EVALUATION OF THE SLAG SYSTEM $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$[1]

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Abstract

Research on the topic 'steel slag' has grown worldwide. In fact, since 2005 the number of articles published per year has nearly doubled. Nevertheless, even the known (pseudo-quaternary) system $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$ presents lack of data regarding the subjects: phases present at the equilibrium state and physicochemical properties. This slag system plays important roles during the secondary refining of steel, such as: protection of refractory, sulfur level adjustment and absorption of non-metallic inclusions. Accordingly, the knowledge of the solid/liquid ratio considering, for instance, binary basicities (CaO/SiO_2) and MgO content, is full of significance. And, with respect to slag properties, the importance of viscosity stands out clearly. This property has an influence, for example, in metal-slag reactions and slag-refractory interactions, among others. Consequently, the objectives of this work are: (i) to perform a thermodynamic study of the phases at equilibrium at a high basicity value; and (ii) to evaluate the slag viscosity (from literature data and *via* thermodynamic software) as a function of the slag composition, establishing therefore a critical analysis with the published data. To achieve the proposed aims, the thermodynamic FactSage v. 6.3 software will be employed.

Key words: Slags; Computational thermodynamics; Steelmaking; FactSage.

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1 INTRODUCTION

Currently there is great pressure for the production of steels with higher technological content, as the market becomes increasingly competitive.

For companies to maintain their competitiveness, knowledge of the fundamentals of steel production is very important. Consequently, there is no quality steels production without the knowledge of the slag behavior.

In the production of iron and steel, slag performs essential functions; some of them can be cited which are especially important for the steelmaking:

- participate in refining reactions;
- act as thermal insulator;
- capture impurities steel;
- increase the lifespan of refractories;
- among other.

To perform these functions adequately to the process, it is important that they have the correct properties. Thus, knowledge of the physico-chemical properties of the slag, such as viscosity, interfacial tension, density, basicity, thermal conductivity, among others, is essential. These properties, in turn, are influenced by the chemical composition and temperature of the system.

Slag composition is fairly diversified, with various types of oxides, sulfides and fluorides. To study the influence of each is a complex task. Generally, the chemical composition determines the structure, so to define the properties, which determines the performance of the slag. Moreover, the slag composition should be considered in terms not only of the steel production process, but also to their further recycling.

As a reflection of this, the interest in the study of slag has grown worldwide. Since 2003, the annual number of publications almost doubled(1) and many of them use thermodynamics as a basis for studying the behavior of the slag.(2-4) However, the thermodynamic models used to understand and evaluate the behavior of real slags are quite complex. Because of this, the so-called 'computational thermodynamics' is a tool increasingly used by researchers.

Among other, the oxide system CaO-MgO-SiO_2-Al_2O_3 (denoted as C-M-S-A) plays an important role in a large number of industrial processes, especially in the steel industry. The high temperature equilibria in this system have been of great importance when selecting slag formers for blast furnace slags. In modern secondary steelmaking, ladle treatment has become increasingly important in the production of clean steels.

In the case of basic ladle slag, C-M-S-A slags close to CaO/MgO saturation with moderate Al_2O_3 and SiO_2 contents are used. As very often ladles are lined with MgO-C refractories, the slag compositions are usually selected close to MgO saturation to prevent severe refractory corrosion.(5,6)

In order to achieve good kinetic conditions for desulfurization and other refining reactions, the steel producers very often prefer completely liquid slag in ladle treatment. Slag with solid pieces might increase the viscosity and retard the refining operations. Hence, reliable *liquidus* data in the high basicity region would be of both industrial and scientific interest.(5,6)

Many phase diagram sections can be found in Slag Atlas,(7) which is based on a number of experimental and theoretical studies.

Figure 1 shows the pseudo-ternary CaO-MgO-SiO_2 diagram with 20 wt.%Al_2O_3 fixed content from this publication.

