₂O₃ as fluxes so that the quaternary system CaO-MgO-Al₂O₃-SiO₂ would be more applicable to steelmaking slags. Unfortunately, adding a fourth component greatly increases the complexity of the phase relations in this system. However, the system can be greatly simplified by considering only slags that are of steelmaking interest. The slags that are optimum for steelmaking and refractory performance are the slags that are dual-saturated with respect to both CaO and MgO. These slags have a high solubility of CaO for good desulfurization and are also compatible with both dolomite and magnesia-based refractories. The following table shows the compositions of slags that are dual saturated as function of Al₂O₃ content at 1600°C

<table>
<thead>
<tr>
<th>% Al₂O₃</th>
<th>% MgO</th>
<th>% CaO</th>
<th>% SiO₂</th>
<th>C/S ratio</th>
<th>B₂ ratio</th>
<th>Opt. Bas (Λ)</th>
<th>-log Cₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.32</td>
<td>44.31</td>
<td>38.37</td>
<td>1.15</td>
<td>1.61</td>
<td>0.696</td>
<td>3.042</td>
</tr>
<tr>
<td>5</td>
<td>15.19</td>
<td>44.79</td>
<td>34.92</td>
<td>1.28</td>
<td>1.50</td>
<td>0.700</td>
<td>2.982</td>
</tr>
<tr>
<td>10</td>
<td>13.11</td>
<td>47.45</td>
<td>29.44</td>
<td>1.61</td>
<td>1.55</td>
<td>0.715</td>
<td>2.763</td>
</tr>
<tr>
<td>15</td>
<td>10.92</td>
<td>51.13</td>
<td>22.95</td>
<td>2.23</td>
<td>1.64</td>
<td>0.737</td>
<td>2.458</td>
</tr>
<tr>
<td>20</td>
<td>8.99</td>
<td>54.69</td>
<td>16.32</td>
<td>3.35</td>
<td>1.75</td>
<td>0.759</td>
<td>2.132</td>
</tr>
<tr>
<td>25</td>
<td>7.68</td>
<td>57.05</td>
<td>10.27</td>
<td>5.56</td>
<td>1.84</td>
<td>0.778</td>
<td>1.856</td>
</tr>
<tr>
<td>30</td>
<td>7.47</td>
<td>57.15</td>
<td>5.38</td>
<td>10.62</td>
<td>1.83</td>
<td>0.789</td>
<td>1.702</td>
</tr>
<tr>
<td>35</td>
<td>8.92</td>
<td>53.88</td>
<td>2.20</td>
<td>24.49</td>
<td>1.69</td>
<td>0.786</td>
<td>1.742</td>
</tr>
</tbody>
</table>

The data from this table showing the variation in CaO and MgO solubility as function of Al₂O₃ content is graphically shown in Figure 23.

Note the increase in lime solubility and sulfide capacity as the Al₂O₃ content of the slag increases (up to about 30%). Even more importantly, note the decrease in the MgO solubility of the slag as the Al₂O₃ content of the slag increases. The table and diagram also show that the solubility of CaO decreases again as the SiO₂ content of the slag becomes very low as the ternary system CaO-MgO-Al₂O₃ system is approached.
It is therefore no surprise that, when considering the above discussion, why the slags from Al-killed steels usually have a high fluidity and good sulfur removal properties. Alumina (Al₂O₃) is the oxidation product of the Al added to steel and acts as a useful flux to bring the added lime into solution. However, to ensure optimum sulfur removal conditions and Al₂O₃ inclusion absorption, it is generally recommended that Al₂O₃ content of the slag should not exceed 25 - 30%. Slags with a high Al₂O₃ content that are not saturated with CaO will be very aggressive to dolomite refractories. The result would be slag penetration into the refractory and a corresponding dissolving of the CaO from the brick in order to fulfill the solution requirements of the slag.

