# Computer Modeling of Refractory/Slag/Metal Interactions

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## ABSTRACT

The use of computer modeling to simulate and predict refractory/slag/metal interactions is illustrated in this paper. The use of these personal computer based programs has become an indispensable tool for the optimization of steelmaking processes. The programs are either used "on-line" to control the steelmaking processes or for process analysis to evaluate the impact and importance of various parameters on steelmaking conditions.

## 1. INTRODUCTION

Most manufacturing processes are characterized by repetitive actions that produce a consistent product within very tight specifications and tolerances. These processes are usually very predictable and can be carefully controlled to achieve the desired result. In contrast, the process of steelmaking is much more dynamic as constant adjustments are needed during a heat to achieve a specific result. The actual energy and material consumption can be significantly different from heat to heat for the identical grade of steel. It is no wonder that to some steelmaking is still considered an art rather than a science.

The use of computer programs to evaluate the variable parameters on the steelmaking process has become an indispensable tool for controlling the process and making the necessary adjustments to achieve steelmaking goals. Although many models and programs are available on various aspects of steelmaking, this paper will primarily focus on the modeling of slag/metal, and slag/refractory interactions. The concept of slag engineering or "slag optimization" is becoming more prevalent in many steelmaking works due to a growing realization that high quality steel and low costs can not be realized by poor slag practices.

## 2. HISTORICAL DEVELOPMENT OF SLAG MODELS

Although the effect of slags on metal properties was recognized by early metallurgists, the reading and adjustment of slag chemistry remained an undocumented and unquantified art until about 100 years ago. Even at the inception of true pneumatic steelmaking, in the 1850's by Bessemer, no provision was made for flux additions. Development of chemical analysis techniques and the recognition of the differences between phosphorous and sulfur-bearing ores, led to the first basic processes: the Open Hearth/Siemens-Martin furnace and the Thomas converter, in which the lining was consumed to provide fluxes. Deliberate additions of lime/doloma in various forms were resorted to for the original purpose (still valid) of extending the consumable lining life [1].

Further basic advances in slag engineering for metallurgical purposes on the shop floor were dependent upon more than 60 years of mineralogy phase identification studies plus phase diagram developments. Combining his mineralogical studies of basic open hearth slags in the 1930's and 40's, with the accumulated mineralogy and phase diagram work, enabled Rait [2] to characterize basic slags and basic refractories sufficiently to allow reasonable estimations of slag conditions prevailing at steelmaking temperatures.

Prior to the development and dissemination of the mineralogical/phase diagram techniques, practical slag control on the shop floor was achieved by establishing empirical correlations between the chemical components of the slag and metallurgical chemistries. This lead to the use of "V" or basicity ratios which reached their ultimate development in the 1960's. Some of the texts of the time document the mineralogy approach [3] which, although effective, required considerable petrographic expertise and was time consuming.

Enter computers! With an increasing database of information, and the advent of computers, true predictive slag engineering could begin. By the 1960's early mainframe-based programs intended for expert users existed for certain areas of phase equilibria, but not necessarily specifically for steelmaking slags. These thermodynamic mainframe- based programs required considerable expertise in mineralogy, mathematics and physical chemistry, an experienced computer operator, and time frames of several days to generate results. They therefore remained primarily research tools not engineering tools. With the advent of the personal computer, both mass balance and phase calculations became available as engineering tools on the shop floor. Many steel and refractory companies very quickly introduced PC based mass balance calculations, but the mineralogical expertise required to program and use phase calculations delayed their application. As the traditional approach (in use for 25 years) using crystallized (solidus) mineralogy was easier to understand and program, it became the base of the early slag programs despite its recognized limitations of not considering temperature effects and not always targeting 100% fluid slags.

Baker Refractories introduced its first PC-based phase calculation program based on Rait's work [4]) in 1986. This program was widely applied in the mini mill sector of the North American steel industry until it was supplanted in 1994 by the first version of the current liquidus based program, which corrects many of the deficiencies inherent in the solidus mineralogy programs. In Europe a spreadsheet-based program using the concept of technical lime saturation [5,6] for calculating the CaO requirement for high alumina slags, has been introduced in the last two years. In early 1996, Baker Refractories went "on-line" using a dial-up computer to allow our customers real time access to interactive phase based liquidus steelmaking slag models.