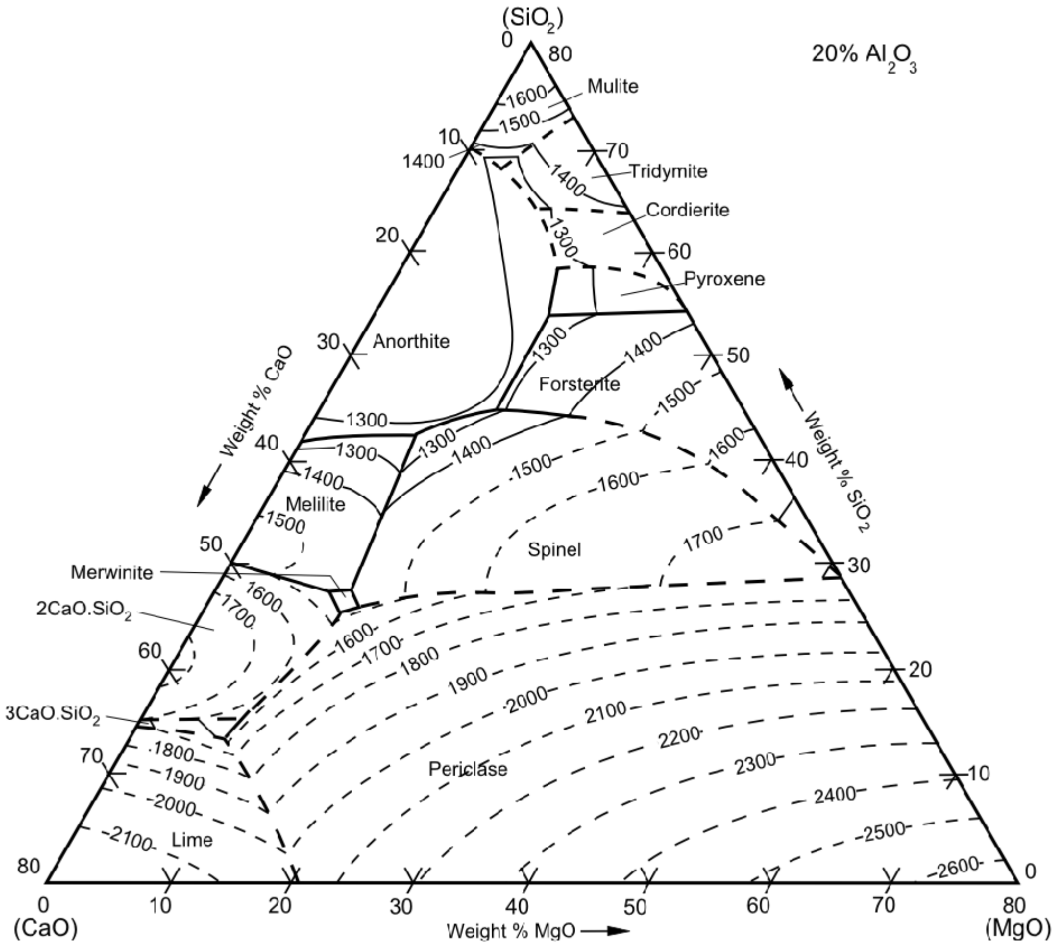

Figure 1. CaO-MgO-SiO_2 pseudo-ternary phase diagram depicting *liquidus* surfaces of system C-M-S-A at 20%Al_2O_3.[7]

It can be seen that are a series of dotted lines in a liquid surfaces of the diagram, showing some data inconsistency.

Gran, Wang and Sichen[6] make considerations about papers used for construction of C-M-S-A diagrams presented in Slag Atlas. Authors describing a lack of experimental data for composition in highest basicities, a lot of dotted lines and disagreement in relation of isotherms location in some areas.

Consequently, the objectives of this work are: (i) to perform a thermodynamic study of the phases at equilibrium at a high basicity value; and (ii) to evaluate the slag viscosity (from literature data and *via* thermodynamic software) as a function of the slag composition, establishing therefore a critical analysis with the published data.

As a reference, a line of binary basicity, B_2, equal to 2 (used later on) in Figure 1, connects the composition point 53.33 wt.%CaO (26.67 wt.%SiO_2) and 100 wt.%MgO.

2 MATERIALS AND METHODOLOGY

The basis for this work is the quinary system Ca-Mg-Si-Al-O. As is tradition, because of the interest in the oxides, a pseudo-quaternary system is used with the following components: CaO-MgO-SiO_2-Al_2O_3. Because of the interest in maintaining fixed levels of Al_2O_3, the focused oxide systems shall become pseudo-ternary systems CaO-MgO-SiO_2 – much more easily visualized.

