

Stainless Steel Slag Fundamentals – From Furnace to Tundish

Eugene B. Pretorius and Robert C. Nunnington
Process Technology Group
Baker Refractories
232 E. Market St
York, PA, USA

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Abstract

This paper will define slag practices and conditions that are optimal for stainless steel quality and good refractory performance. Phase equilibria and computer modeling are used to simulate and predict refractory-slag and slag-metal interactions. The slag principles and requirements for foaming in the EAF are discussed. Aspects of the EAF slags will include the early generation of liquid slags to enhance heat transfer to the bath, and the chemistry and practicalities of foaming with stainless steel heats. With converter slags, specific attention is given to the different effects of MgO and CaO on slag viscosity during the decarburization step, and the dissolution kinetics during the reduction step. The chemical and physical interactions of ladle slags with liquid stainless steel are discussed, and the complex slag-metal interactions during ladle processing of stainless steel are introduced. Clean steel practices are discussed for ladle slags and tundish fluxes.

INTRODUCTION

This paper attempts to illustrate the benefits of applying slag fundamentals to improve stainless steelmaking quality and consistency, and lower refractory costs. Published phase diagrams, and models based on phase equilibria and steelmaking thermodynamics,^{1,2} were utilized to provide practical slagmaking guidelines.

One of the advantages of slag engineering is that customized slags can be designed to fulfill the metallurgical requirements of specific steel grades. An essential requirement is the ability to estimate the composition of the slag at any stage of the process. This is done by mass-balance calculations where all the factors contributing to the slag are considered. By controlling and manipulating slag composition and slag formation rates, the efficiency of stainless steelmaking processes can be improved.

EAF SLAGS AND FOAMING FUNDAMENTALS

Introduction

Two issues will be considered here, the earlier formation of slags to improve the process and electrical efficiency, and foaming slags to enhance these factors and also reduce the effect of arc radiation. The generation of the early liquid slags is a prerequisite to foaming in stainless steel slags.

Foaming slags are desirable in the EAF for reduced arc flare and slag splashing onto refractories and water-cooled panels (shielding of the arc). Equally important is that shielding of the arc reduces the voltage restrictions (arc length), which normally apply when the bath is flat and liquid. By shielding the arc, higher tap settings and thus better thermal efficiency can be attained. The insulating effect of the foam also decreases the radiation to the roof and reduces electrical and audible noise.

Despite the well-documented benefits of slag foaming with C steelmaking, few stainless steel producers have managed to generate a consistent foamy practice. The principal reason for this is the lack of slag chemistry and viscosity control. In many cases the slag tended to be too stiff to sustain an adequate foam.

The following discussion will attempt to provide a better understanding on the key factors that control slag foaming in stainless steel making. There are basically two requirements for slag foaming (C-Steel and stainless steel):

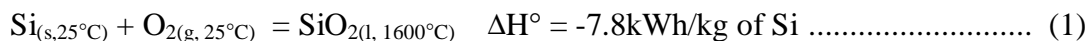
- a) Reactions or processes that generate small gas bubbles.
- b) Suitable slag properties to sustain the bubbles as a stable foam.

Early slag generation

Whether the EAF has a single or double basket charge, the early stages of melting are characterized by short arcs and poor melting efficiency. If the charge contains a significant amount of C steel scrap, then the early oxides generated can be high in FeO, but are discretely distributed and do not play a role in the heat transfer. By generating a continuous liquid slag medium to aid conduction and radiation heat transfer through the bath earlier in the meltdown, the rate of melting can be improved. For example, in one US shop a 20% decrease in "power on time", was observed.

Formation of an early liquid slag is facilitated by the addition of wollastonite (CaSiO_3) with the first scrap charge. The wollastonite will melt at steelmaking temperatures, and provide the fluxing precursor in which the oxidized components and added lime can dissolve rapidly. Lime additions with the first scrap bucket should be matched with the expected amount of Si

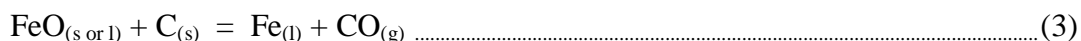
that will be oxidized. The Si in the bath originates from scrap and ferroalloys, or as deliberate FeSi additions. The latter is costly, and not a generally acceptable means of supplying Si units. The quicker the liquid slag forms in the furnace, the quicker the power levels (tap settings) can be increased. However, early liquid slags can also be formed by the oxidation of Si in the bath, or deliberate quartz (SiO_2) and lime additions (although the effectiveness of this mixture will be considerably less than wollastonite additions). The disadvantages of adding quartz is that it requires energy to heat up and melt it, whereas the heating and oxidation of Si overall is exothermic and provides additional energy for melting scrap. i.e.



Irrespective of the source of SiO_2 , the presence of FeO, and CaO from lime additions now allows for the formation of a liquid slag. The FeO generated is a powerful flux for CaO and SiO_2 , and the combination these oxides allows for rapid melting.

Gas generation

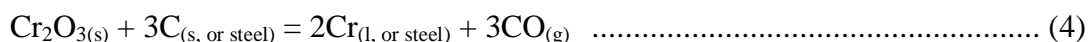
The principal reaction that creates gas bubbles in the slag is:



In C-steelmaking, the FeO is generated in-situ as the major oxidation product of the oxygen blow and is therefore a major component in the slag (>20%). If the consistency of the slag is suitable for sustaining a foam, the simple injection of carbon into the slag will cause the slag to foam. The main reason why poor foaming is sometimes observed in C-steelmaking, is excessive O_2 blowing, leading to a high FeO content, which renders the slag too fluid to sustain a stable foam. The gas generation can also be effected via the reaction of unreduced FeO in DRI, C- O_2 injection, or even millscale-C injection.

In stainless steelmaking, the major oxidation products are SiO_2 and Cr_2O_3 . The SiO_2 is a fluxing component, while the Cr_2O_3 is a very potent refractory component, which stiffens the slag. With stainless steel slags, the Cr-O buffer occurs at a much lower oxygen potential than the Fe-O buffer, and Cr will be preferentially oxidized compared to Fe. It is therefore important that the Cr_2O_3 content of the slag must be carefully controlled, to generate the slag consistency amenable for foaming conditions.

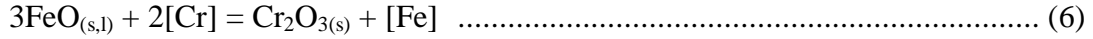
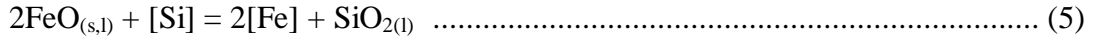
The following reaction is not normally significant in slag foaming, either because the levels of Cr_2O_3 are too low, or more likely the rate of reaction is too slow for sufficient CO gas generation.



More importantly, with conventional EAF processes the Cr_2O_3 is normally not available in a dissolved form in the liquid portion of the slag, but is present as solid spinel (MgCr_2O_4) and CaCr_2O_4 phases.

Also, when the [C] dissolved in the steel is relied on for reducing the oxides in the slag, then the reaction rates are slow, as this involves the mass transfer across a relatively small area of slag-metal interface. This interface is not turbulent as in a converter, and the rapid generation of small bubbles is not as favorable as when the reactions occur directly in the slag.

While FeO is a requirement for slag foaming, the method of FeO addition is critical for a good foamy practice and will be discussed in detail later. The simple addition of iron oxide with scrap (but without additional C) during melting will result in the reduction of the FeO by the Si and Cr in the bath according to the following reactions:



In both reactions the FeO is removed from the slag, but more importantly, in the second reaction Cr₂O₃ is generated which can lead to excessive solids, and thus excessive slag viscosities.

Slag requirements for optimum foaming

Previous research³⁻⁵ has shown that foaming characteristics improve with decreasing surface tension (σ) and density(ρ), and increasing viscosity (η) of the slag. The stability of the foam, or foaming index (Σ) is also determined by the average bubble size (D_B):

$$\Sigma = 115 \eta / (\sigma \cdot \rho)^{0.5} \dots\dots\dots (7)$$

$$\Sigma = \eta^{1.2} / (\sigma^{0.2} \cdot \rho \cdot D_B^{0.9}) \dots\dots\dots (8)$$

D_B determines if the foam is a true foam (like beer foam) or simply expanded slag volume, due to the gas hold-up as the CO passes through the liquid slag. Thus small bubbles are important to generating stable foams.

Another way of expressing Σ is: $\Sigma = h_f / V_{s,g} \dots\dots\dots (9)$

Where h_f is the height of the foam and V_{s,g} is the superficial gas velocity, calculated from the rate of CO gas generation.

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 or viscosity⁵. Thus, these "optimum" slags are not completely liquid ("watery") but are saturated with respect to CaO (Ca₂SiO₄) and/or MgO. These second phase particles serve as gas nucleation sites, which lead to a large number of 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 follows⁶:

$$\eta_e = \eta (1 - 1.35 \Theta)^{-5/2} \dots\dots\dots(10)$$

where

η_e - effective viscosity of the slag,

η - viscosity of the molten slag

Θ - fraction of precipitated solid phases

Figure 1 shows the relationship between the foaming index (Σ)⁷ and the relative effective viscosity(η_e). 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 1, there is an optimum amount of second-phase particles that is beneficial for foam stability (point G). Once this point is exceeded the slag becomes too "crusty" (oversaturated) and the foaming index decreases.

Typical stainless steel EAF slags consist mostly of the components CaO, MgO, Al₂O₃ and SiO₂ so that the phase diagram of the CaO-MgO-Al₂O₃-SiO₂ system can be used to generate target slags with small amounts of second phase particles. Ideally the Cr₂O₃ level of the slag should be less than 5% and can therefore be ignored.

For the sake of simplicity, the 1600°C isothermal section of simple system CaO-MgO-SiO₂ is utilized in Figure 2 to demonstrate the target slags for optimum foaming. Typical target

compositions would be on, or just beyond, the saturation boundaries of CaO (Ca_2SiO_4) or MgO, at the temperature of interest (Figure 2).