The MgO solubility limits for CaO-MgO-Al₂O₃-SiO₂ slags can easily be determined. The MgO solubility in the slag is usually the lowest at CaO saturation (dual saturation) and increases as the basicity of the slag decreases. This is shown in Figure 24, which is a plot of MgO saturation as a function of slag composition (optical basicity). For optical basicity values > 0.69 the following general equation can be used to calculate the MgO solubility in slags of the system CaO-MgO-Al₂O₃-SiO₂ at 1600°C (2912°F) [12].

$$\% \text{ MgO} = 1330.5 \Lambda^2 - 2092 \Lambda + 829.9$$

where $\Lambda$ is the calculated optical basicity of the slag.

---

Figure 23. CaO and MgO solubility as a function of Al₂O₃ content in CaO-MgO-Al₂O₃-SiO₂ slags at 1600°C (2912°F).
The upper applicable basicity limit of the equation is lime saturation which is dependent on the alumina level of the slag. For example, lime saturation is $\Lambda = 0.696$ for $\text{Al}_2\text{O}_3$-free slags and 0.715 for slags containing 10% $\text{Al}_2\text{O}_3$ at 1600°C (Figure 24). Similar equations can be generated for various alumina levels at basicities lower than 0.69 using simple regression techniques.

![Figure 24. MgO saturation levels in slags of the system CaO-MgO-Al$_2$O$_3$-SiO$_2$ at 1600°C](image)

**f) Slags containing fluorspar**

The fluxing potential of $\text{CaF}_2$ to bring $\text{CaO}$ into solution is very similar to that of $\text{Al}_2\text{O}_3$, only stronger. One important difference is the MgO saturation levels in the slag. When the $\text{Al}_2\text{O}_3$ level in the slag increases, the saturation level of MgO in the slag decrease (at CaO saturation). However, when the $\text{CaF}_2$ level in the slag increases, the solubility of MgO in slag stays increases. This is a very important consideration when using Mag-C slag line refractories in contact with slags containing high $\text{CaF}_2$ levels.

Fluorspar can be very effective to increase the solubility of CaO in silicate slags but is not very effective to increase CaO solubility in aluminate slags. The method of fluorspar addition could have a big impact on the effectiveness of fluorspar to bring lime into solution and the amounts required doing so. Fluorspar should never be added in its pure form to a slag but rather in combination with lime and silica. Lime, silica, and $\text{CaF}_2$ mixtures are much more effective to go into solution than lime and $\text{CaF}_2$ mixtures.
The addition of fluorspar to silicate and aluminate slags results in an increase in the solubility of MgO in the slag. This increase in MgO solubility could lead to significant refractory wear if additional MgO is not added to the slag or if CaO-saturation is not maintained at all times. Most steelmaking refining slags are not MgO-saturated, because only lime is typically available as an additive. Furthermore the very high levels of MgO required for saturation might be undesirable from a steel quality perspective. High MgO slags in contact with steel with low oxygen content could result in Mg pickup in the steel and lead to spinel inclusion formation in the steel. Based on the discussion above it is clear that dolomite refractories might be more compatible in contact with fluorspar containing slags than magnesia-based refractories. The simple reason is that lime saturation (a dolomite refractory requirement) is much easier to achieve in practical steelmaking than MgO, or dual saturation.

**The addition of fluorspar to silicate slags**

The effect of fluorspar on silicate slags is shown in the following figures:

![Figure 25. Phase diagram of the CaO-CaF₂-SiO₂ system](image)
The most striking feature of this diagram is the tremendous increase in the solubility of CaO when CaF₂ is added CaO-SiO₂ slags or when SiO₂ is added to CaO-CaF₂ slags. The combined effect of SiO₂ and CaF₂ results in a very high CaO solubility and the maximum solubility at 1600°C is shown by point (a) on the diagram. The composition of the slag at this point is approximately the following:

% CaO – 72  
% SiO₂ – 16  
% CaF₂ – 12

The following figure shows the effect of SiO₂ content in the slag on the solubility of CaO in CaO-CaF₂-SiO₂ slags.