The thermodynamic study was performed with the help of the commercial software FactSage 6.3. A general description of the software and databases was carried out by Bale et al.,[8] as well as its current modifications.[9]
The following databases were used, described at this point according to the FactSage Database Documentation:[10]
The FToxid solution database (FToxid53Soln.sda) contains oxide solutions evaluated/optimized by the FACT group. The FToxid compound database (FToxid53Base.cdb) contains all stoichiometric solid and liquid oxide compounds evaluated/optimized by the FACT group to be thermodynamically consistent with the FToxid solution database. The FToxid databases contain data for pure oxides and oxide solutions of 20 elements (as well as for dilute solutions of S, SO_4, PO_4, H_2O/OH, CO_3, F, Cl, I, C, N and CN in the molten (Liquid, Slag) phase). The major oxide components are: Al_2O_3, CaO, FeO, Fe_2O_3, MgO and SiO_2.
The simulations based on computational thermodynamics were performed under the following conditions:

- wt.% CaO / wt.%SiO_2 ratio (binary basicity, B_2) kept constant (generally B_2=2) for any MgO content;
- fixed amount of 20 wt.% Al_2O_3 for all simulations;
- constant total mass of 100 g;
- constant temperature of 1,600ºC.

Next, an example of slag composition computation for entering input data for the simulation:

Considering 20 wt.%Al_2O_3 and variable amount of MgO
CaO + SiO_2 + MgO = 80   with   CaO / SiO_2 = 2

Results in the following equations:
CaO = 53.33 – 0.66 (MgO)
SiO_2 = 26.66 – 0.33 (MgO)
Al_2O_3 = 20

3 RESULTS AND DISCUSSIONS

3.1 Phases and Phase Diagrams

Some cross sections of the C-S-M-A oxide system (CaO-rich corner) at three Al_2O_3 levels (0 wt.%Al_2O_3, 10 wt.%Al_2O_3 and 20 wt.%Al_2O_3) were built with the help of FactSage 'Phase Diagram' module.
The section at 0 wt.%Al_2O_3 (Figure 2), represents in fact the pseudo-ternary system CaO-MgO-SiO_2. In this diagram phase names are indicated only in areas containing the Liquid (slag) phase. For this section, the *tie lines* are all within the plane and can be presented simultaneously.
The field with Periclase saturation in slag is visible at the top-right portion of the figure. The double MgO-C_2S saturation field, to its left, has a wider MgO range; for low to moderate MgO amounts, however, saturation takes place only with 2CaO·SiO_2. For MgO concentration bellow ~5 wt.% the 'oxide phase' is composed entirely of solid phases. This is also the case with the whole left portion of the diagram. Noteworthy, the C_2S phase is represented by a solid *solution* (dissolving up to ~5 wt.% MgO) in the Fact-oxide database.
At B_2 = 2 (33.33 wt.%SiO_2), only *mono* and *double*-saturated slag can be present in the equilibrium state.

