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

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Abstract

Slag System $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$ - although plays an important role during the secondary refining of steel, such as adjustment of the sulfur level, capture of non-metallic inclusions and refractory protection - still has regions with little data or uncertain data in terms of phases present at equilibrium and isothermal profile heights. It is also important to know the composition and proportion of liquid and solids formed, considering, for example, the basicity ($\%CaO/\%SiO_2$) and the MgO content. With respect to physical properties the slag viscosity stands as the most important. It influences both the reactions between metal / slag as well as slag / refractory interaction. This work, done with the help of computational thermodynamics, is continuing to study the phases present in certain compositions of the system $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$, and to evaluate the viscosity values of this system, calculated via computational thermodynamics, with those of literature.

Key words: Slag; CMSA system; Computational thermodynamics.

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1 INTRODUCTION

Knowledge of the fundamentals of steel production is very important for companies to keep their position – as the market becomes increasingly competitive.

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 steel impurities;
- 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 particles 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 a fixed 20 wt.% Al_2O_3 content from this publication.

A series of dotted lines in the liquid surfaces of this diagram denote a quantity of data uncertainties.

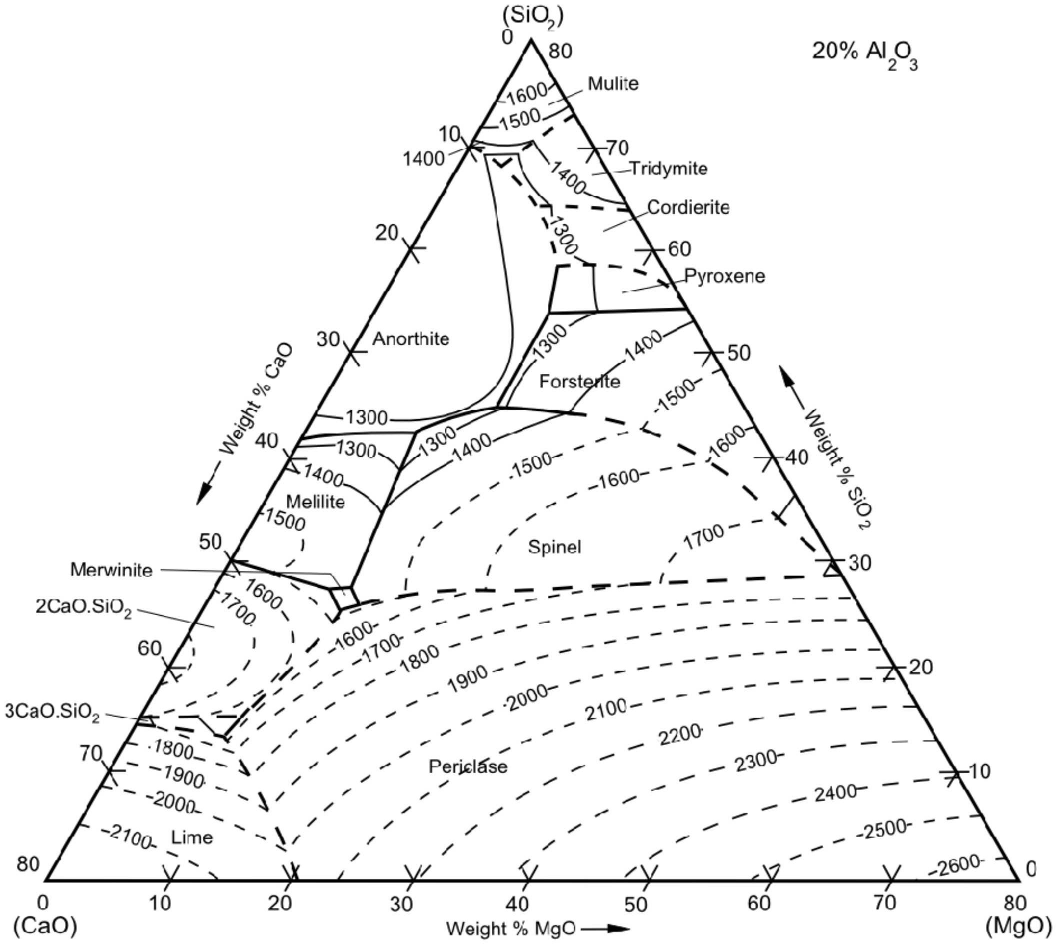

Figure 1. CaO-MgO-SiO_2 pseudo-ternary phase diagram depicting *liquidus* surfaces of system C-M-S-A at 20 wt.% Al_2O_3.(7)

Gran, Wang e Sichen(6) make considerations about papers used for construction of C-M-S-A diagrams presented in Slag Atlas. These authors describe lack of experimental data for composition in highest basicities, too much dotted lines (uncertainties) and disagreement in relation to location of isotherms in some areas of the diagram.