![Figure 26. Solubility of CaO as a function of SiO₂ content in CaO-CaF₂-SiO₂ slags at 1600°C](image)

The maximum in CaO solubility is at about 12% CaF₂ in the slag. The addition of more CaF₂ to the slag, and still maintaining CaO saturation, results in a decrease in CaO solubility because the SiO₂ content of the slag is diluted to levels below 18%. From the above it is clear that the maximum amount of fluor spar that would ever be required in a slag is 12% CaF₂. The addition of more CaF₂ than this number would either result in a decrease in CaO solubility or an increase in fluidity that could lead to an increase in refractory erosion.
The diagrams shown above are especially useful in designing flux recipes for rapid liquid formation. Consider the following mixtures:

Table 9. The combined effect of SiO$_2$ and CaF$_2$ in the solubility of CaO at 1600°C

<table>
<thead>
<tr>
<th></th>
<th>Mixture 1</th>
<th>Mixture 2</th>
<th>Mixture 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>% SiO$_2$</td>
<td>30</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>% CaF$_2$</td>
<td>30</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>% Liquid</td>
<td>0</td>
<td>40*</td>
<td>100</td>
</tr>
<tr>
<td>% Solid</td>
<td>100</td>
<td>60</td>
<td>0</td>
</tr>
</tbody>
</table>

*The composition of the liquid for mixture 2 only contain about 27% CaO in solution.

The combination of CaF$_2$ and SiO$_2$ can create slags in the CaO-CaF$_2$-SiO$_2$ system with excellent desulfurization abilities as shown in the table below. (Using 100000 kg steel, 2000 kg slag, Initial S = 0.05, Oxygen = 15 ppm, 1600°C)

Table 10. Calculated slag and metal parameters for CaO-saturated slags at 1600°C.

<table>
<thead>
<tr>
<th></th>
<th>CaO-SiO$_2$ Slag</th>
<th>CaO-CaF$_2$ Slag</th>
<th>CaO-CaF$_2$-SiO$_2$ slag (slag (a) Fig. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>56</td>
<td>26.6</td>
<td>72</td>
</tr>
<tr>
<td>% SiO$_2$</td>
<td>44</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>% CaF$_2$</td>
<td></td>
<td>73.4</td>
<td>12</td>
</tr>
<tr>
<td>Optical Basicity</td>
<td>0.691</td>
<td>0.744</td>
<td>0.823</td>
</tr>
<tr>
<td>Sulfide Capacity</td>
<td>-3.119</td>
<td>-2.345</td>
<td>-1.208</td>
</tr>
<tr>
<td>Sulfur Distribution Coeff.</td>
<td>13.8</td>
<td>82.16</td>
<td>1127.14</td>
</tr>
<tr>
<td>Final Sulfur (%)</td>
<td>0.0392</td>
<td>0.0189</td>
<td>0.0021</td>
</tr>
</tbody>
</table>

While the theoretical slags discussed above show tremendous potential in terms of desulfurization, they are difficult to attain under real steelmaking conditions. The principal reason is that most real steelmaking slags also contain the components MgO and Al$_2$O$_3$, which will decrease the solubility of CaO. Most slagline refractories are MgO based so that MgO saturation becomes an important requirement in steelmaking slags.

Although the theoretical slags of the CaO-CaF$_2$-SiO$_2$ system has limited applicability as target slags for ladle applications, they are very important in terms of designing flux and additions recipes. This system shows that CaF$_2$-lime-SiO$_2$ mixtures have the potential to go into solution much faster than CaF$_2$-lime mixtures. The phase diagram in Figure 25 also shows that for slags containing SiO$_2$ and CaF$_2$ in approximately a 1:1 ratio is almost parallel to the slopes of the liquidus lines in the diagram. This is a very important observation and should be considered for flux recipes. Consider for example mixtures 2 and 3 in Table 9. Mixtures 3 could potentially melt completely if exposed to steelmaking temperatures whereas Mixture 2 would require SiO$_2$ from another source (steel deoxidation) to become fully liquid. This also shows that amount of CaF$_2$ added to a slag might be minimized by combining the CaF$_2$ with silica sand.
The addition of CaF$_2$ to high-alumina slags

In the previous section on the CaO-SiO$_2$-CaF$_2$ system a tremendous increase in the solubility of CaO was demonstrated for slags containing a combination of SiO$_2$ and CaF$_2$. The question arises whether the same fluxing effect will be present if CaF$_2$ is combined with Al$_2$O$_3$.