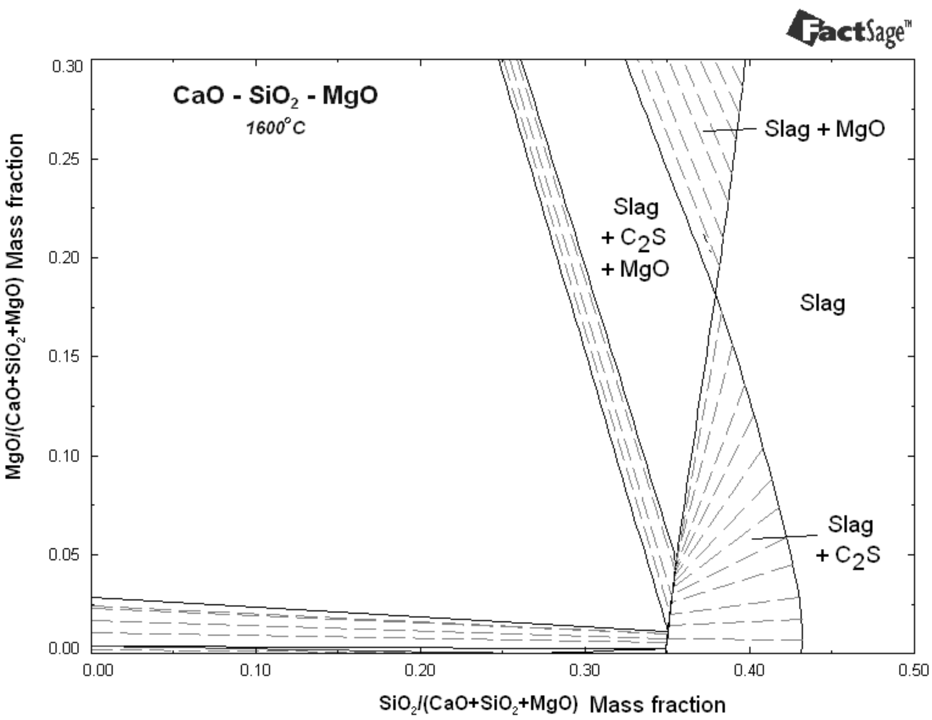

Figure 2. CaO-MgO-SiO$_2$ pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 0%Al$_2$O$_3$) showing the Liquid phase (Slag) and Slag-containing areas; B$_2$ = 2 at 33.33 wt.%SiO$_2$.

At 10 wt.%Al$_2$O$_3$ level (Figure 3), no tie lines are within the plane and consequently cannot be represented in the diagram. Apart from that, the same phase distribution of the previous case can be seen here. B$_2$ = 2 is now at 30 wt.%SiO$_2$ and there will always be some liquid Slag amount in the equilibrium state, for the MgO range in focus.

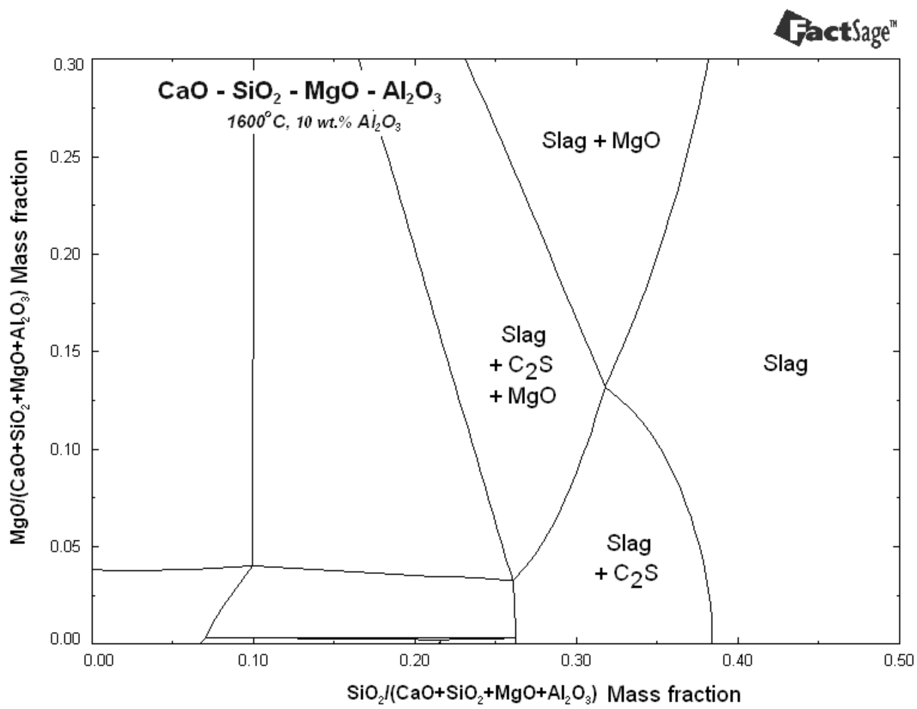

Figure 3. CaO-MgO-SiO$_2$ pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 10%Al$_2$O$_3$) showing the Liquid phase (Slag) and Slag-containing areas; B$_2$ = 2 at 30 wt.%SiO$_2$.

At 20 wt.%Al_2O_3 level (Figure 4), the Slag phase has spread to all covered fields of the pseudo-ternary (CaO-rich corner) system C-M-S. Again, for this section, no tie lines are within the plane and cannot be represented in the diagram.
Comparing the line for the 1,600ºC isotherm in Figure 1 (C-M-S-A system at 20 wt.%Al_2O_3) with that of the single Slag (Liquid) phase field boundary of Figure 4, the same general shape is clearly visible.
Concerning phases, Periclase saturation field is again located at the top-right portion of the figure however there are some fields where the Slag is saturated with CaO, C_3S (Hatrurite) or, with both.
From now on, all analyses will focus on this 20 wt.%Al_2O_3 cross section.