## 3. SLAG MODELS AND STEELMAKING PRACTICE

Before the various slag models are discussed, it is important to illuminate the role (or place) of these models in modern steelmaking practices. The use of a good slag model in a steel plant is no guarantee that good slags will actually be generated during the steelmaking practice. An understanding of slag fundamentals, and what the slag models represent, are essential for the optimum application of the models. Steelmaking is a dynamic process and constant adjustments are made during a heat, which could also affect the composition of the slag. A slag model can only be successful in improving steelmaking results and refractory life if all the factors influencing the composition of the slag are considered. The slag model only provides an optimum target slag. Whether the desired slag is actually achieved depends largely on the consistency and control of the steelmaking process. Slag models are best utilized if combined with a mass-balance approach. The use of a mass-balance calculation enables the steelmaker to adjust his alloy and flux additions to optimize the slag for steelmaking requirements (sulfur removal or retention) and compensate for the effect of carryover slag [7].

One of the major "unknowns" in secondary steelmaking is the amount of oxidized carryover slag from the EAF or BOF. The amount of carryover slag into a ladle is often estimated and historic slag analyses are usually used to approximate the slag composition. The following mass-balance example illustrates the effect of carryover slag and the inconsistencies that can be generated if all the factors are not considered. For illustrative purposes (using a slag model and desulphurization correlations [8,9]) the slag composition below was selected as a target slag because of its desulphurizing properties and its compatibility with the refractory material.

$MgO$ - 11
$CaO$ - 53
$Al_2O_3$ - 6
$SiO_2$ - 23
$CaF_2$ - 7

In order to generate this slag in the ladle, a mass-balance approach was used to estimate and calculate the various contributions to the slag. The following flux addition "recipe" or SOP was then proposed to the ladle operator (carryover slag amount was estimated as 350 kg):

273 kg of lime
180 kg of doloma
70 kg of $CaF_2$
10 kg of $CaC_2$

If the amounts of these additions are fixed and the amount of carryover slag is consistently around 350 kg, then the composition of the ladle slag will approach that of the target slag. However, the age of the taphole in an EBT or BOF can dramatically effect the amount of slag carried over and hence the composition of the slag in the ladle. These variations in ladle slag composition can lead to inconsistent metallurgical results. Table I shows the different ladle slag compositions that will be generated for a fixed flux addition but variable amounts of slag carryover.

This example gives some idea of the inconsistent steelmaking results that could result from inconsistent slags. Slag 3 in Table I was probably extensively oxidized for most of the heat so that effective desulfurization was only possible towards the very end of the heat. This may lead to actual sulfur values in the steel much worse than expected.

**Table I. Calculated changes in slag composition as a function of EAF carryover amount. Units in kg. (100 tons of steel, $S_i = 0.05\%$, $\underline{O} = 15$ ppm)*.**

| | Slag 1 | Slag 2 | Slag 3 |
|---|---|---|---|
| Carryover Amount | 100 | 350 | 1000 |
| Taphole age | 1 day | 4 days | 8 days |
| $CaC_2$ added** | 0 | 10 | 30 |
| % MgO | 11.2 | 10.9 | 10.7 |
| % CaO | 58.1 | 53.3 | 48.9 |
| % $Al_2O_3$ | 7.1 | 6.1 | 5.1 |
| % $SiO_2$ | 13.5 | 22.6 | 30.9 |
| % $CaF_2$ | 9.7 | 7.0 | 4.3 |
| Slag Amount | 700 | 960 | 1582 |
| Optical basicity | 0.795 | 0.752 | 0.717 |
| - Log $C_S$ | -1.62 | -2.23 | -2.74 |
| $S_f$ | 0.005 | 0.012 | 0.02 |

* The calculation includes slag/metal interactions

** $CaC_2$ added for slag deoxidation

Slag 1 was probably not fully liquid for most of the heat so that the calculated desulfurization will be greatly over estimated. Optical basicity and sulfide capacity calculations are only applicable to fully liquid slags [10,11].