The following figure shows the isothermal section of the CaO-Al$_2$O$_3$-CaF$_2$ system at 1600°C.

From this figure it is clear that CaF$_2$ in combination with Al$_2$O$_3$ does not show that same behavior as it does in combination with SiO$_2$. The addition of Al$_2$O$_3$ to the CaF$_2$-CaO system does result in a significant increase in the solubility of CaO but the addition of CaF$_2$ to the CaO-Al$_2$O$_3$ system results in a decrease in the solubility of CaO. It is therefore clear that CaF$_2$ is not a good flux to increase the solubility of CaO in CaO-Al$_2$O$_3$ slags. The replacement of Al$_2$O$_3$ with CaF$_2$ results in a decrease in the solubility of CaO as indicated by the two CaO-saturated slags in the following table:

Table 11. CaO-saturated slags in the CaO-Al$_2$O$_3$-CaF$_2$ system at 1600°C

<table>
<thead>
<tr>
<th></th>
<th>Slag (a)</th>
<th>Slag (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>61</td>
<td>50</td>
</tr>
<tr>
<td>% Al$_2$O$_3$</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>% CaF$_2$</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>
Consider the CaO-MgO-SiO$_2$-CaF$_2$ system

The inferred phase relations for this system at 1600°C are shown in the next figure.

![Figure 28. The system CaO-MgO-SiO$_2$-CaF$_2$ at 1600°C (2912°F)](image)

This diagram shows the following important features:

1. An increase in CaO solubility as the CaF$_2$ content of the slag increases.
2. A decrease in CaO solubility on the CaO-saturation curve as the MgO content of the slag increases towards dual saturation.
3. An increase in MgO solubility at dual saturation as the CaF$_2$ content of the slag increases.

One of the most important features of this diagram is the increase in MgO solubility (at dual saturation) as the CaF$_2$ content of the slag increases. This has significant implications for magnesia-based slaglines. If fluorspar-containing slags are in contact with magnesia refractories, then significant refractory wear can occur if the slag is not MgO or CaO saturated. If the slag is CaO-saturated but MgO-unsaturated (“creamy” consistency), then the extent of refractory wear could be minimized even though the slag is not fully chemically compatible with the refractories. However, if the slag is also CaO unsaturated (very liquid or “watery” in consistency) then severe refractory wear can occur in just one heat. The above is true for any slag, CaF$_2$-containing or not, but the presence of CaF$_2$ accelerates the wear because of its depression of the solidus temperature of the slag, which causes deeper penetration into the refractory matrix.
Consider the CaO-MgO-Al₂O₃-CaF₂ system

It was shown earlier in the CaO-Al₂O₃-CaF₂ system that the addition of CaF₂ did not increase the solubility of CaO. Similar phase relations are observed in the CaO-MgO-Al₂O₃-CaF₂ system, which is shown in the next figure.

![Phase Diagram](image)

Figure 29. Phase diagram of the CaO-MgO-Al₂O₃-CaF₂ system at 10% Al₂O₃

The compositions of the slags at dual saturation in the systems CaO-MgO-Al₂O₃ and CaO-MgO-Al₂O₃-CaF₂ are shown in the next table. The addition of CaF₂ to the CaO-MgO-Al₂O₃ system results in only a small increase in the solubility of CaO but a very large increase in the solubility of MgO in the slag. This diagram and table once again demonstrate the vulnerability of magnesia-based slagline refractories to CaF₂-containing slags. The use of CaF₂ in high-Al₂O₃ slags therefore should be avoided if possible. The benefits of using CaF₂ as a cheap fluxing precursor might be offset by the potential of increased refractory wear.