3.2 Phase Amount for Binary Basicity Equal to 2

When B_2 = 2, at 20 wt.%Al_2O_3, for MgO ranging from ~5 to ~10 wt.%MgO, the Slag is fully composed by the Liquid phase. Outside this range, C_2S or Periclase precipitation will occur (Figure 5). Moreover, as is easy to see, the Liquid phase amount is at least 75% of the system mass for any chosen composition.

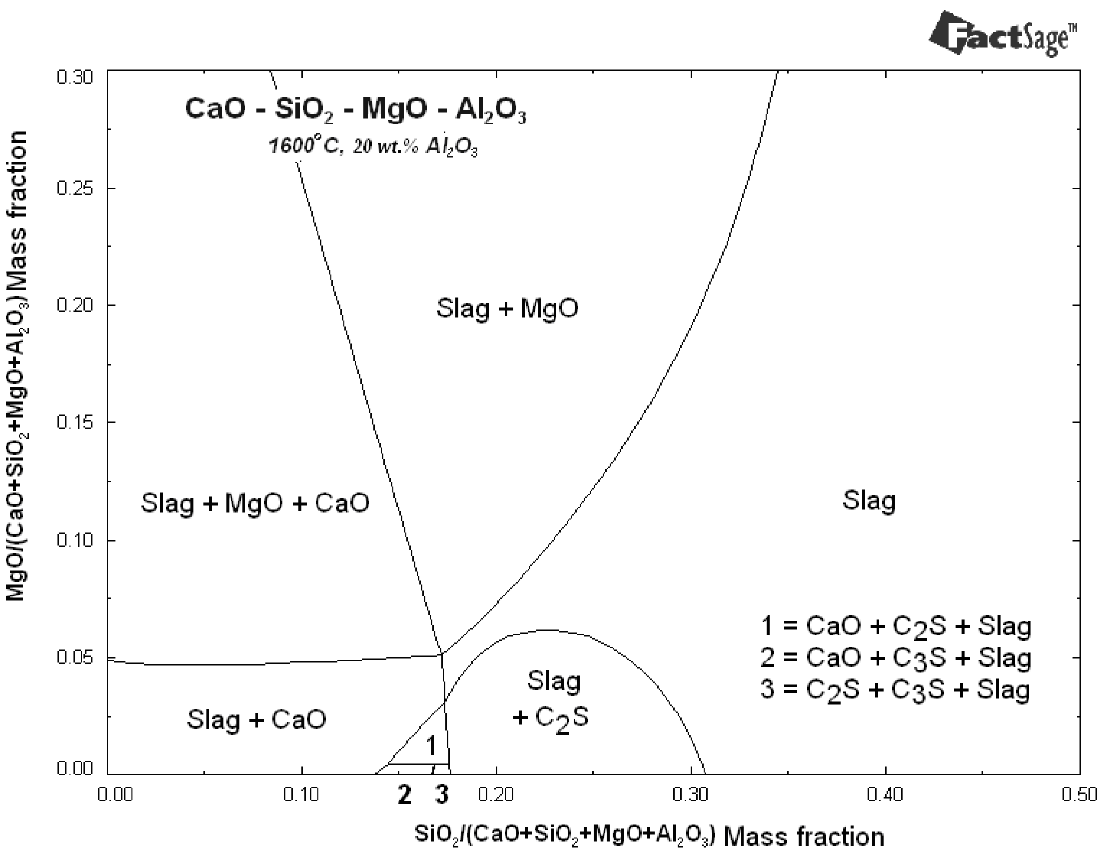

Figure 4. CaO-MgO-SiO_2 pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 20%Al_2O_3) showing the Liquid phase (Slag) and Slag-containing areas; B_2 = 2 at 26.67 wt.%SiO_2.