## 4. SLAG MODELS

Following is a brief overview of some of the slag models that have been utilized in steelmaking over the past three decades. The latter part of this paper will focus on the application and use of a liquidus slag model.

### 4.1) Models based on simple component ratios

The most common slag models that have been used for a number of years in stainless steelmaking are those based on simple $CaO/SiO_2$ or $V_B$ ratios in the slag. The process of stainless steelmaking is somewhat more predictable than C-steelmaking which made the implementation of the models easier. However, as the number of Al-killed stainless grades has increased dramatically over the last decade, the slags that are now generated in the stainless steel vessel are significantly more complex; so that the old slag models have become ineffective as extensive refractory wear in the vessel has become a major problem. For example consider the two slags in Table II where the target $V_B$ ratio is 1.5. Slag A would be compatible with a dolomite refractory but Slag B would be incompatible as it is CaO unsaturated and could lead to extensive refractory wear. Lime saturation is a major requirement for slags in contact with dolomite refractories as the matrix (bonding phase) of these refractories is lime based.

**Table II. Two stainless reduction slags. Slag A - Si-killed steel, Slag B - Al killed steel.**

| | Slag A | Slag B |
|---|---|---|
| % MgO | 12 | 12 |
| % CaO | 48 | 48 |
| % $Al_2O_3$ | 2 | 35 |
| % $SiO_2$ | 33 | 5 |
| % $CaF_2$ | 5 | |
| $V_B$ ratio | 1.5 | 1.5 |

$$V_B = \frac{CaO + MgO}{SiO_2 + Al_2O_3 + CaF_2}$$

### 4.2) Models based on crystallized mineralogy

With the introduction of personal computers in the early eighties, the use of slag models based on solidus (crystallized mineralogy) phase relations became popular. These models were mainly based on Rait's mineralogical work [2] and estimated slag compatibility with basic refractories. Unfortunately, these models have severe limitations: They do not accurately show the effect of temperature variations on the solubility of CaO and MgO. Furthermore, they do not accurately predict the melt phase amounts, or the different effects of fluidizing components such as $Al_2O_3$, $SiO_2$, FeO or $CaF_2$.

A comparison of the results of the solidus mineralogy approach to the liquidus slag model may be informative. Two solidus slag models were used:

1) A "simple" solidus model, using the approach from Rait's work.
2) A "modified" model developed by Baker Refractories that considers $CaF_2$ and limits CaO saturation. The various models were applied to the slags in Table II and the results are listed in Tables III and IV for slags A and B, respectively.

**Table III. Adjusted slag compositions using the various models (For 100 kg of slag A).**

| | Slag A | Solidus models "S" - simple "M" - modified | | Liquidus slag model (Temp. - °C) | |
|---|---|---|---|---|---|
| | | "S" | "M" | 1600 | 1700 |
| % MgO | 12 | 0 | 12 | 15 | 15 |
| % CaO | 48 | 61 | 50 | 50 | 53 |
| % $Al_2O_3$ | 2 | 2 | 2 | 2 | 2 |
| % $SiO_2$ | 33 | 32 | 31 | 29 | 26 |
| % $CaF_2$ | 5 | 5 | 5 | 4 | 4 |

For the slags in Table III resulting from Si-killed deoxidized steels (Slag A), the "simple" mineralogical approach yields excess lime, but with a magnesia deficiency at 1600°C; and becomes significantly CaO and MgO deficient at 1700°C by comparison to the liquidus slag model. The "modified" solidus model partially corrects for this error, but remains CaO and MgO deficient at higher temperatures.