<table>
<thead>
<tr>
<th>Table 12. Slag compositions at dual saturation in the systems CaO-MgO-Al₂O₃ and CaO-MgO-Al₂O₃-SiO₂ at 1600°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System</strong></td>
</tr>
<tr>
<td>% CaO</td>
</tr>
<tr>
<td>% MgO</td>
</tr>
<tr>
<td>% Al₂O₃</td>
</tr>
<tr>
<td>% CaF₂</td>
</tr>
</tbody>
</table>
The extent of MgO-dissolution and refractory wear can be minimized if CaO-saturation is maintained at all times, but if the slag is both CaO and MgO unsaturated (very watery) then extensive refractory wear could occur.
a) Definition of terms

The following is a brief overview of the principles related to steel desulfurization. For the sake of brevity and simplicity, a significant amount of the detailed information (such as reactions and equations) have been omitted.

**Sulfide Capacity (C₅)**

The term sulfide capacity (C₅) is used to describe a completely liquid slag's potential ability to remove sulfur. Sulfide capacities for various slags have been calculated from experimental data and examples are shown in Figures 30 and 31.

![Figure 30. Iso-sulphide capacity curves for CaO-Al₂O₃-MgO slags at 1600°C. Numerical values show - log C₅.](image-url)

Sulfide capacity is defined as:

\[ C₅ = \left(\%S\right) \frac{pO₂^{1/2}}{pS₂^{1/2}} \]

where (\%S) is the sulfur content of the slag, pO₂ is oxygen partial pressure, and pS₂ is sulfur partial pressure.
Sulfide capacities are usually expressed in log units, for example: \( \log C_S = -3.2 \). The less negative the logarithmic unit (larger the actual number), the better the sulfur removing capacity of the slag, i.e., a slag with \( \log C_S = -1 \) has a better sulfur removing capacity than a slag with a \( \log C_S = -3 \).

The fact that a slag might have a favorable \( C_S \) value is no guarantee that good steel desulfurization will occur. It only means that the slags has the potential to remove sulfur from the steel. Other factors that have a profound impact on the extent of sulfur actually removed from the steel are:

- The extent of mixing between the steel and the slag
- The amount of slag
- Temperature
- Oxygen content of the steel
- Oxidation state of the slag
- Viscosity of the slag

The importance of these factors will be illustrated later. The relationship between sulfide capacity and optical basicity (\( \Lambda \)) is given by:

\[
\log C_S = \frac{[22690 - (54640 * \Lambda)]}{T} + [(43.6 * \Lambda) - 25.2]
\]
Figure 32 shows the correlation between sulfide capacity and calculated optical basicity of slags at 1500°C (2732°F).

**Figure 32.** Correlation between sulfide capacity and calculated optical basicity of slags at 1500°C.

**Sulfur Distribution Ratio (L$_S$)**

The sulfur distribution ratio is defined as:

\[
L_S = \frac{\%S}{[\%S]}
\]

where (%S) is the sulfur content of the slag, and [\%S] is the sulfur content of the metal.

From the above definition it is obvious that higher L$_S$ values are desired for good sulfur removal. L$_S$ is usually determined experimentally. Is it possible to calculate L$_S$ for a particular slag?
The relationship between $C_S$ and $L_S$ can be shown as:

$$L_S = (C_S) \frac{K}{[\%O]}$$

where $[\%O]$ is the oxygen content of the steel, and $K$ and $C_S$ are a function of temperature.

The only problem with this equation is determining a reliable value for $[\%O]$. $[\%O]$ is a function of temperature and the activities of aluminum and silicon in the steel which are difficult to measure. The value of equilibrium constant for the reaction:

$$\frac{1}{2} O_2 + [\%S](1 \text{ wt%}) = \frac{1}{2} S_2 + [\%O](1 \text{ wt%}); \quad \log k_{eq} = -935/T + 1.375$$

can be used as an approximation for $K$ in the equation above.

$C_S$ and $K \uparrow$ as $T \uparrow$ so that $L_S \uparrow$ as $C_S$ and $T \uparrow$.