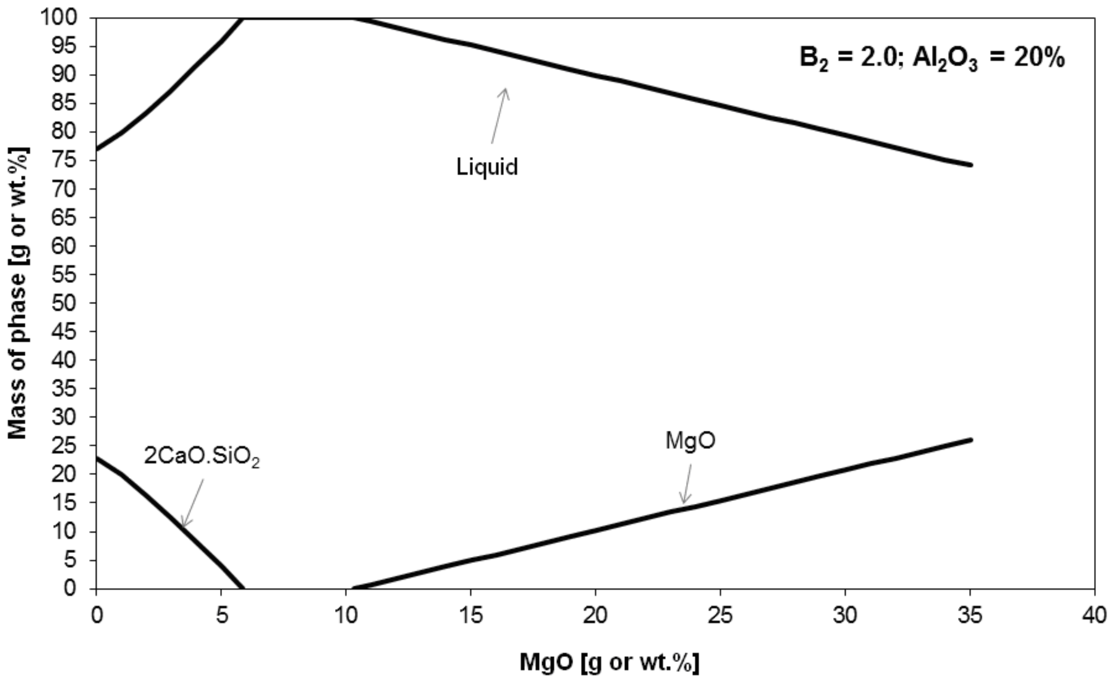

Figure 5. Mass of phases in the equilibrium state for $\%CaO/SiO_2$ = 2, Al_2O_3 = 20 wt.% and variable amount of MgO (0 to 35 wt.%); FactSage.

With reference to the diagram of Figure 1, a comparison can be made with Figure 5 in respect to the composition. Although the general behavior observed in both diagrams is the same, comparing in detail the minimum MgO content required to form 100% Liquid phase and for Periclase saturation, (i) from Slag Atlas diagram (Figure 1); and (ii) from the thermodynamic simulation *via* FactSage (Figure 5), some small differences can be cited (Table 1).

Table 1. Comparison between Slag Atlas data (C-M-S-A system at 20 wt.%A) and simulation results (FactSage)

	Slag Atlas[7] **C-M-S phase diagram (20%A)**	**FactSage**
100% Liquid	8.0 wt.%MgO	5.9 wt.%MgO
Periclase saturation	12.7 wt.%MgO	10.3 wt.%MgO
Δ MgO	4.7%	4.4%

It can be noted by this comparison that regarding FactSage data the content of MgO for the cited targets is somewhat lower than that from Slag Atlas diagram. However, the interval between the two points, namely the ‘width’ of the Liquid phase in this region is similar for both sources.

3.3 Analysis as a Function of Three B_2 Basicities

Table 2 compares the MgO saturation values for Periclase precipitation as a function of basicity at 20 wt.%Al_2O_3 found with FactSage *versus* Slag Atlas data. As it can be seen, a small difference between the two sources is noticeable, the major is located at B_2 = 2.5.