**Table IV. Adjusted slag compositions using the various models (For 100 kg of slag B).**

| | Slag B | Solidus models "S" - simple "M" - modified | | Liquidus slag model (Temp. - °C) | |
|---|---|---|---|---|---|
| | | "S" | "M" | 1600 | 1700 |
| % MgO | 12 | 0 | 6 | 8 | 9 |
| % CaO | 48 | 62 | 58 | 57 | 58 |
| % $Al_2O_3$ | 35 | 33 | 31 | 31 | 29 |
| % $SiO_2$ | 5 | 5 | 5 | 4 | 4 |
| % $CaF_2$ | | | | | |

In Table IV a similar comparison of slags from Al deoxidation (Slag B) shows a closer correlation between the liquidus and solidus models, but still with significant errors - especially the undersaturation with respect to MgO. The deviations would be greater for slags containing fluorspar.

### 4.3) Thermodynamic slag models

The most sophisticated of these slag models are the complex statistical thermodynamic models which allow a very accurate description of the properties of multi-component systems [12,13,14,15]. Unfortunately, these models are not commercially available and most have not yet been ported for use on personal computers.

### 4.4) Models based on multi-dimensional phase equilibria

In this study the liquidus surfaces of selected phase diagrams have been utilized to design a slag model. The selection of particular areas on these multi-component and multi-dimensional phase diagrams that are of special interest to the steelmaker, can greatly simplify the modeling possibilities, allowing quicker results and the use of a PC platform[11]. Since most steelmaking slags are basic in nature, the models described in this paper have been designed for basic slags. The models utilize a statistical and mathematical approach to describe the liquidus surface and solidus phase relations as a function of temperature and composition for basic slags that are compatible with magnesia and dolomite refractories [16,17].

As a default option, at a given temperature for any composition, the models seek the CaO/MgO saturated liquidus boundary (Point O on Figure 1).

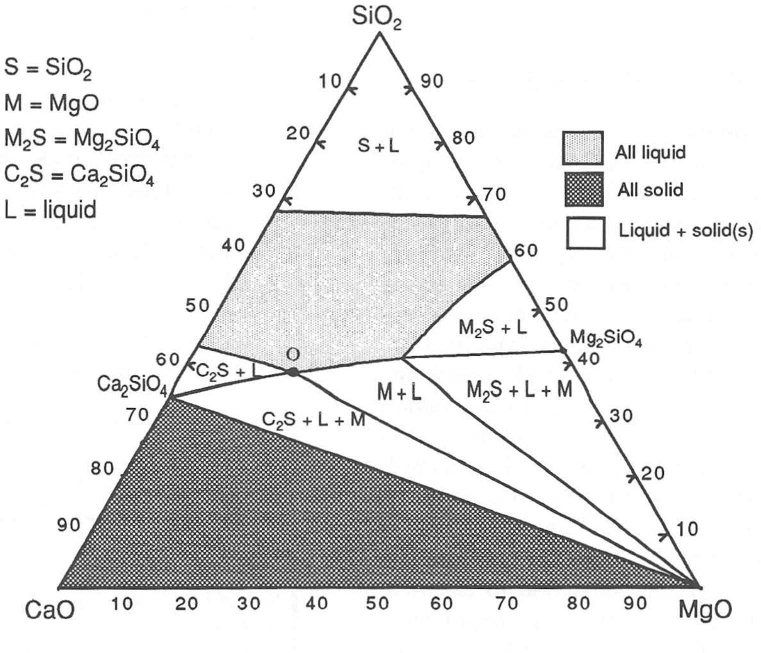

Figure 1. Isothermal section for the CaO-MgO-$SiO_2$ system at 1600°C.

The adjustment of CaO/MgO levels to achieve the 100% fluid boundary is calculated, and desulfurization (for reduced slags) is estimated for the 100% fluid slags using published optical basicity correlations [8,9]. Currently two models have been developed: The first model is applicable to "oxidized" slags and incorporates the components CaO, MgO, $SiO_2$, $Al_2O_3$, FeO, and MnO, and can be used for EAF and BOF slags. This model defines the compositions of slags with good foaming properties that are also compatible with magnesia slag-line refractories.