Consequently, the objectives of this work are: (1) to perform a thermodynamic study of the phases at equilibrium at a high basicity value (binary basicity, B_2, equal to 2), and (2) evaluate the slag viscosity values (checking results obtained *via* thermodynamic software with data coming from the literature) as a function of the slag composition and temperature, establishing therefore a critical analysis.

As a reference, a line of binary basicity, B_2, equal to 2 (used later on) would connect (Figure 1) the composition points 53.33 wt.% CaO (26.67 wt.% SiO_2) – at the axis CaO-SiO_2 – with point 100 wt.% MgO.

2 MATERIALS AND METHODOLOGY

The basis for this work is the quinary system Ca-Mg-Si-Al-O. As is tradition, in this type of study, a 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 a pseudo-ternary system CaO-MgO-SiO_2 – much more easily visualized.

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The thermodynamic approach was executed 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 thermodynamic simulations based on computational were performed under the following conditions:

- wt.% CaO / wt.% SiO_2 mass 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;
- temperatures of 1,500°C; 1,550°C; 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:

$$\text{wt.\% CaO} + \text{wt.\% SiO}_2 + \text{wt.\% MgO} = 80$$
with
$$\text{wt.\% CaO} / \text{wt.\% SiO}_2 = 2$$

It results in the following equations:

$\text{wt.\% CaO} = 53.33 - 0.66\ (\text{wt.\% MgO})$

$\text{wt.\% SiO}_2 = 26.66 - 0.33\ (\text{wt.\% MgO})$

$\text{wt.\% Al}_2\text{O}_3 = 20$

3 RESULTS AND DISCUSSIONS

3.1 Phases and Phase Diagrams

Some cross sections of the quaternary C-M-S-A oxide system (CaO-rich corner), at fixed 20 wt.% Al_2O_3 composition (Figure 2), were drawn with the help of FactSage ‘Phase Diagram’ module in order to show the phases which are stable in the equilibrium state as a function of composition.

Three temperatures of interest were used in these cross sections: 1,500°C, 1,550°C and 1,600°C.

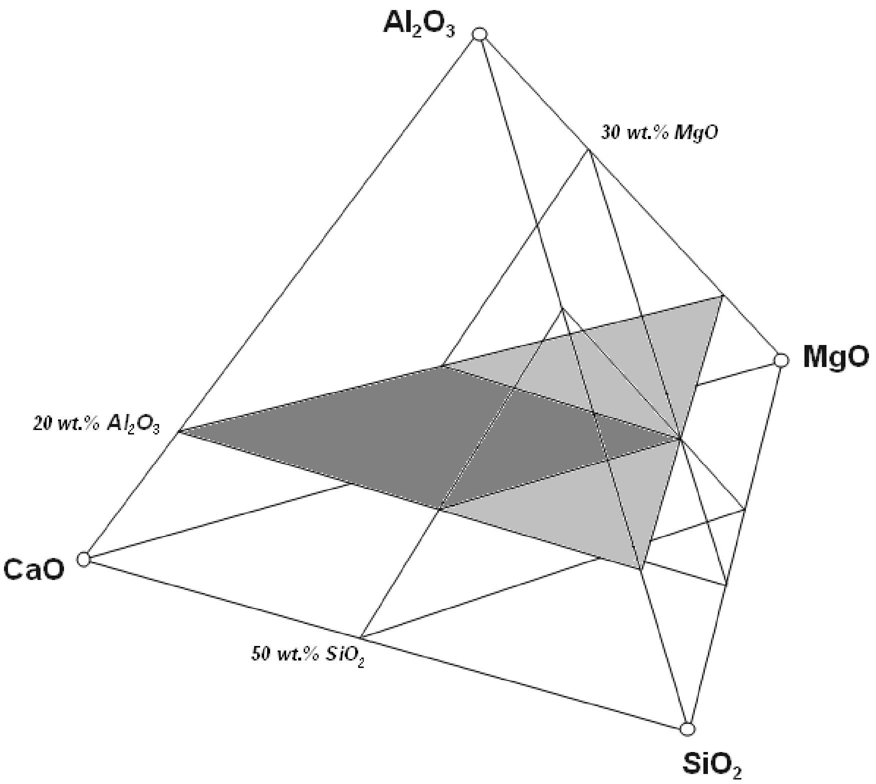

Figure 2. Schematic diagram of the quaternary system C-M-S-A indicating the *plane* at 20 wt.% Al_2O_3 (light gray) and the area used to plot the phase equilibrium diagrams (dark gray) which illustrate this work (*not to scale*).

