MgO Saturation Analysis of CaO-SiO₂-FeO-MgO-Al₂O₃ Slag System

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Electric arc furnace (EAF) slag has a range of functions, including improving energy efficiency through the "slag foaming" phenomenon. As such, the study of slag is important in EAFs. One of the factors that determine foaming quality and efficiency is the presence of solid particles. MgO saturation is highly significant since, in addition to ensuring the presence of solid particles, it also ensures chemical compatibility to minimize refractory consumption. The present study aims to examine MgO saturation, using the software FactSage v.6.4 for all calculations, in the CaO-SiO₂-FeO-MgO-Al₂O₃ slag system and the influence of binary basicity, FeO and Al₂O₃ content on this system. Ternary diagrams revealed the influence of Al₂O₃ content on the liquid field and other phases present. Isothermal saturation diagrams (ISDs) were constructed, showing the same dual saturation points found in the ternary diagrams. The ISDs were validated by comparing the results of different heats in terms of the electrical energy consumption. The closer the heat is to the MgO saturation line, the less energy is consumed.

Keywords: EAF, MgO saturation, Dual saturation.

1. Introduction

Slag plays different roles in electric arc furnaces, from protecting refractories against arc radiation to absorbing phosphorus and improving energy efficiency. However, in order to satisfactorily perform these roles, slag composition must be compatible with the refractories used in the furnace. They are typically made of basic oxides (MgO, CaO, etc.) and end up being incorporated to the slag throughout the EAF process, as primary refining slag is rich in acidic oxides (SiO₂, MnO, FeO, etc.). Thus, it must have the correct basicity and be MgO saturated. Table 1 shows an example of EAF primary refining slag. Excess MgO and proper basicity minimize refractory consumption and contribute to the foaming phenomenon. For foaming to occur, slag must contain excess oxygen and carbon, according to the following reactions 1 and 2.

\[ C + \frac{1}{2}O_2 \rightarrow CO \] (Reaction 1)
\[ C + (FeO) \rightarrow CO + Fe \] (Reaction 2)

As CO bubbles are generated by these reactions, slag expands and covers the arc. There are several parameters that a good foaming slag: adequate viscosity, low surface tension, low density, and the presence of solid particles. Slag saturation in CaO and MgO produces solid particles that serve as bubble nucleation sites, generating a larger amount of small bubbles.

Studying slag foaming is highly complex and involves variables such as temperature, basicity, the chemical composition of slag, and MgO saturation. Thus, the present study aimed to analyze MgO saturation behavior in the CaO-SiO₂-FeO-MgO-Al₂O₃ system according to different slag chemical composition parameters, at a temperature of 1600°C, using FactSage 6.4 thermodynamic simulation software.

2. Materials and Methods

FactSage was created in 2001, resulting from the merge of two well-known software packages in the field of computational thermochemistry: FACT-Win (formerly F*A*C*T) and ChemSage (formerly SOLGASMIX). According to Bale et al.4-6, this software is under constant development, whether upgrading or adding new database. Several studies have been carried out to validate the database, from binary7,8, quaternaries9,10, and even more complex systems11-14. In these studies the "quasichemical" model15 was used for the thermodynamic description and, among them, some were performed to evaluate systems containing iron oxide (both FeO and Fe₂O₃)9,11,13,14. The software FactSage 6.4 was used for all calculations in this study. This software has been used in several studies of primary16,17 and secondary18,19 refining slag.
The following databases were used:
- FToxid: this database consists of two sections: FToxid53Soln.sda, which contains evaluated/optimized oxide solutions, and FToxid53Base.cdb, for evaluated and optimized solid and liquid compounds. The main oxides in this database are: Al$_2$O$_3$, CaO, FeO, Fe$_2$O$_3$, MgO, SiO$_2$.
- FactPS: pure substance database.

In iron and steel production slags, not all iron oxide present is in the form of FeO. In fact, Fe$_2$O$_3$ also exists. The higher valence iron oxide (Fe$^{3+}$), probably located in the slag region in contact with air, will be unstable in the slag region that is in physical contact with liquid iron. This study adopted the system CaO-SiO$_2$-MgO-Al$_2$O$_3$-FeO, using FeO instead of Fe$_2$O$_3$.