The second model has been designed for "reduced" slags and incorporates the components CaO, MgO, $SiO_2$, $Al_2O_3$ and $CaF_2$, and can be applied to ladle slags and stainless steel reduction slags. This model defines slag compositions that are not only optimum slags for metallurgical practice, but are also fully compatible with magnesia and dolomite refractories. Compatible slags are defined as being just CaO and MgO saturated and having a high fluidity. Considering the various combinations of fluidizers ($SiO_2$, $Al_2O_3$, and/or $CaF_2$), an infinite number of slag compositions can be generated that will have different sulfide capacities, so that slag compositions can be engineered for a specific steel grade or heat.

## 5. APPLICATION OF LIQUIDUS SLAG MODELS

Liquidus slag models are generally used in three ways:

1) The evaluation of existing slag in a post-mortem fashion.
2) The design of optimum target slag recipes in order to achieve specific metallurgical goals.
3) Combining the slag model with a mass-balance approach in order to calculate the required lime and MgO additions during the steelmaking process.

### 5.1) Using slag models to evaluate existing slags

Slag models are commonly used to evaluate existing slags in a "postmortem" fashion. While this approach provides some idea of the compatibility of the slag, erroneous conclusions can sometimes be made. The following composition represents a slag sample taken from a ladle with a magnesia slag line (Slag X):

% MgO - 12
% CaO - 45
% $Al_2O_3$ - 26
% $SiO_2$ - 17

Evaluating this slag with the liquidus slag model and using the default slag criteria[1] indicates that this slag is CaO unsaturated but MgO over-saturated. For 100 kg of slag (at 1600°C) the calculated slag requirements would be 22.5 kg CaO and -1.5 kg MgO, respectively. The adjusted "optimum" slag composition would be the following:

% MgO - 9
% CaO - 56
% $Al_2O_3$ - 21
% $SiO_2$ - 14

However, since the slag is in contact with a magnesia refractory material, only MgO saturation is required for refractory compatibility. The liquidus slag model allows the user to specify MgO saturation as a target slag option. Evaluating the slag with magnesia saturation as the criteria now shows the CaO and MgO requirements of the slag to be zero, i.e. fully compatible with a magnesia slag line refractory. Hence it can be concluded that Slag A is compatible with magnesia slag line refractories but not compatible with dolomite slag line refractories.

By evaluating published phase diagrams the MgO solubility limits for various slags can easily be determined. The MgO solubility in the slag is usually the lowest at CaO saturation and increases as the basicity of the slag decreases. This is shown in Figure 2 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 $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ at 1600°C.

$$\% \, MgO = 1330.5 \, \Lambda^2 - 2092 \, \Lambda + 829.9 \qquad (1)$$

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

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 $Al_2O_3$-free slags and 0.715 for slags containing 10% $Al_2O_3$ at 1600°C (Figure 2). Similar equations can be generated for various alumina levels at basicities lower than 0.69 using simple regression techniques.

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[1] The default slag criteria is CaO and MgO saturation. It target slags of "optimum" desulfurization and compatibility with dolomite refractories