The ideal aim (final) slag composition is at dual saturation with respect to both CaO and MgO. These dual saturated slags are basic enough to minimize Cr_2O_3 losses to the liquid portion of the slag but will also be compatible with magnesia-chrome and magnesia-carbon refractories.

From the discussion above it is clear that establishing target slags is relatively simple, since the liquidus phase relations of the CaO-MgO- SiO_2 - Al_2O_3 system are well known, and target slags at any Al_2O_3 content can be determined. A slag model was developed using a mathematical and statistical approach to define these target slags^{1,2}. A critical requirement for these target slags to foam adequately is the control of the Cr/ Cr_2O_3 equilibrium in the bath. The solubility of chromium oxide (CrO_x) in the targeted slags above is very low ($< 5\%$ CrO_x). The moment the solubility of CrO_x is exceeded in the slag, chromium-containing phases will precipitate, which will drastically increase the viscosity of the slag and negatively impact the slag's ability to foam.

The first parameter that has to be established is the volume of slag that will be required to cover the arcs when foaming. This in turn will indicate the amounts of SiO_2 , CaO, MgO, and Al_2O_3 needed to achieve the desired volume of slag in the furnace. A mass-balance approach is then used to perform a Si balance and calculate the amount of SiO_2 that will report to the slag. It is very important that Si level in the bath does not drop below a certain critical level ($> 0.2\%$ Si), otherwise significant amounts of Cr could be lost to the slag. The amount of Si remaining in the bath will depend on the balance of chemical and electrical energy that will be utilized to melt the scrap and heat the charge. If chemical energy from oxidation of Si is used then the amount of oxygen blown should be linked to the available Si in the metal and the aim tap Si ($> 0.25\%$). Blowing much more oxygen than the stoichiometric amounts could again lead to excessive chrome oxidation. If charge chrome with high Si content is available, then enough Si might be in the bath to match the oxygen input. However, additions of FeSi (or any other source of Si) with the scrap might be required to increase the Si load in the furnace, to achieve the targeted chemical energy inputs.

When oxygen is blown into a molten pool of metal, the metals will oxidize according to the affinity for oxygen and their activities in the bath. While Al and Si have a greater affinity for oxygen, some of the Cr in the bath will also oxidize because of its high activity. If the CrO_x is absorbed into a liquid slag, then equilibrium conditions can be approached after the oxygen blow, and the chrome could revert back to the bath, providing the Si content is high enough. In the liquid slag enhances the mass transfer between slag and metal. However, if the oxidized chrome is present as a solid phase (MgCr_2O_4 , CaCr_2O_4) in a stiff slag, the recovery of chrome into the metal will be poor even if the Si content of the steel is high.

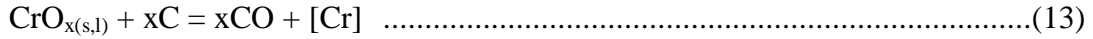
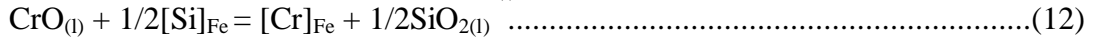
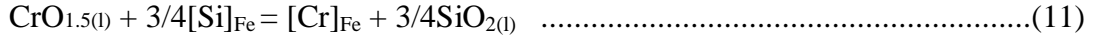
Another very important parameter that influences slag foaming in stainless steelmaking is the timing of additions. The path the slag composition takes to achieve its final target composition is crucial for controlling chrome losses and optimizing the foamability of the slag. The generation of an early liquid slag during melt down is an important requirement to enhance oxidation/reduction kinetics in the bath, and control the amount of chrome lost to the slag. The early liquid slag is facilitated by the addition of wollastonite (CaSiO_3) as discussed earlier.

Another important consideration is the initial MgO content of the slag. The addition of MgO to "wollastonite" type slags will decrease the solubility of Cr oxide because the primary Cr saturation phase changes from eskolaite (Cr_2O_3) to spinel (MgCr_2O_4)⁹. However, the addition of MgO to a CaO- SiO_2 slag will lower the melting point of the slag and increase the fluidity of the slag until the MgO content of the slag becomes too high ($> 15\%$) and periclase or spinel

start to precipitate. It is therefore important to distribute the MgO (doloma) additions so that MgO content of the slag never exceeds the target MgO value. The suggested path of slag formation based on the discussions above is shown in Figure 2.

Cr chemistry in foaming stainless steel slags

From the above discussion, it is clear that the management of Cr in the slag is an important aspect of controlling foaming in stainless steel slags. Essentially the equilibria governing the reactions of Cr species can be described as follows:



In order to compare the oxides in terms of one mole of Cr per mole of oxide, Cr_2O_3 is normally expressed as $\text{CrO}_{1.5(l)}$. Thus the relationship can be thermodynamically described by the free energy of formation

$$(\Delta G^\circ_f) \text{ of } \text{CrO}_{1.5} \text{ i.e. } \Delta G^\circ_{f, \text{CrO}_{1.5}} = 0.5 \Delta G^\circ_{f, \text{Cr}_2\text{O}_3} \quad \text{.....(14)}$$

$\text{CrO}_{1.5(l)}$ has some solubility in the liquid phase, although it is much lower than CrO. Equations 11 and 12 describe the minimum Si required to prevent Cr losses to the slag for any activity of SiO_2 and Cr oxide. If the oxygen potential in the bath rises to the Cr-CrO_x buffer, Cr will be lost to the slag, which will happen when the Si level in the alloy drops below a critical level. The equilibrium involving carbon (Equation 13) should be considered separately to those involving Si. However, at the levels of C in the EAF (1-2%), equilibria involving Si predominate.

The work done by Pretorius and Muan⁹⁻¹¹ on CrO_x solubility at 1500°C can be extrapolated to higher temperatures, at moderate levels of CrO_x , as confirmed by the results of Xiao and Holappa^{12,13} at 1600°C. Figure 3 shows the calculated values for $a_{\text{CrO}_{1.5}}$ and a_{CrO} in equations 11 and 12, for an 18%Cr steel, where

$$K_{15} = [\% \text{Cr}]_{\text{Fe}} * f_{\text{Cr}} * a_{\text{SiO}_2}^{3/4} / ([\% \text{Si}]_{\text{Fe}}^{3/4} * f_{\text{Si}}^{3/4} * a_{\text{CrO}_{1.5}}) \quad \text{.....(15)}$$

$$K_{16} = [\% \text{Cr}]_{\text{Fe}} * f_{\text{Cr}} * a_{\text{SiO}_2}^{1/2} / ([\% \text{Si}]_{\text{Fe}}^{1/2} * f_{\text{Si}}^{1/2} * a_{\text{CrO}}) \quad \text{.....(16)}$$

and f_{Cr} and f_{Si} refer to the activity coefficient of Cr and Si with respect to the 1wt% standard state in Fe. The various thermodynamic data were taken from references 9 to 22.

The diagram shows several important features:

- The Wollastonite starting slags have a high a_{SiO_2} , while at the end of melting, the final aim slags with a higher CaO/SiO₂ ratio drop the a_{SiO_2} , thereby maximizing the recovery of Cr to the alloy.
- As a result, the amount of Si required in the alloy to maintain the activities at a minimum falls as the a_{SiO_2} falls. So while a high Si level is required in the alloy at the beginning of foaming, the final level is approximately 0.2%.
- The recoveries of Cr will be poor if the Si drops below 0.1% after tapping, as the activities of both CrO and $\text{CrO}_{1.5}$ rise steeply with increasing oxygen potential at <0.15%Si.

It is known from the work described in references 9-13 that the amount of liquid in the CrO_x -CaO-SiO₂ system is strongly dependent on oxygen potential. Thus the Si level and slag composition are manipulated to ensure the oxygen potential does not fall significantly below that for the Cr buffer ($\log P_{\text{O}_2} = -12.6$). This ensures that both the precipitation of solid Cr_2O_3 is minimized, and recovery of CrO_x from the liquid slag is maximized at the end of the heat.

Foaming the slag

Following the principles outlined in the discussion above could significantly decrease chrome losses to the slag, and improve electrical efficiency in the furnace, even without any attempt at foaming. The slags will be liquid, and the action of tapping the slag with the steel will recover additional chromium oxide from the slag. This will also lower the transfer Si in the steel somewhat, to more acceptable levels for refining in the converter.

Up to this point the focus has been to create a slag in the furnace that could sustain a foam. The next step is to create the bubbles that will make the slag foam. Injection of only gas (Nitrogen or Argon) into a slag with a suitable viscosity would create some foam. However, the extent of foaming would be limited and be directly proportional to the amount of gas injected (an expensive option). The more effective and cheaper option is to create CO gas bubbles by the reduction of iron oxide by carbon according to reaction (3). This is achieved by the injection (or roof feeding) of a **mixture** (preferably pelletized) of carbon and iron oxide. The mixture particle size should be as fine as possible, as the reduction rate with finely divided particles is very fast at steelmaking temperatures (a few seconds for >95% reduction). Maintaining an adequate Si level in the steel, together with continuous feeding of the mixture, will discourage the involvement of Cr in the steel bath as a reductant.

Furthermore, Zhang and Fruehan³ determined that the presence of free particles of coke or coal char act as foam destabilizers, and thus intimately mixing the iron oxide and reductant will decrease this effect.

It is important to note that the effect of [C] dissolved in the steel may not play a vital role in the reduction of FeOx in the slag. However, it does have an important role in reducing the activity of [Cr].