$L_S \uparrow$ as $[\%O] \downarrow$

**Calculating the final metal sulfur content**

The following equation can be used to calculate the potential final metal sulfur content assuming good mixing and completely liquid slags.

$$[S_F] = \frac{[S_i] \cdot W_M}{W_M + (L_S \cdot W_S)}$$

where $[S_F]$ is the final sulfur content of the steel

$[S_i]$ is the initial sulfur content of the steel

$W_M$ is the weight of the metal

$L_S$ is the sulfur distribution ratio

$W_S$ is the weight of the slag

**Slag Fluidity and Effective Slag Volume**

One of the most important aspects that is frequently overlooked when evaluating and discussing slags, is that most slags consist of two fractions, i.e., a liquid fraction and a solid fraction. Slag fluidity in basic slags is controlled by the liquid and solid fractions of the slag. The higher the solid fraction of the slag - the lower the fluidity of the slag (higher viscosity). A basic slag that is completely liquid has maximum fluidity.

The following example illustrates the importance of fluidity and effective slag volume.
Consider the following two slags at 1600°C (2912°F):

<table>
<thead>
<tr>
<th></th>
<th>Slag O (Figure 33)</th>
<th>Slag K (Figure 33)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% SiO₂</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>% CaO</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>% MgO</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Phases present</td>
<td>100% liquid (Optimum slag)</td>
<td>56% liquid, 39% Ca₂SiO₄, 5% MgO</td>
</tr>
</tbody>
</table>

In many calculations of sulfur removal, the total composition of the slag is sometimes mistakenly considered. It is the lime dissolved in the liquid fraction of the slag that is removing sulfur from the steel and not lime as determined by the chemical analysis of the "total" slag. The undissolved lime in the slag does not remove any sulfur. The liquid fraction of slag K has the identical composition as slag O. The addition of more lime than required (slag O to slag K), only resulted in a decrease in the amount of liquid available for desulfurization (liquid composition stayed constant) and an increase in the viscosity of the slag.
The errors that can be made by not considering only the liquid portion of a slag is illustrated by the following example:

Table 13. Example of possible errors in the calculation of final metal sulfur content

<table>
<thead>
<tr>
<th></th>
<th>Considering the total slag chemistry (Slag O)</th>
<th>Considering the total slag chemistry (Slag K)</th>
<th>Considering only the liquid fraction of slag K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1600</td>
<td>1600</td>
<td>1600</td>
</tr>
<tr>
<td>Si (wt%)</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
<tr>
<td>WM (tons)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>WS (lb.)</td>
<td>2000</td>
<td>2000</td>
<td>(2000*0.56) = 1120</td>
</tr>
<tr>
<td>λ</td>
<td>0.698</td>
<td>0.717</td>
<td>0.698</td>
</tr>
<tr>
<td>[% O] (ppm)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>log CS</td>
<td>-3.01</td>
<td>-2.74</td>
<td>-3.01</td>
</tr>
<tr>
<td>LS</td>
<td>17.83</td>
<td>32.84</td>
<td>17.83</td>
</tr>
<tr>
<td>SF (wt%)</td>
<td>0.0297</td>
<td>0.0263</td>
<td>0.0318</td>
</tr>
<tr>
<td>Calculated result</td>
<td>Correct</td>
<td>Wrong!!</td>
<td>Correct</td>
</tr>
</tbody>
</table>

Metal Oxygen Content and Oxidation State of the Slag

The oxygen content of the steel has a profound impact on the sulfur distribution ratio (LS).

\[
LS = (CS) \frac{K}{[\%O]}
\]

If the temperature and slag composition is fixed the effect of [%O] can be evaluated as shown in Table 14 below:

Table 14. Calculation showing the effect of oxygen content on LS

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1600</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log CS</td>
<td>-2.04</td>
<td>-2.04</td>
</tr>
<tr>
<td>[% O] (ppm)</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>LS</td>
<td>49</td>
<td>246</td>
</tr>
</tbody>
</table>

Note the significant increase in the value of LS when the oxygen content of the steel decreases from 50 to 10 ppm.