It is known that the Fe$^{3+}$/Fe$^{2+}$ relation decreases when the silica content is increased, increases with increasing slag basicity and with decreasing FeO content in basic slags. Tayeb et al. performed calculations of the Fe$^{3+}$/Fe$^{2+}$ ratio in FactSage software, comparing to experimental results published by other authors. For an iron oxide ranging from 10 to 20 wt pct, FactSage predict a Fe$^{3+}$/Fe$^{2+}$ ratio of 0.12 to 0.18, which is in good agreement with the literature.

Because the Fe$_2$O$_3$ phase is acidic in a basic slag, the MgO solubility could be increased. However Tayeb et al. calculated the change in solubility of MgO by replacing FeO by Fe$_2$O$_3$ in FactSage, resulting in a small increase on MgO solubility (<1 wt. pct). Thus, considering that all the iron oxides are in the form of FeO will not lead to errors in the MgO saturation calculated by FactSage.

The effect of binary basicity on MgO saturation was analyzed for FeO contents between 15 and 35 weight %. The calculations were done for different basicities (1.5, 2.0, 2.5, and 3.0). In this analysis the chemical compositions were pre-established by the authors. As FeO increases in the analysis, the CaO and SiO$_2$ decrease, but the basicity relation (B$_{2+}$=CaO/2SiO$_2$) is constant.

To study the behavior of the MgO saturation due to temperature change, data were pre-established, the FeO content for all the analysis was constant (30% wt.) and the basicity varied between 1.5 and 3.0. The calculations were done for different temperatures (1500, 1550, 1600 and 1650 °C).

In order to make comparisons and determine the effect of Al$_2$O$_3$ on the CaO-SiO$_2$-FeO-MgO system, CaO-SiO$_2$-FeO pseudo-ternary diagrams with 5% MgO and different Al$_2$O$_3$ values (0, 5 and 8%) were made using FactSage software v. 6.4.

Isothermal Saturation Diagrams (ISDs), introduced by Pretorius can also be used to analyze MgO saturation. ISDs are compiled considering two main boundary conditions: constant basicity and constant temperature. Figure 1 shows a generic ISD.

![Figure 1. Generic isothermal saturation diagram.](image)

**Table 1.** Main EAF slag components and final composition %.

<table>
<thead>
<tr>
<th>Component</th>
<th>Component range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>25 - 40</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>5 - 20</td>
</tr>
<tr>
<td>MgO</td>
<td>7 - 13</td>
</tr>
<tr>
<td>FeO</td>
<td>20 - 45</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2 - 10</td>
</tr>
<tr>
<td>MnO</td>
<td>2 - 5</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>&lt; 1.5</td>
</tr>
</tbody>
</table>

Figure 1 shows some of the main information provided by ISDs: FeO and MgO content necessary for dual saturation to occur; the point C (whose chemical composition can be obtained from the chemical composition of the liquid in the FeO-MgO diagram); and the line connecting the dual saturation point and point C, named MgO saturation line.

It is known that ISDs reflect MgO saturation and that slag foaming is favored by the presence of solid particles. Therefore, when the MgO content in the heat is slightly above the saturation line but close enough to it, it is going to provide higher quality foaming and increase energy efficiency.

In order to evaluate the ISDs, historic data provided by a special steel mill was used. This data corresponded to heats produced using very similar scrap loads, regarding amount and scrap grades. Additionally, heats with the same chemical composition (basicity and Al$_2$O$_3$ content), similar refining times, and tapping temperatures varying by a maximum of 10°C were compared, based on their position in the ISD and their energy consumption.

### 3. Results and Discussion

#### 3.1 Effects of binary basicity and FeO content

It is known that higher binary basicity slags, require lower MgO content for saturation and that the FeO content significantly influences MgO saturation. This can be seen in figure 2, which shows MgO saturation levels for different FeO contents for binary basicities ranging from 1.5 to 3.0.
Figure 2. Effect of basicity on MgO saturation levels for different FeO contents at 1600°C.