The addition of the iron oxide separately with the scrap or through the roof without the simultaneous addition of carbon will lead to excessive chrome losses to the slag which, will greatly diminish the ability of the slag to sustain a foam (too stiff). The **combined** addition of iron oxide with carbon into a liquid slag ensures the immediate availability of C to react with the iron oxide as it is dissolved into the slag. This decreases the possibility of FeO reacting with Cr in bath according to reaction (6). The amount of carbon required in the mixture will depend on the type of carbon source. The efficiency of the carbon to react with the iron oxide is not 100% so that an excess amount of carbon should be added with the mixture. Note that the recovery of any Cr oxidized to the slag is complex²³ as it appears to require the presence of droplets of Fe in the slag, into which the Cr can dissolve.

The carrier gas for the injection of the foamy mixture could be nitrogen or air. If air is used then the amount of oxygen injected should be adjusted based on the projected air injection.

Foamy slags processes in the EAF for stainless steelmaking have been reported in the literature.^{24,25} These however, require separate carbon and millscale additions, or other foaming agents (such as limestone -graphite briquettes), together with air or oxygen injection. One process uses large amounts of oxygen (>2000Nm³ for a 140t heat) and relies on several FeSi additions. Any process that uses batch type additions will by default have cyclic periods of foam stability and instability.

The requirements for slag foaming in stainless steelmaking can be summarized as follows:

- The early generation of a liquid slag of sufficient volume that will remain liquid for the duration of the heat.
- A mass balance approach to calculate the Si and the oxygen inputs required.
- Sufficient Si early in the heat to prevent cycling of slag foamability due to excessive oxidation of Cr.

- Control of the $\text{Cr/Cr}_2\text{O}_3$ equilibrium by maintaining adequate Si levels in the steel.
- A final aim slag that is dual saturated with respect to CaO and MgO, with the appropriate viscosity to sustain a foam.
- The combined injection of carbon and iron oxide to efficiently generate the CO gas bubbles.

DECARBURIZATION SLAGS

Introduction

The primary decarburization slag requirements can be summarized as follows:

Aim for a) a solid (dry) slag, and (b) the smallest possible slag volume. A solid slag during decarburization will be compatible with any type of basic refractories and will be a permeable media through which the CO gas bubbles can escape (lower the p_{CO} pressure). A liquid or partially liquid slag during decarburization could cause refractory wear and inhibit carbon removal efficiency (CRE). A large slag volume and the addition of very large amounts of basic oxides (lime/doloma) during the decarburization step could inhibit CRE and negatively impact the dissolution and desulfurization reactions during reduction.

The poor quality of lime/doloma sometimes used leads to excessive amounts of basic oxide additions during the decarburization step. The lime/doloma cannot be added during the reduction step because of the high carbonate levels. The addition of soft-burned lime/doloma will lead to unpredictable amounts of carbon pickup during reduction, which could result in reblows. It is therefore very important to use hard-burnt lime and doloma in stainless making. The argument that soft burnt lime/doloma added during decarburization will go into solution faster is not valid. The lime/doloma added during decarburization will be exposed to very high temperatures which will densify it more than any kiln could do.

A solid decarburization slag can be achieved as follows:

Option 1: Add sufficient amounts of basic oxides (lime, doloma, magnesia) during the decarburization step to completely absorb the fluxing oxides (SiO_2 , Al_2O_3 , Nb_2O_5 , CaF_2) present in the slag. This is a conservative approach and is only possible if SiO_2 is the major fluxing component in the slag. The quaternary and ternary phase diagrams of the CaO-MgO- Al_2O_3 - SiO_2 system can be used to calculate the amounts of CaO/MgO needed to form solid slags. These slags stay completely solid during the whole decarburization step.

Option 2: Add just enough of the basic oxides to ensure refractory compatibility (CaO or MgO saturation), but rely on the Cr_2O_3 that is formed to stiffen and dry up the slag. This approach is typically used when significant amounts of Al_2O_3 or Nb_2O_5 are present in the decarburization slag. These slags might go through a partially liquid state before stiffening up.

Using the CaO-MgO- Al_2O_3 - SiO_2 system to calculate CaO and/or MgO requirements

The minimum amount of basic oxide that is required to make a slag solid or refractory compatible, will depend on the type of fluxing oxide (SiO_2 , Al_2O_3 , Nb_2O_5 , CaF_2) and the type of basic oxide used (CaO, MgO). The oxides SiO_2 , Al_2O_3 , CaF_2 , and Nb_2O_5 are not equal in fluxing ability to bring lime into solution. Only SiO_2 can be combined with CaO and/or MgO to form completely solid slags below 1700°C . For this reason the amounts of Al and Nb transferred in the steel or added during decarburization should be kept at a minimum!

a) Consider the reaction of SiO_2 with CaO and MgO

Figure 4 shows the isothermal section of the system CaO-MgO- SiO_2 at 1700°C.

In this diagram slag basicity can be defined in two ways:

$$\% \text{CaO} / \% \text{SiO}_2 \text{ or } (\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2$$

The line A-B represent slags that have a constant basicity of $\% \text{CaO} / \% \text{SiO}_2 = 2.0$. Any slags falling on or below this line in the diagram will be completely solid at 1700°C.

The line C-D represent slags that have a constant basicity of $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 = 2.0$. The phase relations of slags falling on this line will change greatly as the MgO content of the slag increases. This is demonstrated in Figure 5 which shows a significant increase in the amount of liquid in the slag as the MgO content of the slag increases.

From Figures 4 and 5 it is clear that at a constant SiO_2 content, MgO is acting as a fluxing component (up to 30% MgO). Great care should therefore be taken to use the appropriate basicity ratio in order to aim for a solid decarburization slag. Consider the following target basicities and basic oxide additions if SiO_2 is the major fluxing component in the decarburization slag ($\text{Al}_2\text{O}_3 + \text{Nb}_2\text{O}_5 < 5\%$).

Lime addition only during decarburization

The target basicity should be $\% \text{CaO} / \% \text{SiO}_2 \geq 2.0$ to form completely solid slags. The addition of only lime provides the lowest basic oxide requirement when SiO_2 is the major fluxing component in the slag.

Doloma addition only during decarburization

The target basicity should be $\% \text{CaO} / \% \text{SiO}_2 \geq 2.0$ or $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 \geq 3.33$. A target basicity of $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 \geq 2.0$ will not be adequate to ensure a fully solid slag above 1700°C. From Figure 5 it can be calculated that for this ratio the slag would contain more than 80% liquid in the CaO-MgO- SiO_2 system. However, in reality these slags still appear to be fairly dry (stiff) after decarburization with almost no liquid. This is due to the reaction of Cr_2O_3 with MgO to form a very refractory solid spinel phase, which essentially removes the MgO from the slag so that the slag will be dry. The effectiveness of the Cr_2O_3 to stiffen the slag will obviously depend on the amount of MgO in the slag and, when the Cr is oxidized, and the amount of Cr oxidized.

For a mixture of lime and doloma addition during decarburization

Target Basicity should be $\% \text{CaO} / \% \text{SiO}_2 \geq 2.0$ or
 $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 \geq 2x(\% \text{MgO} / \% \text{CaO}) + 2$

b) Consider the reaction of Al_2O_3 with CaO and MgO

The isothermal section of the CaO-MgO- Al_2O_3 system at 1700°C is shown in Figure 6.

In this system the following basicity ratios could be considered:

$$\% \text{CaO} / \% \text{Al}_2\text{O}_3 \text{ or } (\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3$$

From this Figure it can be seen that the only "all-solid" region in this system at 1700°C, is close to the Al_2O_3 apex. Since there are no all-solid areas towards the CaO or MgO corners of the diagram, slags with very high basicity ratios would be required to minimize the amount of

liquid present. The target basicity ratios (2.0 and 3.33) that were used in the CaO-MgO-SiO₂ system are totally inadequate in the CaO-MgO-Al₂O₃ system to ensure completely solid slags. A slag with a basicity ratio of $(\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3 = 2.0$ will contain about 91% liquid at 1700°C, and slag with a basicity ratio of $(\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3 = 3.33$ will contain about 70% liquid at 1700°C (using doloma). The basicity ratios required to aim for slags that contains less than 30% liquid are:

$\% \text{CaO} / \% \text{Al}_2\text{O}_3$ and $(\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3 \geq 9.0$, for lime and doloma additions, respectively.

The amounts of lime or doloma required to meet this basicity target are extremely high and totally impractical. It also defeats the aim of minimizing the amount of slag during decarburization. However, one of the more promising features of the CaO-MgO-Al₂O₃ system is the behavior of MgO. In contrast to the CaO-MgO-SiO₂ system, MgO is acting as a stiffener (refractory oxide) in this system at MgO levels > 15%. This graphically shown in Figure 7.

A practical target basicity ratio for slags that contain significant amounts of Al₂O₃ therefore is $(\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3 \geq 3.33$. It is also recommended that doloma instead of lime be used as the basic oxide addition during decarburization. The resultant higher MgO slags will be less liquid and also more likely to react with Cr₂O₃ to form refractory Mg(Al,Cr)₂O₄ spinel solid-solution phases which will dry up the slag rapidly. From the above it is clear that minimizing the Al₂O₃ level of decarburization slags is very important to minimize basic oxide addition requirements to form slags with low fluidity.

Lime versus doloma as the basic oxide addition during decarburization

There are different opinions in the industry regarding the benefits or disadvantages of using lime or doloma as the basic oxide decarburization addition.

The Case for Lime addition.