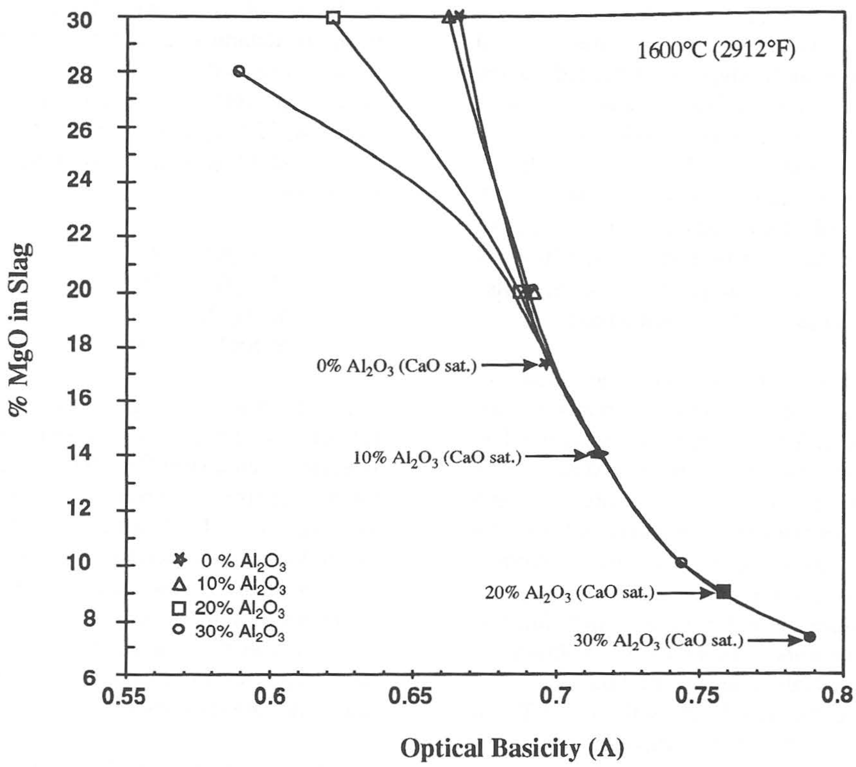

Figure 2. MgO saturation levels in slags of the system CaO-MgO-$Al_2O_3$-$SiO_2$ at 1600°C

The calculated optical basicity for Slag X is 0.727 and substituting this value into equation (1) gives the % MgO = 11.96 to be the saturation value at 1600°C.

From the evaluation of Slag X using the slag model, the conclusion might be made that Slag X would be compatible with the magnesia slag line. However, in actual plant experience, extensive wear was observed in the magnesia slag line during the ladle campaign. In order to elucidate the obvious discrepancy a mass-balance approach was employed to calculate the MgO inputs to the slag. From the mass-balance calculation it was immediately clear that the only addition of MgO to the ladle originated from the EAF carryover slag, and could be calculated to a maximum level of 4% MgO.

Only lime and alloys were added for the remainder of the heat so that the increase in MgO content in the slag from 4% to 12% can be attributed to refractory wear. Due to very long heat times in the ladle furnace and high fluidity slags, extensive dissolution of the refractory occurred so that the final MgO value in the slag approached the saturation value.

This demonstrates a major limitation of slag models and mass-balance calculations which is: they ignore kinetic barriers and only provide the final calculated result. The "path" that the slag took to reach its final composition is usually not considered.

## 5.2) The use of liquidus slag models to design target slags.

The liquidus slag model is a very useful tool to evaluate and design desulfurization slags since it calculates to a 100% fluid slag. The model provides information on the solid-liquid phase equilibrium relationships for multi-component slags as a function of temperature and composition which is critical for the engineering of slags to achieve desulfurization goals. The choice of fluidizers ($SiO_2$, $Al_2O_3$ 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. The slags listed in Table V were generated with the "reduced" slag model, and the effect of fluidizer on the solubility of CaO and MgO is clearly illustrated. All of the slags in Table V have a high fluidity and are just saturated with respect to CaO and MgO and are therefore compatible with magnesia and dolomite refractories. From Table V it can be inferred that $Al_2O_3$ and $CaF_2$ are much "stronger" fluidizers than $SiO_2$ for increasing the solubility of CaO in the slag. Using the liquidus slag model with various combinations of fluidizing agents, an infinite number of slags with varying sulfide capacities can be designed to attain specific metallurgical goals.

**Table V. Compositions of slags that are just CaO and MgO saturated at 1600°C ($\Lambda$=optical basicity, $C_s$ = sulfide capacity, and $S_f$ = final sulfur)**

| | Slag 1 | Slag 2 | Slag 3 | Slag 4 |
|---|---|---|---|---|
| % CaO | 45 | 52 | 54 | 58 |
| % MgO | 17 | 10 | 13 | 8 |
| % $Al_2O_3$ | | 17 | | 23 |
| % $SiO_2$ | 38 | 21 | 22 | 9 |
| % $CaF_2$ | | | 11 | 3 |
| $\Lambda$ | 0.696 | 0.744 | 0.766 | 0.788 |
| -Log $C_s$ | 3.04 | 2.35 | 2.04 | 1.72 |
| $S_f^*$ | 0.035 | 0.017 | 0.010 | 0.005 |

*Using 100 tonnes of steel, 1000 kg of slag, $S_i = 0.05\%$, $\underline{O} = 15$ ppm

The effect of $CaF_2$ on the solubility of CaO is similar to that of $Al_2O_3$, but higher amounts of CaO can be dissolved in certain composition ranges. However, the MgO requirements of $CaF_2$ fluidized slags are high (> 12% MgO) so that extensive refractory wear can occur for fully liquid $CaF_2$-containing slags if insufficient MgO is added to satisfy solution requirements.