A general recommendation is the total reducible oxides in ladle slags should be less than 2%. (Reducible oxides = FeO, MnO, and Cr2O3).
The effect the amount of reducible oxides in ladle slags on the desulfurizing efficiency is shown in Figure 34.

![Figure 34. Effect of (FeO + MnO) in slag on desulfurization.](image)

**The importance of good mixing between slag and steel**

A fully reduced slag with a good desulfurizing capacity and a steel with a low oxygen content will, based on theoretical calculations, result in a high sulfur distribution ratio $L_S$ which is required for good sulfur removal. However, this is still no guarantee that efficient sulfur removal will actually occur in practice. Extensive intimate mixing between the slag and the steel is required to overcome the kinetic barriers. The thermodynamic calculations only predict that the reactions are possible but do not say anything as to whether or not they will actually occur. The addition of fluxes during tap at the arc-furnace and/or high stirring rates at the ladle furnace, are therefore required to ensure good sulfur removal, provided that the other parameters discussed earlier are optimized.

b) **The design of flux recipes to achieve specific steelmaking goals**

Published phase diagram and liquidus slag models can be used to design slags for specific metallurgical requirements. It was mentioned earlier that the choice of fluidizers (SiO$_2$, Al$_2$O$_3$, and/or CaF$_2$) in the design of these slags is very important because the solubility of CaO and MgO is strongly dependent on the type of fluidizer used. This is clearly illustrated by the slags in Table 15. All of the slags in Table 15 have a high fluidity and are just saturated with respect to CaO and MgO ("creamy") and are therefore compatible with magnesia and dolomite refractories. Using available phase diagrams or liquidus models, various combinations of fluidizing agents can be used so that an infinite number of slags with varying sulfide capacities can be designed to attain specific metallurgical goals.
Table 15. Compositions of slags that are just CaO or CaO and MgO saturated at 1600°C  
($\Lambda$=optical basicity, $C_s$ = sulfide capacity, and $S_f$ = final sulfur)

<table>
<thead>
<tr>
<th></th>
<th>Slag 1</th>
<th>Slag 2</th>
<th>Slag 3</th>
<th>Slag 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>% CaO</td>
<td>45</td>
<td>52</td>
<td>53</td>
<td>57</td>
</tr>
<tr>
<td>% MgO</td>
<td>17</td>
<td>10</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>% Al$_2$O$_3$</td>
<td>17</td>
<td></td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>% SiO$_2$</td>
<td>38</td>
<td>21</td>
<td>23</td>
<td>9</td>
</tr>
<tr>
<td>% CaF$_2$</td>
<td></td>
<td></td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>$B_5$ Ratio</td>
<td>1.63</td>
<td>1.63</td>
<td>1.94</td>
<td>1.86</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>0.698</td>
<td>0.742</td>
<td>0.758</td>
<td>0.785</td>
</tr>
<tr>
<td>-Log $C_s$</td>
<td>3.01</td>
<td>2.38</td>
<td>2.14</td>
<td>1.76</td>
</tr>
<tr>
<td>$S_f^*$</td>
<td>0.0424</td>
<td>0.0285</td>
<td>0.0217</td>
<td>0.0121</td>
</tr>
</tbody>
</table>

*Using 100 tonnes of steel, 1000 kg of slag, $S_f = 0.05\%$, $O = 15$ ppm

Slags can also be “designed” for resulfurized steel grades. This usually requires substitution of MgO for CaO in order to generate slags that are still fluid but with a decreased thermodynamic sulfide capacity (while maintaining basicity for basic refractory compatibility). These slags will have lower CaO/SiO$_2$ ratios which will increase the solubility of MgO in the slag. The MgO saturation values as a function of slag composition are shown in Figures 19 and 24. All these slags are 100% fluid at steelmaking temperatures and compatible with magnesia slag line refractories.
VIII References


G. Trömmel, W. Fix, and H. Kaup, Arch. für das Eisenhüttenwesen, 38, No 8, 1967, pp. 595-605.