1. Adding lime only results in the lowest volume of basic oxide required to form a solid slag. The target basicity ratio $\% \text{CaO} / \% \text{SiO}_2$ is ≥ 2.0 , provided that SiO₂ is the major fluxing component.
2. The thermodynamic activity of chromium in the slag is close to unity. Cr₂O₃ is the stable phase in contact with Ca₂SiO₄ and Ca₃SiO₅ at elevated temperatures according to the CaO-Cr₂O₃-SiO₂ phase diagram. A high activity of chromium oxide in the slag improves the reduction reaction.
3. Burnt lime is more readily available than burnt doloma.
4. Fluorspar (CaF₂) and/or Al will be required in the reduction step, in order to improve the kinetics of lime dissolution. Lime and SiO₂ (from the FeSi) first reacts to form the intermediate phase Ca₂SiO₄, then the Ca₂SiO₄ reacts with SiO₂ to form CaSiO₃, which then gradually melts. Ca₂SiO₄ is a very refractory phase and could form a coating around lime grains and hence delay the dissolution of lime into the reduction slag (Figure 8). This could result in a non-equilibrium slag that is CaO-saturated but with a liquid portion that is not CaO-saturated and aggressive to the refractories. Fluorspar and/or Al additions are therefore required during the reduction step to increase the dissolution of Ca₂SiO₄, and hence lime into the slag. It is not uncommon to see undissolved particles of lime floating around in a reduction slag, if the CaF₂ addition was very low, or the particle size of the lime was very large.

The Case for Doloma

1. SiO_2 reacts with doloma to form the phases Ca_2SiO_4 , Ca_3SiO_5 and MgO . This "free" MgO is now available to react with Cr_2O_3 to form very high melting MgCr_2O_4 spinel phases which rapidly dries up the slag.
2. Doloma addition is a necessity if the decarburization slag contain significant amounts of Al_2O_3 or Nb_2O_5 . Doloma will be more effective than lime to react with these components and Cr_2O_3 to form solid slags faster and minimize refractory wear.
3. The addition of doloma during decarburization can enhance the kinetics of the reduction step and the dissolution of the decarburization slag. The reaction between SiO_2 and the MgO -containing decarburization slags forms low melting intermediate CaMg -silicate phases which reduces (or eliminates) the need for CaF_2 additions during reduction.

Mass-Balance Calculations

A mass-balance approach is normally utilized to calculate the amounts of fluxing components formed and the amounts of basic oxides required. In the mass-balance calculation the following is considered:

- The amount and composition of the carryover slag from the electric-arc, induction furnace, or primary converter. (The amount of carryover slag should be minimized in order to minimize the volume of decarburization slag.)
- The amounts of Si, Al, and Nb in the transfer steel.
- The amounts of Si, Al and Nb that are contributed from alloy additions during decarburization (such as charge chrome and scrap).
- The amounts of FeSi/Al that are added as fuel during the decarburization step.

From the total amounts of Si, Al, and Nb input and the expected levels after decarburization, the amounts of SiO_2 , Al_2O_3 and Nb_2O_5 released to the slag can be calculated.

Special exceptions for VOD operations

One of the principal requirements for the VOD decarburization step is to minimize the slag volume in order to maximize the amount of steel exposed to the oxygen jet from the top lance. This is achieved by minimizing or eliminating carryover slag from the EAF or MRP and by transferring steel with low Si levels ($< 0.1\%$ Si). If the above is true, the amount of lime required to completely absorb the SiO_2 generated is small and can usually be added without inhibiting the CRE. Lime is normally added instead of doloma because of the lower amounts required to form completely solid slags. Consider the following example:

For 50 MT of steel containing 0.1% Si : $50\,000 \times 0.001 \times 2.13 = 107 \text{ kg SiO}_2$ released

For a 400 Kg addition of FeCr (4.5% Si) $400 \times 0.045 \times 2.13 = 38.3 \text{ kg SiO}_2$ released

The amount of lime required during decarburization to render the slag completely solid would be the amount of $\text{SiO}_2 \times 2.0$ (Basicity target $\text{CaO/SiO}_2 = 2$):

$$\text{Lime Required} = (107 + 38.3) \times 2 = 290.6 \text{ kg}$$

In the above example a standard decarburization addition of 300 kg lime would be recommended. The addition of fuel such as FeSi or Al during the decarburization step for temperature completely changes the picture. A 100 kg addition of FeSi (75% Si) will release 160 kg of SiO_2 to the slag which would increase the amount of lime required to 611 Kg. If 100 kg of Al was used, the slags would never completely solidify and the amount of lime required would be 1113 kg just to maintain a basicity ratio of $\% \text{CaO} / (\% \text{Al}_2\text{O}_3 + \% \text{SiO}_2) \geq 3.33$.

Because of the partially liquid state of these slags, there is an increased possibility of foaming. If insufficient lime is added, the slags that are formed will be very aggressive to the refractories, and a partially liquid slag will inhibit CRE. The amounts of lime needed to absorb the Al_2O_3 or SiO_2 generated from fuel addition are normally excessive and impractical. It is therefore recommended to eliminate the use of fuel during decarburization wherever possible.

If the addition of fuel cannot be eliminated, then it is recommended that no basic oxides be added during the decarburization step. The resultant slags that will form will consist essentially of SiO_2 and Al_2O_3 . Although these slags are not compatible with the refractories, they will be fairly viscous and slow to react with the brick. Any addition of basic oxide (lime or doloma) to such a slag will decrease the slag viscosity and hence increase the reactivity of the slag. A "standard" addition of 300 kg lime (95% CaO) during decarburization and the addition of 100 kg of Al for fuel will result in the following slag composition:

% SiO_2 - 23.4 (145 kg), % Al_2O_3 - 30.5 (189 kg), % CaO - 46.1 (285 kg)

This slag lies in the all liquid region and could foam in the VOD vessel. Furthermore, such a slag is not compatible with a basic refractory and could cause significant refractory wear.

Summary

The following table (Table 1) summarizes the basicity requirements for various stainless steel grades using lime and doloma additions, respectively.

REDUCTION SLAGS

Introduction

The target compositions for stainless steel reduction slags are similar to that of the EAF slags discussed earlier. Most reduction slags consist of CaO , MgO , Al_2O_3 , SiO_2 , and CaF_2 as major components with Cr_2O_3 , TiO_2 and Nb_2O_5 as the minor components. The quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ can once again be utilized to define target slags that would be optimum for steel quality and refractory compatibility. Most reduction slags also contain CaF_2 as a component so that the target slags from the quaternary system will provide the **minimum** levels of CaO and MgO that should be aimed for because the addition of CaF_2 will increase the solubility of CaO and MgO in the slag. The effect of CaF_2 on selected areas of this diagram can be inferred from the available CaF_2 -containing phase diagrams. A slag model was developed utilizing selected areas of $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, which also incorporated the effect of CaF_2 on the liquidus relationships in this system^{1,2}.

The compositions of the target slags will depend on the type of refractory in the vessel and the grade of steel produced. For magnesia-chromite and magnesia-carbon refractories, a typical target slag composition will be dual saturation (CaO and MgO). For doloma refractories, only CaO saturation could be targeted, since the matrix (bonding phase) of these refractories is lime based.

While defining target slags is a relatively simple task, the manner by which these slags are achieved in practice could have a significant impact on the efficiency (time and cost) of the reduction step. The following discussion will highlight some of the most important parameters.

The importance of a small decarburization slag volume

A low decarburization slag volume is essential for rapid dissolution and optimum reductant utilization. It is much easier to fluidize a small amount of solid slag and gradually add lime to maintain compatibility, than attempting to fluidize a large volume of basic oxides. A low decarburization slag volume could also improve the efficiency of the reduction reaction. It is not a chemical (thermodynamics) effect but simply a physical dilution effect. The oxidized chromium in a small amount of slag is much more readily available to react with the added reductant, than the case where the slag amount is large, i.e. when the bulk of the reduction lime requirement was added during the decarburization step.

The effect of reductant type and decarburization slag composition

If FeSi is the main reductant, then SiO₂ will be the primary fluxing component in the slag. If mostly lime was added during the decarburization step, then extensive amounts of fluorspar would be required to facilitate the solution of lime into the slag. It was mentioned previously that an intermediate layer of Ca₂SiO₄ could form around the undissolved particles, which will delay their dissolution into the slag. The addition of CaF₂ dissolves this phase and enhances the kinetics of slag formation.

For some grades of steel some of the FeSi can be replaced with Al which will release some Al₂O₃ to the slag. The Al₂O₃ will help to bring the lime into solution, but it is not as effective as fluorspar. If doloma was the major decarburization addition, then Al and/or fluorspar additions might be minimized (or eliminated). The reaction between SiO₂ and the MgO-containing decarburization slags forms low melting intermediate CaMg-silicate phases, which will rapidly generate a liquid slag.

The importance of adding a fluxing precursor before reduction

In the previous section it was emphasized that a solid slag is important for decarburization efficiency. Unfortunately, this solid slag is not ideal for reduction efficiency and rapid slag dissolution. The fluxing oxides available to fluidize the decarburization slag are: SiO₂, Al₂O₃ and CaF₂. Both the SiO₂ and Al₂O₃ are the oxidation products of the FeSi and Al added for reduction. Fluxing of the slag will not occur until significant amounts of SiO₂ and/or Al₂O₃ are generated.

As was pointed out for the EAF slags, the generation of a small amount of early liquid slag could greatly enhance the reduction efficiencies and kinetics. This early liquid slag could be generated by adding fluorspar to the decarburization slag just before the reduction mix is added. The added fluorspar will melt immediately and create some liquid in the slag so that when the reductant is added it will be immersed in a partially liquid slag (eliminating atmosphere oxidation). The kinetics of liquid-liquid reactions are faster than liquid-solid reactions. Furthermore, the addition of the fluorspar just before the reduction mix is added, will calcine any residual carbonate in the fluorspar, eliminating any unexpected carbon pickup.

The effect of Fluorspar in stainless steel reduction slags.

Fluorspar is utilized for the following reasons:

1. To act as a fluxing precursor at the beginning of the reduction step.
2. To increase the solubility of CaO in the slag and hence improve desulfurization.
3. To maintain fluidity in the slag as the slag temperature decreases (VOD slags).
4. To increase the mass transfer rate for the reduction reactions.²⁶

Fluorspar is very effective in bringing lime into solution as shown by the phase diagram of the CaO-CaF₂-SiO₂ system in Figure 9. Unfortunately, no phase diagrams are available for the CaO-MgO-SiO₂-CaF₂ system.