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 Figure 2. All these slags are 100% fluid at steelmaking temperatures and compatible with magnesia slag line refractories.

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. The liquidus slag model allows the user to specify the maximum tolerable MgO level in the slag so that the model will iterate to a slag that is only CaO-saturated. Figure 3 shows the areas of CaO-saturation in CaO-MgO-$SiO_2$ slags at 1600°C. These slags will be fully compatible with dolomite refractories and reasonably compatible with magnesia refractories.

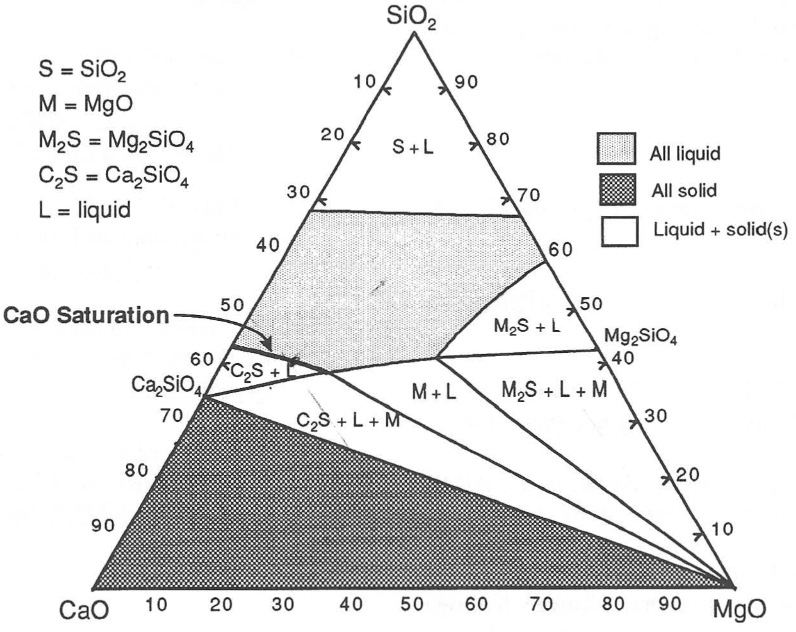

Figure 3. Isothermal section for the CaO-MgO-$SiO_2$ system at 1600°C
The area of CaO saturation is indicated by the thicker line.

### 5.3) Combining slag models with mass-balance calculations

The most common combination of computer models and mass-balance calculations is in stainless steelmaking. The temperatures, blow rates, alloy and flux additions are calculated using this approach. As the amounts of reductants (FeSi and/or Al) are known before the reduction step, the amounts of lime and dolomite required for refractory compatibility can be easily calculated. A mass-balance calculation will track all the possible input components into the slag; whereas the process models will give an indication on the amount of $SiO_2$ and $Al_2O_3$ that will be released into the slag. The application of a liquidus slag model in stainless steel making allows the operator to evaluate the effect of temperature and overblown heats on his flux requirements to achieve refractory compatibility. Since the model also predicts desulfurization values, the choice of fluxes ($CaF_2$ vs. $SiO_2$ vs. $Al_2O_3$) becomes very important in order to increase the solubility of CaO in the slag, and hence desulfurization.

## 6. CONCLUSIONS

We have attempted to demonstrate the benefits of computer modeling to simulate and predict refractory/slag/metal interactions. These personal computer-based models can be utilized to optimize the thermodynamics and kinetics of various steelmaking reactions, which is the key to improve the overall efficiency of the steelmaking process. This paper focused on the use of a liquidus slag program, based on the multi-dimensional modeling of phase equilibria, in conjunction with mass-balance calculations.

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