Table 2. MgO for Periclase saturation for several basicities B_2 at 20 wt.%Al_2O_3; all composition figures given in wt.%

	wt.%MgO for Periclase precipitation	
B_2 = wt.%CaO/wt.%SiO_2	Slag Atlas[7]	FactSage
1.5	16.7	13.9
2.0	12.7	10.3
2.5	10.8	6.0

3.4 Pure Liquid Slag Viscosity

The viscosity of the pure Liquid slag was calculated *via* FactSage (using *melts* database). For the composition of Periclase saturation: 10.3 wt.%MgO; 20 wt.%Al_2O_3; 46.5 wt.%CaO e 23.3 wt.%SiO_2, the viscosity value obtained for 1,600ºC was 0.931 Poise.
The Slag Atlas does not give viscosity values for slags of this composition. Still five partial pseudo-ternary diagrams are given which show composition ranges in close proximity; all for the temperature of 1,500ºC though. They consist of cross-sections of the C-M-S-A system at 35 wt.%SiO_2, 40 wt.%SiO_2, 45 wt.%SiO_2 and 50 wt.%SiO_2 and also at 10 wt.%MgO.
In order to verify the FactSage model against the Slag Atlas experimental and modeled viscosity data, the viscosity for a slag with 10 wt.%MgO; 20 wt.%Al_2O_3; 30 wt.%CaO e 40 wt.%SiO_2, was calculated using FactSage, which resulted in 4.917 Poise at 1,500ºC. For this composition, the 40 wt.%SiO_2 cross-section from Slag Atlas reads 6 Poise; on the other hand, the 10 wt.%MgO shows 14-16 Poise. When rising the temperature to 1,600ºC, FactSage model determines 2.752 Poise.

3.5 Liquid-solid Slag Viscosity

The FactSage model is able to compute the viscosity of the single-phase Liquid only. Nevertheless, the software is capable of displaying the *solid fraction* within the state of equilibrium.
No word however is said about the way in which the *second* phase is present at equilibrium: in the form of precipitates forming an emulsion or concretions adhered on the refractory, or a mixture of both.
Pretorius e Carlisle[11] provided the concept of *effective viscosity*, which was defined to relate viscosity to the amount of second phase particles, as follows:

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

Where:

- η_e effective viscosity of the Slag;
- η viscosity of the molten (Liquid) Slag;
- Θ fraction of precipitated solid phases.

The Figure 6 shows the solid fraction calculated for the slag shown in Figure 5: B_2 = 2.0; Al_2O_3 = 20 wt.% and MgO content from 0 to 35 wt.%; T = 1,600ºC.
With the calculated solid fraction, bearing in mind that the solids are making an emulsion with the Liquid slag, the effective viscosity was determined for the following

Liquid Slag composition: 10.3%MgO; 20%Al_2O_3; 46.5%CaO e 23.3%SiO_2 at 1,600ºC, using Equation 1; the results can be seen in Figure 7.
One can observe that in the presence of 25% solid fraction in the slag, the viscosity is almost 2.5 times greater than the viscosity of the simple Liquid slag.