The most striking feature of this diagram is the tremendous increase in the solubility of CaO, when CaF₂ is added to CaO-SiO₂ slags, or when SiO₂ is added to CaO-CaF₂ slags. The combined effect of SiO₂ and CaF₂ results in a high CaO solubility, as shown by point (a) on the diagram (1600°C). The composition of the slag at this point is approximately the following:

% CaO – 72 % SiO₂ – 16 % CaF₂ – 12

The saturation solubility of CaO at 1600°C in CaO-CaF₂-SiO₂ system, is plotted as a function of SiO₂ content in Figure 10.

The maximum in CaO solubility is at about 12% CaF₂ in the slag. The addition of more CaF₂ to the slag, results in a decrease in CaO solubility along the CaO-saturation boundary. This is because the SiO₂ content of the slag is diluted to below 16%. Again this shows why the maximum amount of fluorspar that would ever be required in a slag is 12%. The addition of more CaF₂ would also result in an increase in fluidity that could lead to increased refractory erosion.

If fluorspar is added as a fluxing precursor then the typical aim CaF₂ levels in the final slag should be about 3%, provided the slag contains considerable amounts of MgO (approximately 10%). If the MgO content of the final slag is less than 10% then higher CaF₂ levels might be required to obtain adequate dissolution rates. The higher CaF₂ level will require a significantly larger lime addition to maintain refractory compatibility, as shown in Table 2.

Table 2 also shows the increased desulfurization as the CaF₂ content increases and CaO saturation is maintained by lime additions. The initial slag is just CaO-saturated at 1600°C.

For some grades with very low sulfur specifications, a second reduction slag might be required. Typically a mixture of lime and fluorspar is utilized. From Figure 9 it is clear that the amount of residual slag in the vessel, in combination with the lime and fluorspar additions, can yield slags with high desulfurization capabilities.

In VOD operations all the reduction slags stays in the ladle until the steel is cast. An important requirement is that the slag stays reasonably liquid down to casting temperatures to facilitate alloy and wire additions. When all the fluorspar is added in a single step during reduction for fluidity control, then extensive slagline refractory wear will occur. The preferred method is to add the fluorspar in steps after reduction as the slag cools, and only as needed. This could result in significant refractory performance improvements and also decreased fluorspar consumption.

Fluorspar can be very effective in increasing the solubility of CaO in silicate slags but it is not very effective to increase CaO solubility in aluminate slags. The only benefit fluorspar could have for Al-killed grades is that it could act as the fluxing precursor before the Al is added. In these grades fluorspar is not normally necessary because the reaction of CaO and Al₂O₃ will form a liquid slag without high-melting intermediate phases such as Ca₂SiO₄. The only intermediate phase that can form, Ca₃Al₂O₆, melts at 1535°C

Can CaF_2 be replaced by Al_2O_3 in stainless steelmaking?

Some plants, and indeed countries, are considering the elimination of fluorspar from the shop floor because of environmental concerns. The question now arises whether fluorspar can be replaced by something else. While certain alkali-containing minerals have been suggested as a replacement for fluorspar, the only practical replacement is Al_2O_3 . The Al_2O_3 is generated by the partial replacement of FeSi by Al as a reductant. Unfortunately, Al_2O_3 is not as potent as CaF_2 to bring lime into solution, and considerably higher levels of Al_2O_3 would be required in the slag to get the same desulfurization. Furthermore, the pickup of Al in the steel and the resultant lower dissolved oxygen levels, will have a significant impact on the inclusion chemistry and the timing of Al_2O_3 precipitation.

From the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system the saturation levels of CaO was determined as a function of the Al_2O_3 content for slags containing MgO levels of 5% and 10%, respectively (Figure 11).

This figure has the following important features:

- The solubility of CaO initially decreases as Al_2O_3 replaces SiO_2 as flux.
- The solubility of CaO decreases as the MgO content of the slag increases
- For slags containing 5% MgO, the solubility of CaO increases rapidly as the Al_2O_3 content of the slag increases beyond about 22%. However, this increase only occurs when the SiO_2 content of the slag has been diluted below 15%. For example consider slags (A) and (B) in Figure 11 that contain 22.5 and 23% Al_2O_3 , respectively. Slag (A) contains 22.5% SiO_2 and only has 50% CaO in solution, whereas slag (b), which contains only 12% SiO_2 , has 59% CaO in solution. This has a significant implication in terms of desulfurization. Not only are high levels of Al_2O_3 required in the slag (>22%), but the SiO_2 level should be below 15%. These lower levels of SiO_2 , together with the higher levels of [Al], will result in a decreased oxygen potential in the steel.
- High solubilities of CaO are only observed at the 5% MgO level. From the quaternary system it can be determined that the maximum MgO level of the slag should be below 7.5 % to obtain the high CaO solubilities shown in Figure 11.
- For slags containing 10% MgO, less Al_2O_3 (19%) is required to reach the maximum CaO limit (51%), however, the maximum solubility limit is much less compared to slags containing 5% MgO (59%).

This figure clearly shows that partial replacement of FeSi by Al as a reductant will be ineffective to increase the solubility of CaO. To obtain similar dissolved CaO levels as silica-fluorspar slags, the bulk of the reductant should be Al. The SiO_2 that is transferred from the EAF slag, together with the transfer Si and Si in alloy additions, must be considered to determine the Al required in the reduction mix to ensure adequate SiO_2 dilution (<15%).

Another important consideration is the MgO content of the slag. If the slags generated in the process are not compatible with the refractories then significant amounts of MgO can be dissolved from the brick, which could increase the MgO content of the slag above the 7.5% level. The above considerations have serious implications for many steel grades and many practices. The replacement of FeSi by Al will result in higher reduction temperatures, which will require more coolant additions. In addition Al as a reductant is more expensive than FeSi.

LADLE SLAGS

There are some basic requirements for ladle slags for stainless steel production, namely:

- Additional desulphurization, or prevention of [S] reversion for resulphurised grades.
- Prevention of contact of steel with air
- Absorption of inclusions
- Control of oxygen potential in the steel
- Maximizing recovery of alloying additions to the melt
- Minimized reaction with the ladle refractories, particularly at the slag-metal line
- Rapid melting and formation of a homogenous liquid slag

Most ladle slags are based on the Al_2O_3 -CaO-MgO-SiO₂-CaF₂ system, and the same slag model can be used to determine the liquidus phase relations. Ladle slags are normally a mixture of some remnant AOD slag, together with mixtures of alumina, lime, dolomite and fluorspar. The lime and alumina may be added individually or as pre-fused or pre-melted calcium aluminate. Two aspects will be briefly mentioned here; those involving inclusions and the physical phenomena occurring between slag, metal and inclusions.

When the steel is tapped from the AOD, there is a sequence of events which dictates the final slag- steel- inclusion equilibria. Some of the events are shown in Figure 12.

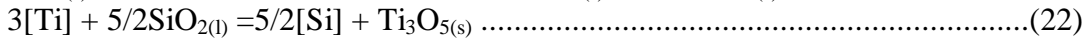
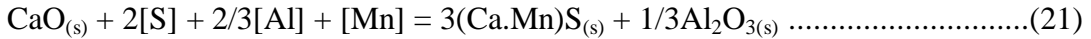
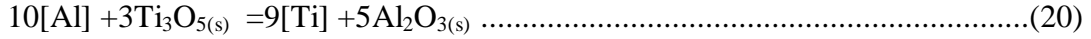
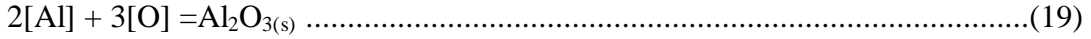
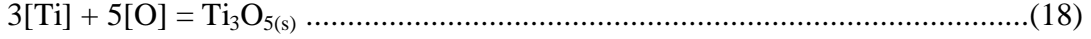
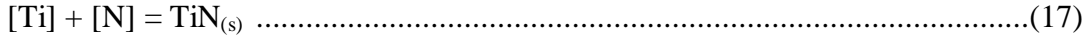
- Initially the steel will contain some entrapped AOD slag from tapping. Depending on the imposed stirring behavior and the chemistry of the slag, the inclusions will agglomerate to some extent, and some will be removed by absorption in the slag or attachment to the ladle walls. At the same time, the most reactive deoxidant in the steel will react with dissolved [O] in the bath and the inclusions, changing their overall composition.
- If reactive elements such as Si, Ti or Al are now added as alloying elements, there will be a burst of solubility product inclusions, as the oxygen potential of the steel is lowered locally in the volume of addition. Now, for a period the steel approaches equilibrium with the solubility product, not the slag. If Ti is added, some TiN formation will occur, the extent depending on the initial [N] content. An important point here is that the melting characteristics of the alloying addition, the amount added and the method of addition will determine the local concentration. For instance FeTi melts at ladle temperatures, whereas FeNb has a melting point higher than liquid stainless steel, and so must dissolve. Thus the localized activity of [Ti] in the bath will differ to [Nb] for similar mass additions.
- During stirring the concentration and thus activity of the element will decrease, some of the solubility product inclusions being removed to the slag or sidewalls, or being absorbed into the original slag inclusions. In the case of further Al additions or other alloys containing Al as an impurity, a higher than equilibrium amount of [O] will stay in solution due to supersaturation. Elements which promote supersaturation include Ti, Cr and Mn. This does not, however occur with the Si-SiO₂ equilibrium.²⁸
- At some point (where sufficient inclusions are removed) the steel will now equilibrate with the slag again, unless some additional reactive element is added.
- If Ca treatment is then applied, the [Ca] will react with Al_2O_3 inclusions or [Al] to form calcium aluminates of various ratios, and even possibly CaS if the oxygen potential is sufficiently low. These inclusions will be removed to some extent as before, the liquid inclusions having the advantage of greater buoyancy and thus ability to float.
- After some further time period, the Ca level in the steel will drop, and the steel will equilibrate with the slag until the ladle is teemed. Here the slag – steel equilibrium will

dictate the oxygen potential, and this in turn will dictate the composition of any further solubility product inclusions.