Figure 2 shows that different behaviors occur at different basicities. For lower basicities, such as 1.5, MgO saturation varied slightly as FeO content changed. A different behavior is observed for basicities above 2.0 and 2.5; MgO saturation increases with increasing FeO contents. When basicity is increased even further, slag is MgO saturated until FeO content reaches approximately 25%. For higher FeOs, MgO is no longer saturated and behaves as it did in the previous cases. These last three cases show the fluxing effect FeO has on primary refining slag. Additionally, for the same FeO content, MgO saturation declines as basicity increases.

3.2 Effect of temperature

As the temperature rises, the liquid slag fraction increases and viscosity declines. That requires the MgO necessary for saturation to increase as well. Figure 3 shows the behavior of MgO saturation with binary basicity at temperatures of 1500, 1550, 1600, and 1650 °C and 30% FeO.

Regarding temperature, MgO varies more with temperature at lower basicities, from 16.3% MgO at 1650°C to 13.3% MgO at 1500°C. The variation was smaller at a basicity of 3.5, from 3.6% MgO at 1650°C to 2.2% MgO at 1500°C.

3.3 Effect of $\text{Al}_2\text{O}_3$ content

3.3.1 Ternary diagrams

Another parameter that affects MgO saturation is $\text{Al}_2\text{O}_3$ content. In his study, Pretorius used $B_3 = \%\text{CaO}/(\%\text{SiO}_2 + \%\text{Al}_2\text{O}_3)$ to analyze this parameter, substituting a certain amount of silica with alumina to keep basicity constant. Pretorius compared an alumina-free slag, resulting in binary basicity, with slag containing alumina, producing ternary basicity. To study the effect of $\text{Al}_2\text{O}_3$, the present study constructed CaO-SiO$_2$-FeO pseudo-ternary diagrams with fixed $\text{Al}_2\text{O}_3$ and MgO contents for comparison purposes. Figures 4 and 5 show the pseudo-ternary diagrams at 5% MgO, with and without $\text{Al}_2\text{O}_3$.

Figure 3 shows that, as basicity increases, MgO contents behave the same at all temperatures. Initially, there is a sharp decline (approximately 10%) between basicities from 1 to 2. At higher basicities, MgO can be considered constant.

Figure 4. CaO-SiO$_2$-FeO pseudo-ternary diagram at 5% MgO and $T = 1600°C$.

Figure 5. CaO-SiO$_2$-FeO pseudo-ternary diagram at 5% $\text{Al}_2\text{O}_3$ and 5% MgO, $T = 1600°C$. 
The fields of particular interest for this study are 2, 3, and 5, consisting of: liquid, liquid + C\textsubscript{2}S \text{ and liquid + (Mg, Fe)} \text{O, respectively. In other words, in field 3 CaO precipitates as C\textsubscript{2}S (2CaO.SiO\textsubscript{2}), and in field 5, MgO saturates as (Mg, Fe)O (magnesium wüstite). As such, A-C and A-B are C\textsubscript{2}S \text{ and MgO saturation lines, respectively. At 5\% Al\textsubscript{2}O\textsubscript{3} (figure 5), the field consisting of C\textsubscript{2}S \text{ + magnesium wüstite (field 8 in figure 4) is suppressed, as is the field comprising solid CaO + C\textsubscript{2}S \text{ + magnesium wüstite (field 9 in figure 4).} }

Figure 6 shows the overlapping of the liquid fields from the two ternary diagrams and the addition of liquid field lines for an Al\textsubscript{2}O\textsubscript{3} content of 8%.

![Figure 6](image)

**Figure 6.** Superimposed liquid fields of the pseudo-ternary diagrams at 0\%, 5\%, and 8\% Al\textsubscript{2}O\textsubscript{3} and 5\% MgO.

Figure 6 shows the differences in the liquid slag field (field 2) caused by Al\textsubscript{2}O\textsubscript{3}. The presence of Al\textsubscript{2}O\textsubscript{3} causes the expansion of the liquid slag field, evident in the change in lines A-C and A-B.