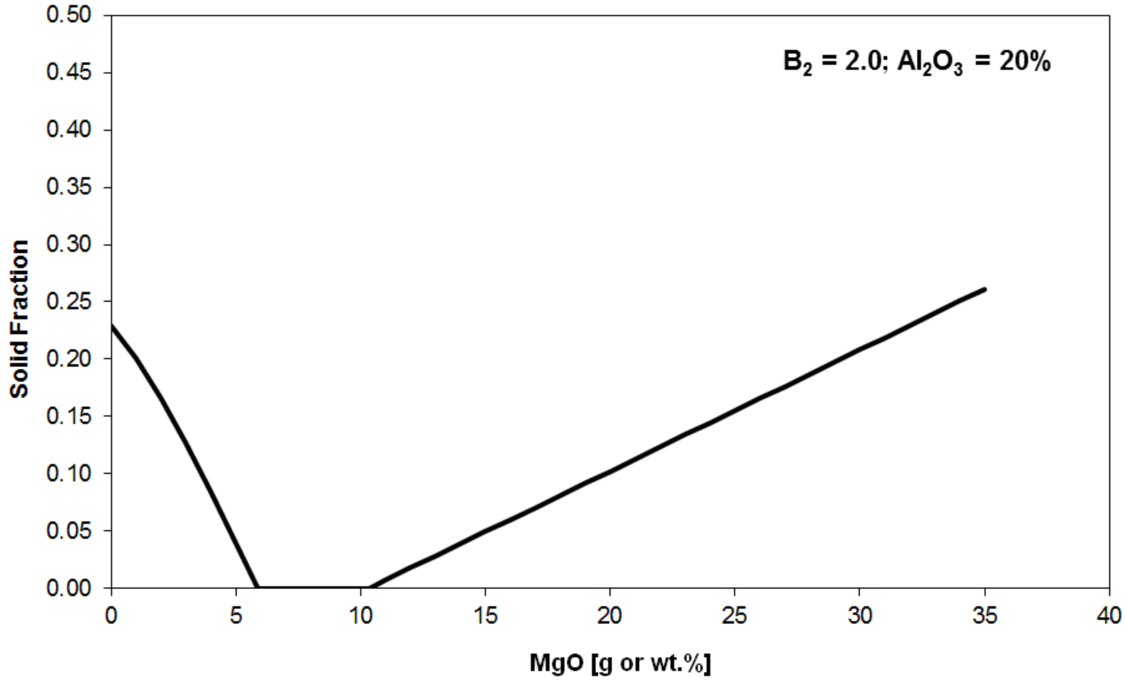

Figure 6. Solid fraction for Slags in Figure 5 at 1,600ºC.

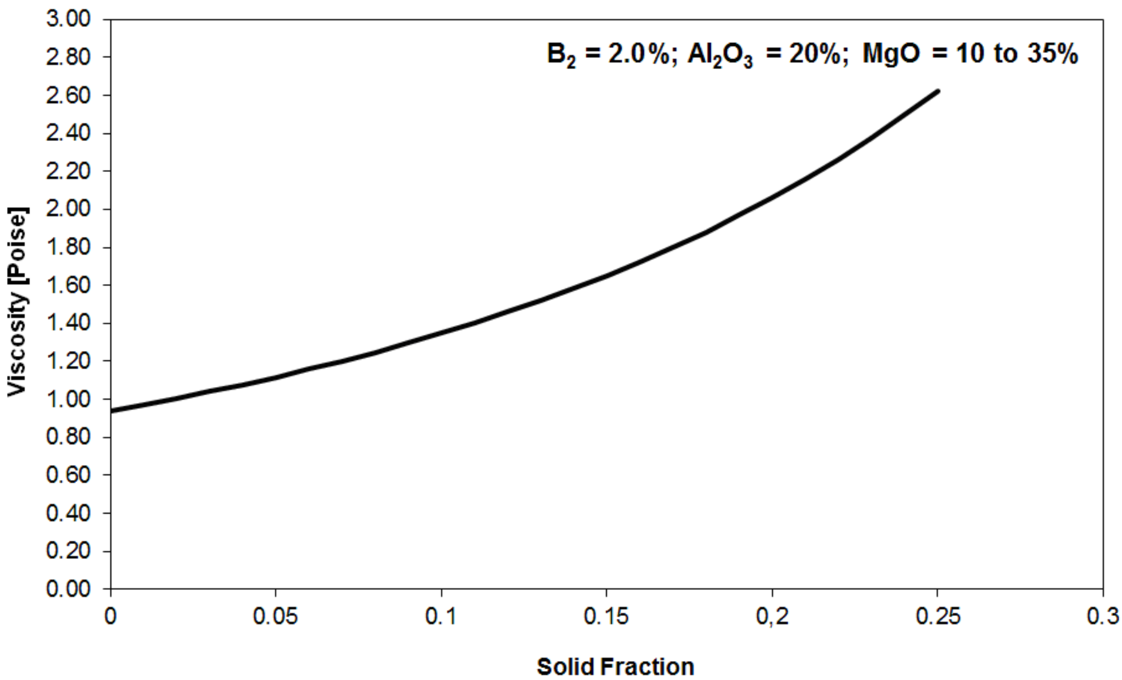

Figure 7. Effective viscosity determined for the Liquid Slag: 10.3%MgO; 20%Al_2O_3; 46.5%CaO e 23.3%SiO_2 at 1,600ºC.

4 CONCLUSIONS

Some conclusions that can be drawn from this work will be described next.

Comparing the line for the 1,600ºC isotherm in Figure 1 (C-M-S-A system at 20 wt.%Al_2O_3) with that of the single Slag (Liquid) phase field boundary of Figure 4, it can be said that there is an acceptable similarity between them. However, it can be noted also that, regarding FactSage data, the content of MgO for some Periclase saturation points is somewhat lower than that from Slag Atlas diagram.

The Slag Atlas does not give viscosity values for slags of the studied compositions and shows some inconsistencies within diagrams depicting the same composition for the C-M-S-A system. Nevertheless, when the same composition and temperature was used, the value determined by the F model gave results lower than those described in the reference work.

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