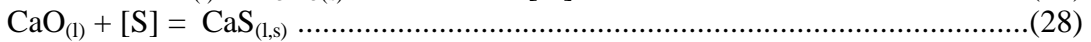
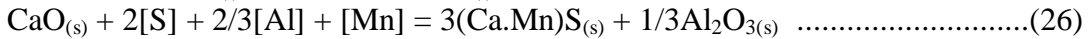
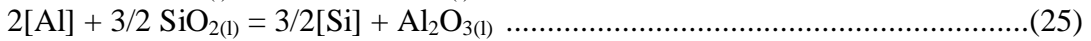
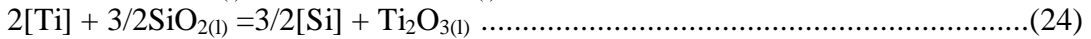
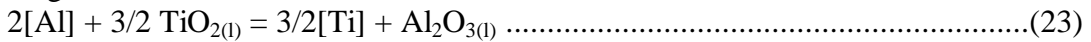
- As the steel continues to cool, further inclusions will precipitate without any additional change to the steel composition, simply due to the lowered solubility product value.

Some of the critical reactions taking place are then as follows:

Inclusions



Slags



It can be seen that the chemistry is complicated considerably by the presence of Ti, where Ti fades as a result of reaction with SiO_2 or Al_2O_3 . The extent of reaction will be dictated by the activities of the slag and steel species. Models have been developed to describe these complex equilibria, particularly those involving Ti, and will be the topic of a future paper.

In addition to the chemical reactions taking place between slag and steel, there are other phenomena to consider which play a role in determining the final slag and steel compositions. For instance, the role of interfacial tension has been studied extensively in recent years, and it is known that Ti in steels undergoes dynamic interfacial tension effects.²⁹ Here, the interfacial tension drops to levels lower than the equilibrium level, as a result of chemical reactions involving oxygen transfer across the interface. As the interfacial tension drops to low levels, emulsification of slag in alloy and alloy in slag is possible, thereby adding to the inclusions already present.

Slags which contain titanium oxides have been found to lower the interfacial tension with steels, which will encourage slag entrainment in the steel.³⁰ MgO also has this effect, while CaF_2 and Al_2O_3 have the opposite effect, where significant increases in it can occur. There are some anomalies regarding Na_2O , as it reduces the interfacial tension in $\text{CaO-SiO}_2\text{-CaF}_2$ slags, but has been found to increase it in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags. Also, CaF_2 tends to increase the interfacial tension more in calcium aluminate slags than silicate slags.³⁰ The absolute value of interfacial tension between any slag-steel system is dependant, therefore, on the relative amounts of components in the slag, and the composition of the alloy, particularly with respect to $[\text{O}]$, $[\text{S}]$, $[\text{Al}]$ and $[\text{Ti}]$. From the aspect of selecting slag compositions, it can be seen that sometimes properties such as viscosity and surface tension can have conflicting effects, and the optimum slag for any metallurgical operation is not so easily attained!

Other aspects of interfacial tensions include the interaction of TiN with the steel and slag. As TiN has a contact angle with liquid steel of $>90^\circ$, it is not wet initially by liquid steel. However, work by Chung²⁹ has shown that this is time dependent, and surface reactions

render the TiN particles wetting after some incubation time. However, TiN has a low solubility in liquid slags, due to their low nitride capacity. As a result, the slags cannot absorb TiN inclusions, unless they are first oxidized to an oxynitride or oxide. Consequently, any TiN collecting at the slag-metal interface, will remain there, as the TiN is wet by the slag.³¹ This leads to the formation of a slurry with high viscosity and reduced potential to perform the metallurgical duties required of the slag.

New work on the attraction and agglomeration of solid and liquid inclusions using the Confocal Scanning Laser Microscope has shown the importance of short range interfacial tension interactions, and different behavior of inclusions of different compositions.³² This technique allows the study of inclusion ejection at an interface, and for optically transparent slags, it will lead to a better understanding of how the types of inclusions found in stainless and other steel behave at a slag-metal interface.

TUNDISH SLAGS

The primary functions of tundish covers are to prevent oxidation and nitridation of the steel, and heat loss prior to casting. By the time the steel reaches the tundish it should be clean, and the efforts in making it so can be wasted by poor tundish practice. On the other hand, tundish covers have only limited opportunity for cleaning the steel, and if the steel from ladle is still dirty; the tundish as a reactor has limited scope to remove inclusions. The reasons for this are the relatively small amount of cover and the normally limited contact time by the bulk of the steel as it passes through the tundish. Much of the steel does not see the cover at all, and short-circuiting along the bottom of the tundish exacerbates the issue. Modern tundishes have furniture such as weirs, baffles and flow arresters, which aim to prevent short-circuiting and homogenize the steel temperature. The aims are to maximize the amount of steel that contacts the tundish cover, and to prevent temperature stratification. These devices, however, require water and CFD modeling to characterize a particular tundish design and desired practice, before optimizing flows and retention times.

Tundish covers are of 2 main types, reactive and insulating. The former can be referred to as fluxes, while the latter are strictly covers. The reactive covers are generally either Wollastonite or calcium aluminate. As with ladle slags, there is a wide range of pre-fused and pre-melted calcium aluminates, the best performance is normally achieved by the pre-melted versions, which melt rapidly and homogeneously to quickly cover the steel surface.

One particular problem with tundish covers is the control of the thermal profile through the relatively thin layer of flux. Even quite low melting point fluxes can become crusty as a result of the steep temperature profile through the thin layer of flux (with the ambient temperature on the upper surface). This is particularly a problem where Al_2O_3 or TiO_x is absorbed in fluxes with low capacities for these oxides. The use of insulating covers is often used here – but care must be taken to minimize the reaction between the active slag and the insulating cover. This is particularly important with regards to SiO_2 . With Al killed grades or at least where Al controls the oxygen potential of the steel, the reaction with SiO_2 in the flux leads to the generation of inclusions at the worst possible time, just prior to the steel entering the mould. Here, instead of the tundish slag cleaning up the steel, it is making it dirtier!

One ideal tundish cover, which is often overlooked, is crushed and recycled ladle slag. This slag is potentially the best cover for a tundish, as it was the previous flux in equilibrium with

the steel! Providing the [S] level of the slag is not at the CaS saturation level, the slag will provide a cheap source of reactive tundish cover.

SUMMARY

Defining target slags using phase diagrams and slag models, is a fairly simple task. However, the method by which this final target slag is achieved, and the path to this final slag, can have a significant impact on the efficiency of the steelmaking process. The generation of early liquids in the EAF and the reduction step converter is very important to enhance the kinetics of the redox reactions. The type and quality of the raw materials used will also have a significant influence on the extent to which the slag guidelines could be implemented. The chemical kinetics, phase equilibria, and other physical phenomena need to be understood to manage the slag for metallurgical process efficiency.

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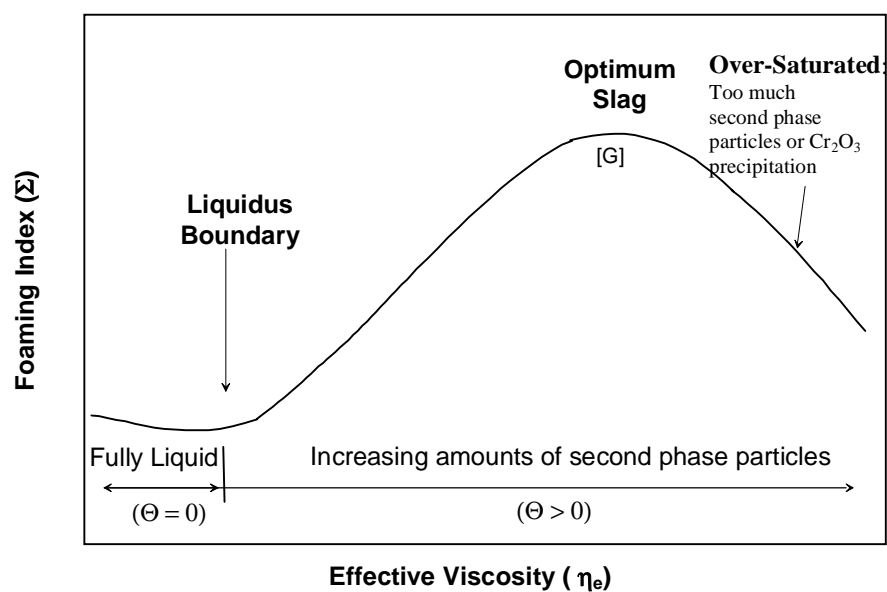


Figure 1: The Relationship between the Foaming Index⁷ and Effective Viscosity.