Another important difference occurs for point A, which, according to Paulino\textsuperscript{27}, is the dual saturation point. In other words, this is the point where fields 2, 3, and 5 in figures 4 and 5 intersect, and where saturation occurs for both CaO as C\textsubscript{2}S \text{ and MgO in the form of magnesium wüstite.}

There was a significant change to point A with the change in Al\textsubscript{2}O\textsubscript{3} content, as shown in table 2.

Al\textsubscript{2}O\textsubscript{3} content significantly influences point A. Table 2 shows that the higher the Al\textsubscript{2}O\textsubscript{3} content, the greater the basicity (from 2.15 at 0\% to 2.78 at 8\% Al\textsubscript{2}O\textsubscript{3}) and lower the FeO content needed for dual saturation. This indicates the flux effect of alumina, as demonstrated by Kim et al.\textsuperscript{26}.

### 3.3.2 Isothermal Saturation Diagrams

Given that ISDs are constructed using constant basicity and temperature, ISDs were compiled using the chemical compositions at point A in figure 6. The same basicities found and the same Al\textsubscript{2}O\textsubscript{3} content were used, at the temperature of 1600°C. The FeO and MgO contents obtained in the pseudo-ternary diagrams for the dual saturation point (point A) were compared to the values found in the ISDs of figures 7, 8, and 9.

![Table 2](image)

**Table 2.** Chemical composition of dual saturation points (point A) for slag at: a) 0\% Al\textsubscript{2}O\textsubscript{3}, b) 5\% Al\textsubscript{2}O\textsubscript{3}, and c) 8\% Al\textsubscript{2}O\textsubscript{3}.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>20.21</td>
<td>19.40</td>
<td>18.35</td>
</tr>
<tr>
<td>CaO</td>
<td>43.60</td>
<td>48.46</td>
<td>51.12</td>
</tr>
<tr>
<td>B\textsubscript{2}</td>
<td>2.15</td>
<td>2.50</td>
<td>2.78</td>
</tr>
<tr>
<td>FeO</td>
<td>30.59</td>
<td>22.13</td>
<td>17.50</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>0</td>
<td>5.0</td>
<td>8.0</td>
</tr>
<tr>
<td>MgO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

![Figure 7](image)

**Figure 7.** Isothermal Saturation Diagram B\textsubscript{2}=2.15 and T = 1600°C.

![Figure 8](image)

**Figure 8.** Isothermal Saturation Diagram B\textsubscript{2}=2.5, 5\% Al\textsubscript{2}O\textsubscript{3}, T=1600°C.

![Figure 9](image)

**Figure 9.** Isothermal Saturation Diagram B\textsubscript{2}=2.78, 8\% Al\textsubscript{2}O\textsubscript{3}, T=1600°C.

The ISD in Figure 7 was compiled for basicity of 2.15 and without the presence of Al\textsubscript{2}O\textsubscript{3}. The dual saturation point in this graph had the following chemical composition: FeO
content = 30.5 % and MgO content = 5.07 %. The ISD in figure 8 was constructed with basicity equal to 2.5; the dual saturation point was identified at FeO = 22.25% and MgO = 5.01%. In the ISD in figure 9, the dual saturation point found was: FeO = 16.95% and MgO = 5.14. When comparing these values to those shown in table 2, it is seen that the values are the same. That shows the ISDs can be used to predict the behavior of slag containing complex chemical composition that include Al₂O₃, for example.

The present study used ISDs to evaluate the effect of Al₂O₃ on MgO saturation. Differences are shown in figure 10. The graphs were superimposed in order to more easily visualize the binary basicities of 1.5, 2.0, 2.5, and 3.

Alumina has the same effect for all four basicities. Higher Al₂O₃ content leads to an increase in the MgO necessary for saturation and a decline in the FeO required for dual saturation, as observed in the ISD for basicity of 2.0, where the FeO necessary for dual saturation dropped from 30% (without Al₂O₃) to 15% (at 8% Al₂O₃). These two effects combined produce the same results seen in the pseudo-ternary diagrams, that is, the liquid field expands.