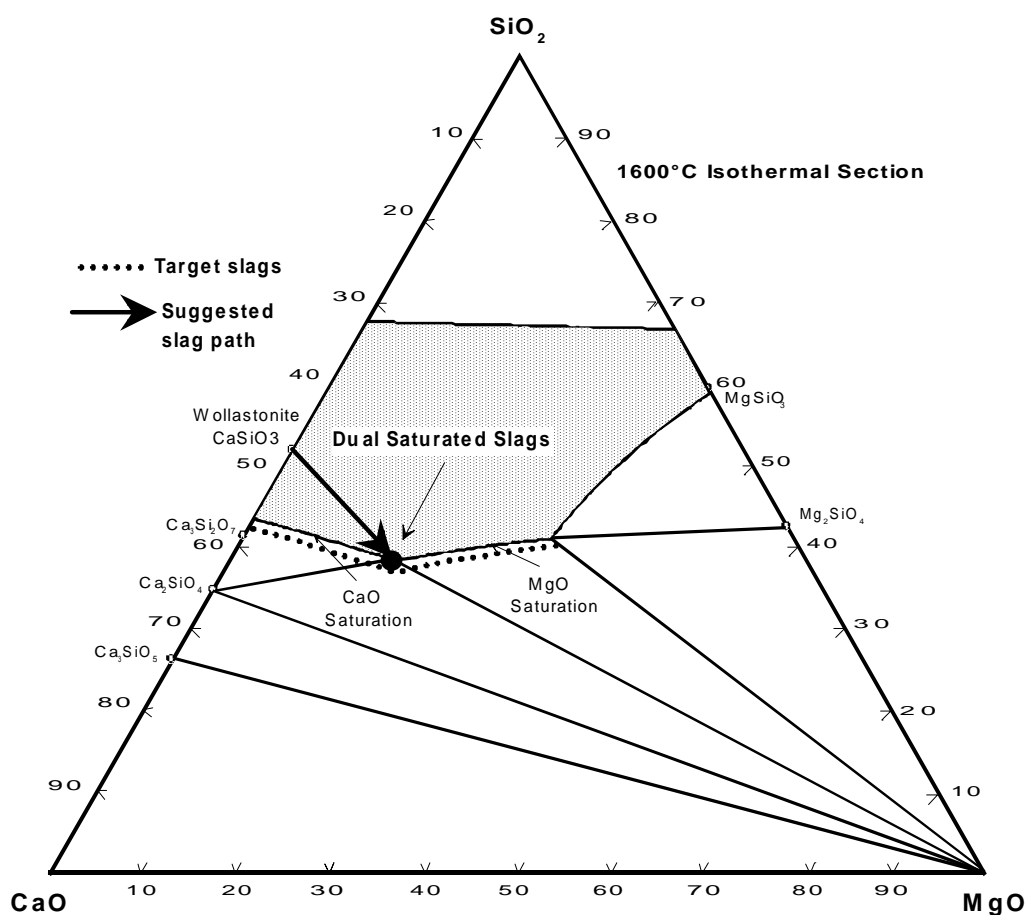


Figure 2: Isothermal section of the CaO-MgO-SiO_2 system at 1600°C .⁸

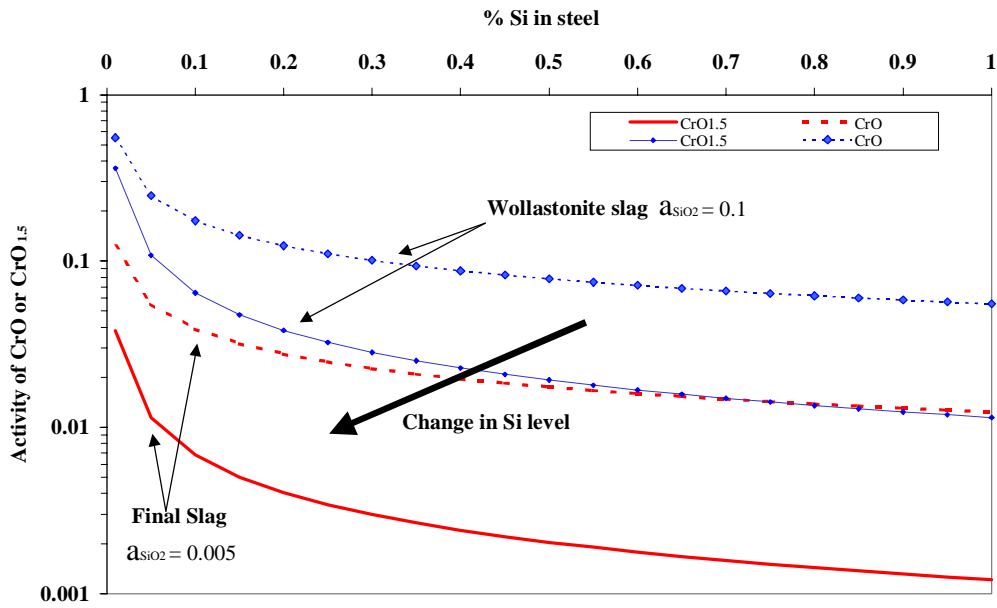


Figure 3: Calculated activities of CrO and $\text{CrO}_{1.5}$ for various Si levels in the alloy and activities of SiO_2 in the slag. An 18% Cr alloy was assumed.

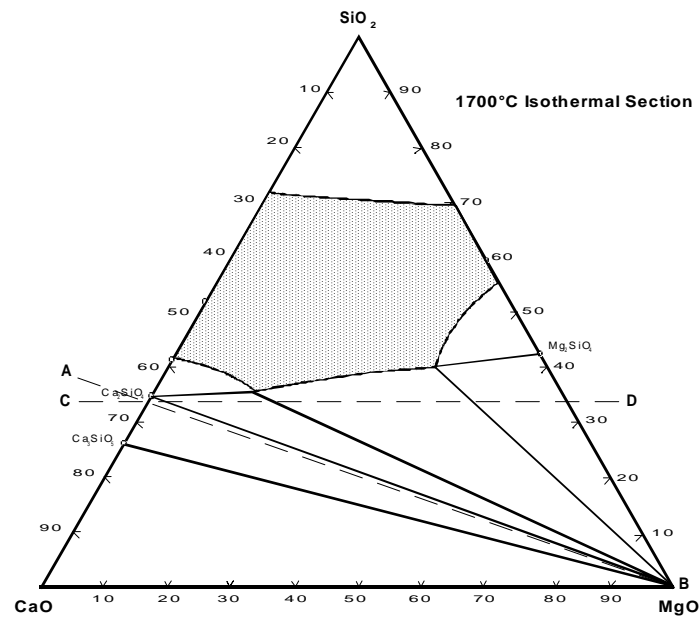


Figure 4: Isothermal section of the CaO-MgO-SiO_2 system at 1700°C .⁸

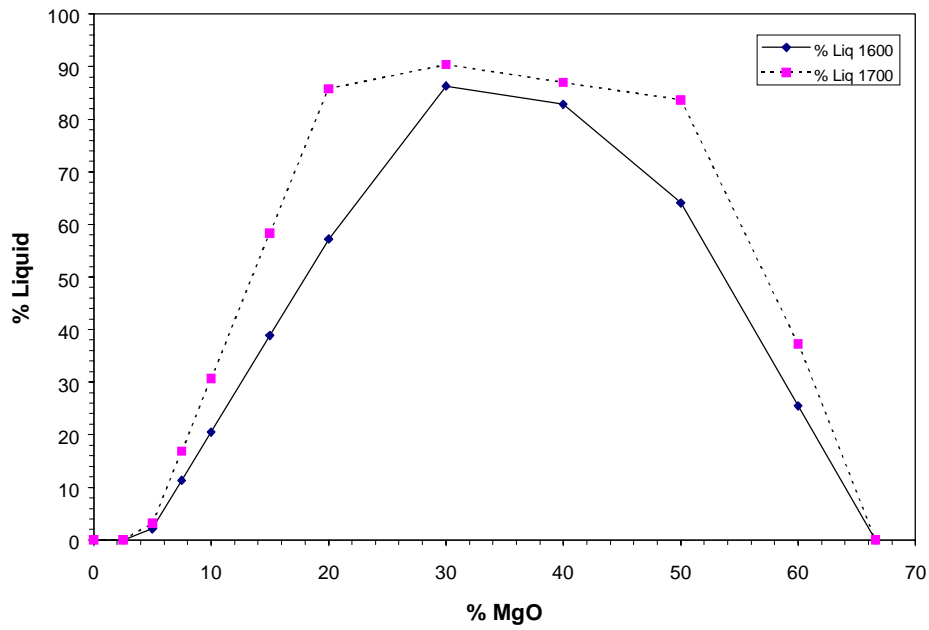


Figure 5: % Liquid in the slag as a function of MgO content, $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 = 2.0$

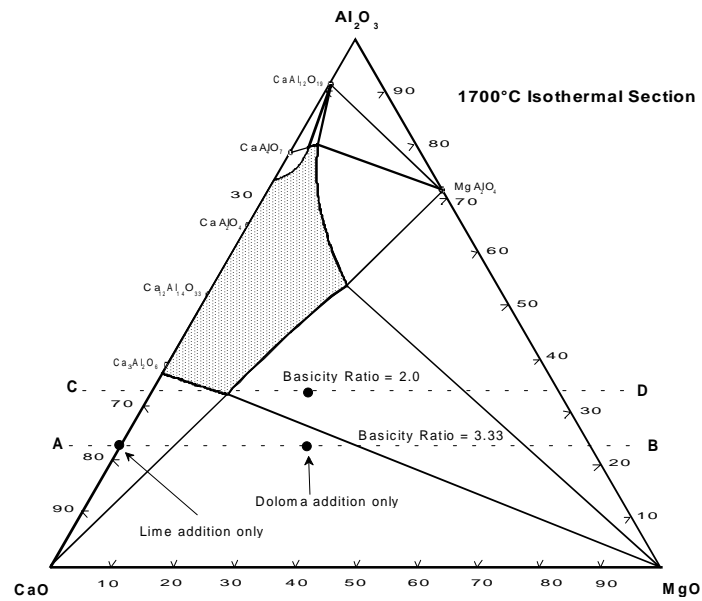


Figure 6: Isothermal Section of the CaO-MgO- Al_2O_3 system at 1700°C

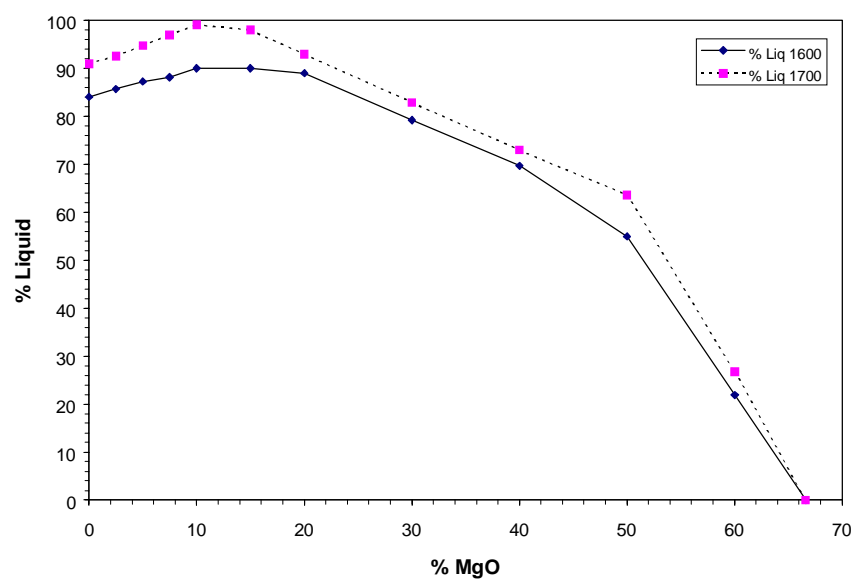


Figure 7: % Liquid in the slag as a function of MgO content, $(\% \text{CaO} + \% \text{MgO}) / \% \text{Al}_2\text{O}_3 = 2.0$