3.3.3 Tests using industrial data

It is known that solid particles serve as bubble nucleation sites, generating a larger amount of small bubbles, so slags saturated either in CaO or MgO should have a better foaminess than slags without solid particles or slags that are oversaturated in solid particles, resulting in less electric energy consumed.

Tests based on industrial data were conducted using electrical energy consumption during refining (E_{refining}) and the refining time (T_{refining}). The electrical energy consumption during refining (E_{refining}) is considered to be energy used after a flat bath state is reached inside the furnace (around 70% of the total electrical energy used in the heat). The heats plotted in the ISDs in figures 11, 12, and 13 had the same alumina content and basicity that were used to construct these ISDs. They show, for each heat, the E_{refining}, T_{refining} and also the average electrical power (E_{Power}). The electrical power is relevant as it influences the refining time.

Figures 11 to 13 show the same behavior for all heats. Heats closer to the saturation line showed better results in terms of electrical energy consumption during refining and
power (short electrode, for example). Excluding external
data, this heat could have had a higher power, using the
same electrical energy but in shorter refining time.

Figure 12 shows the comparison between the three heats
closer to the saturation line (heats 2, 3 and 4) and heat 1,
farther from it. Despite the difference in refining times,
there is a slight increase in energy consumption, and a significant
decline in power. For a refining time of 12.8 min (4 min
difference), the energy increased by 1062 kWh. The energy
increase was 1403 kWh when refining time was 13.7 min (5.9
min difference). A significant decrease in energy consumption
(1543 kWh) was observed for the heat with a refining time
of 7.6 min (1.2 min difference).

Except for 2 heats (heat 1 of figure 11 and heat 1 of
figure 13) all other heats have similar FeO content, causing
the variation of the electrical conductivity to be very low.
Regarding the heats with different FeO, they had the same
basicities as the other heats in their ISD. This indicates that
these heats have higher CaO content. According to Jiao28,
the slag electrical conductivity can be expressed as a function
of FeO, CaO and MgO. As all these oxides change
(FeO decreases, and CaO and/or MgO increase), it can be
considered that the electrical conductivity of these heats
will be very similar. For this reason, electrical conductivity
variations will not be taken into account.

4. Conclusions

- Results obtained using FactSage were in accordance
  with those expected for the relationship between
  basicity and MgO saturation, where the MgO
  necessary for saturation decreases as basicity
  increases. Regarding the relationship between FeO
  contents and MgO saturation: when basicities were
  2.0 or higher, there was an increase in the MgO
  saturation. A different effect was observed for
  basicity of 1.5, with MgO saturation decreasing
  as FeO contents increased.

- The effect of Al2O3 was analyzed using CaO-SiO2-
  FeO pseudo-ternary diagrams with 5% MgO and
  no Al2O3, as well as 5% and 8% Al2O3. Significant
differences were observed in the liquid field and
dual saturation points, with chemical composition
  changing from SiO2 = 20.21%, CaO = 43.60% FeO
  = 30.59%, and MgO = 5% to SiO2 = 19.40%, CaO
  = 48.46%, FeO = 22.13%, MgO = 5%, and Al2O3
  = 5%, and SiO2 = 18.35%, CaO = 51.12%, FeO
  = 17.50%, MgO = 5%, and Al2O3 = 8%, showing
  a major decrease in FeO content and an increase
  in basicity from 2.15 (without Al2O3) to 2.78 (8%
  Al2O3), for dual saturation to occur.

- The ISDs made for the points mentioned in the
  pseudo-ternary diagrams showed the same dual
  saturation points, with an MgO content of 5% and
FeO = 30.5% for a basicity of 2.15. MgO content = 5% and FeO = 22.25% for basicity 2.5, and FeO = 16.95% and MgO = 5.14 for basicity 2.78. The comparison of ISDs with and without alumina showed the flux effect of alumina, with a higher MgO content needed for saturation and lower FeO level required for dual saturation. ISDs can be used to analyze MgO saturation and energy consumption. Heats closer to the MgO saturation line resulted in lower power (around 33000 kW) than the farther ones (above 40000 kW).

5. Acknowledgements

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6. References