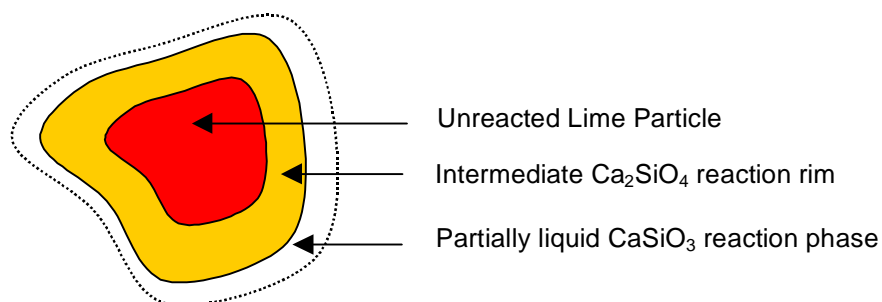


Figure 8: Schematic showing the dissolution of lime in silicate slags

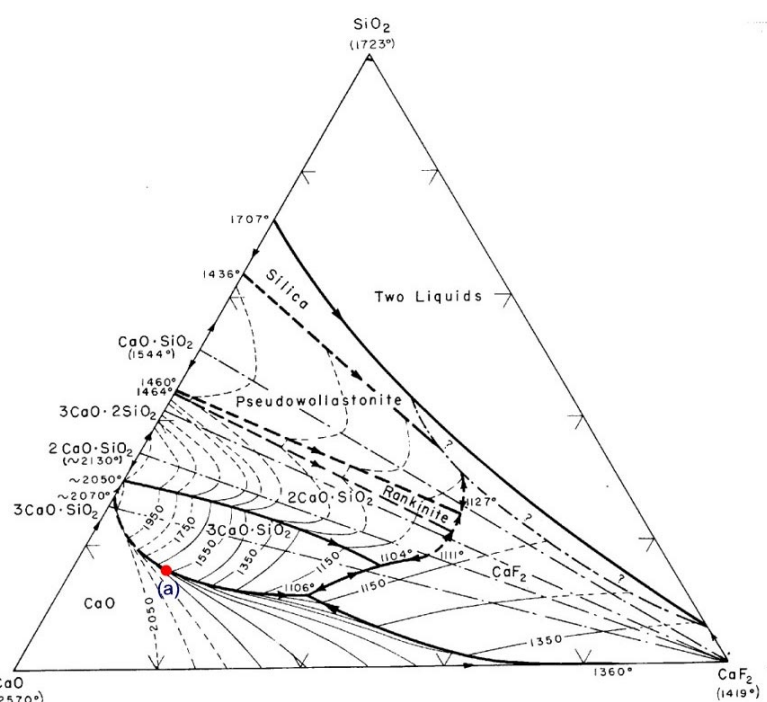


Figure 9: Phase diagram of the $\text{CaO}-\text{CaF}_2-\text{SiO}_2$ system²⁷

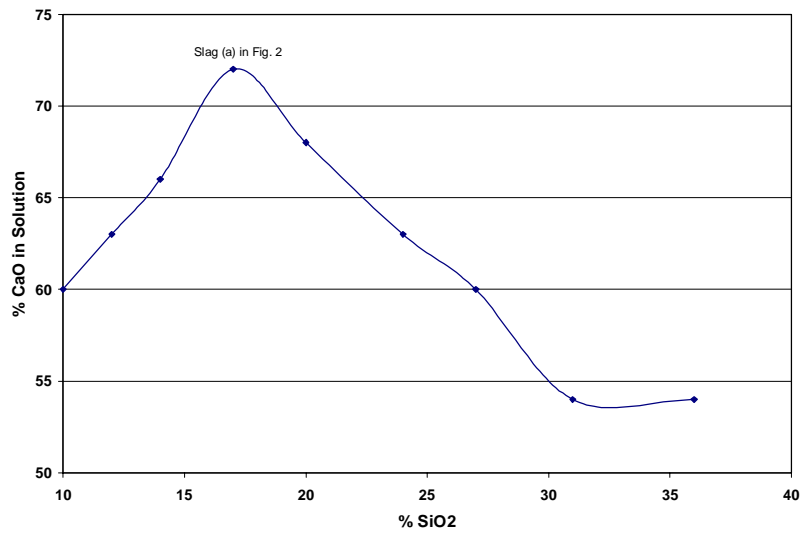


Figure 10: Solubility of CaO as a function of SiO₂ content in CaO-CaF₂-SiO₂ slags at 1600°C

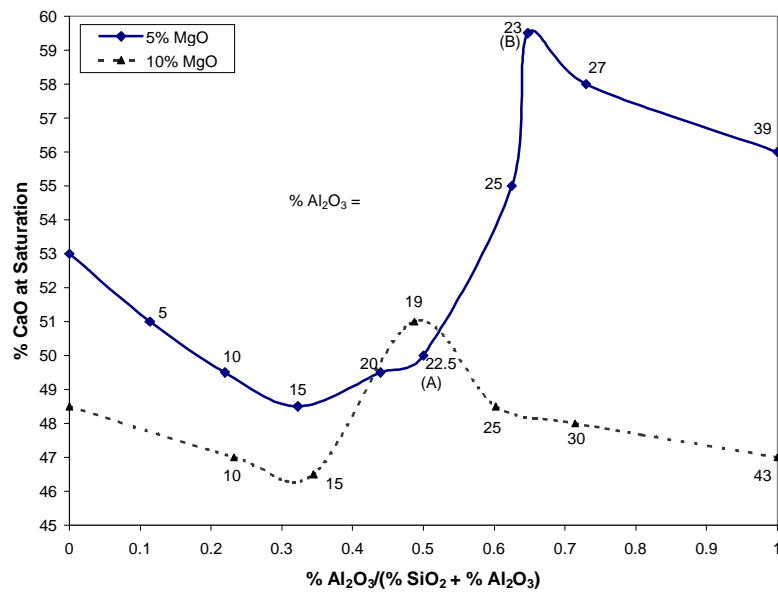


Figure 11: The solubility of CaO as a function of Al₂O₃ content at 1600°C (The actual Al₂O₃ levels of the slags are indicated in the figure)

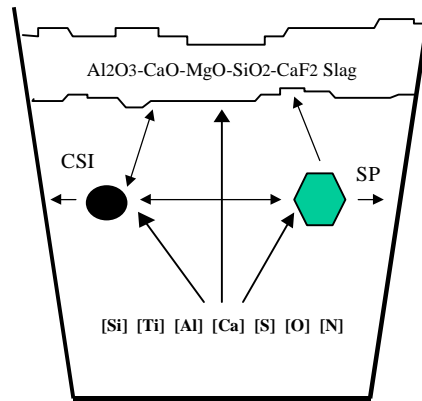


Figure 12: Showing possible reactions between inclusions, steel and slag. CSI refers to converter slag inclusion, while SP refers to solubility products such as Al_2O_3 or TiN

Table 1. Basicity ratios for refractory compatible slags, and solid decarburization slags.

Typical steel grades (Low Al_2O_3 and Nb_2O_5)	Minimum basicity ratios for refractory compatibility	Recommended basicity ratios (solid slags)
Lime addition only	$\% \text{CaO} / \% \text{SiO}_2 \geq 1.6$	$\% \text{CaO} / \% \text{SiO}_2 \geq 2.0$
Doloma or Doloma/Lime	$(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 \geq 2.0$	$\% \text{CaO} / \% \text{SiO}_2 \geq 2.0$ or $(\% \text{CaO} + \% \text{MgO}) / \% \text{SiO}_2 \geq 3.33$
Special Steel Grades (High Al_2O_3 and Nb_2O_5)		
Doloma or Doloma/Lime	$(\% \text{CaO} + \% \text{MgO}) / (\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3 + \% \text{Nb}_2\text{O}_5) \geq 2.0$	$(\% \text{CaO} + \% \text{MgO}) / (\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3 + \% \text{Nb}_2\text{O}_5) \geq 3.33$

Table 2. Calculated lime requirements and desulfurization potential as a function of CaF_2 content

% CaF_2 in Final Slag	0	3%	6%
Additional Lime required	0	379	909
Optical Basicity	0.698	0.713	0.729
Sulfide Capacity ($\log C_S$)	-3.02	-2.80	-2.57
Sulfur Distr. Ratio (L_S)	18.08	29.53	50.2
Final Sulfur	0.0089	0.006	0.0036

The following parameters were used in the calculation: Initial slag weight 5000 kg, Steel Weight = 50 tons, Temperature = 1600°C , Initial Sulfur = 0.025%, $[\text{O}]$ in steel = 40 ppm.