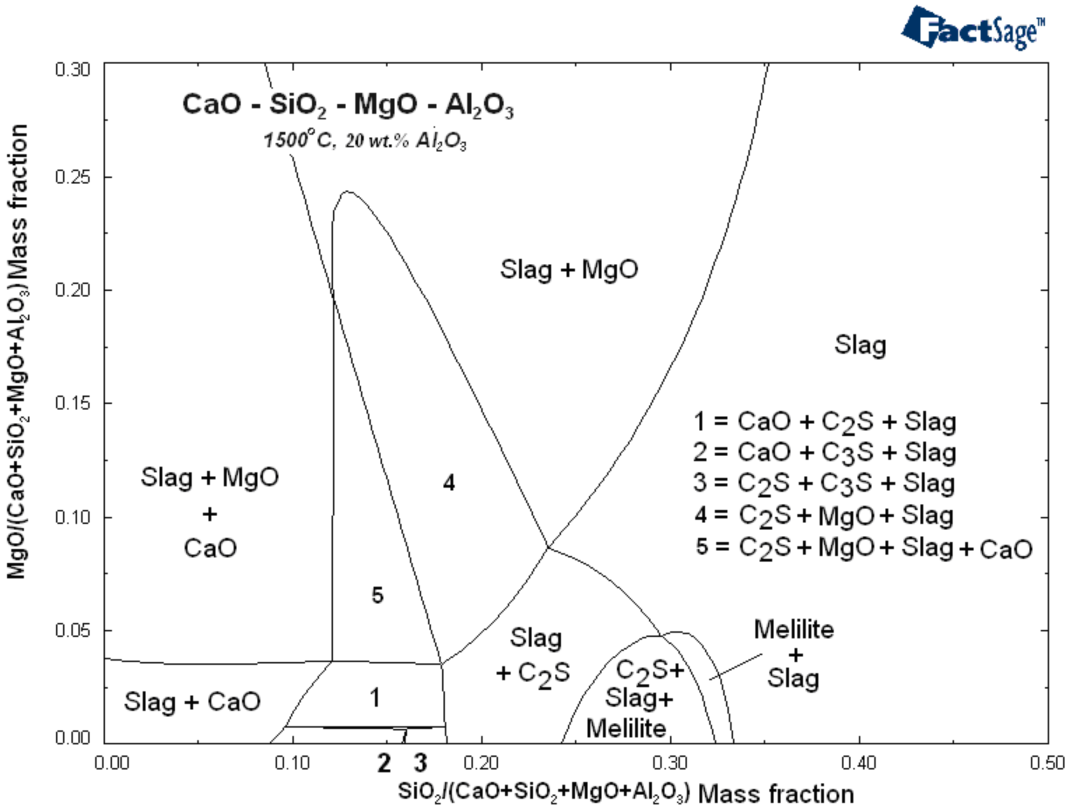

Figure 3. CaO-MgO-SiO_2 pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 20 wt.% Al_2O_3) at the temperature of 1,500ºC.

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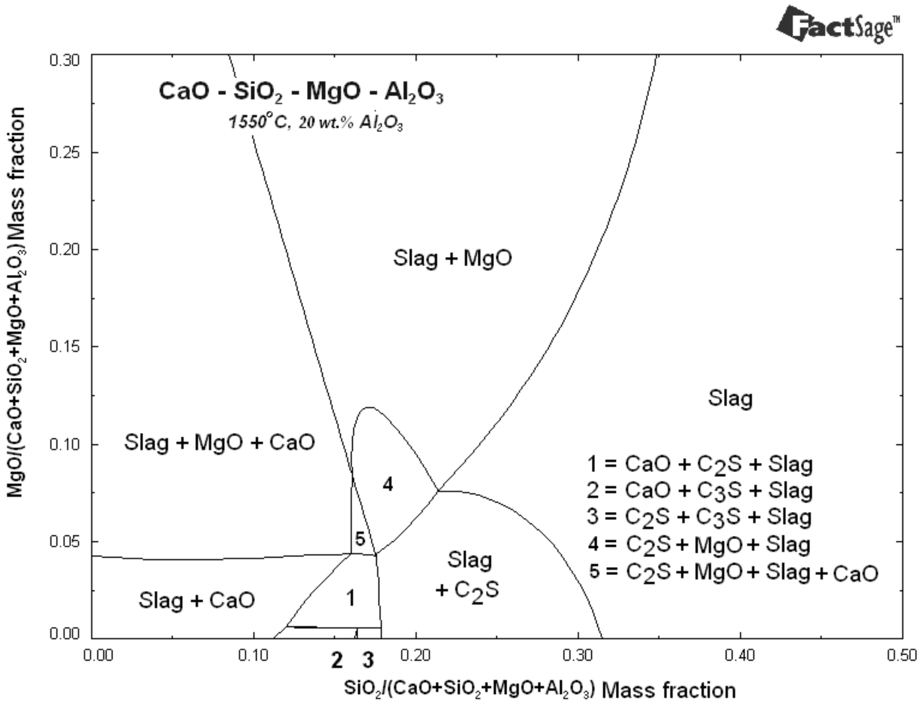

Figure 4. CaO-MgO-SiO$_2$ pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 20 wt.% Al$_2$O$_3$) at the temperature of 1,550ºC.

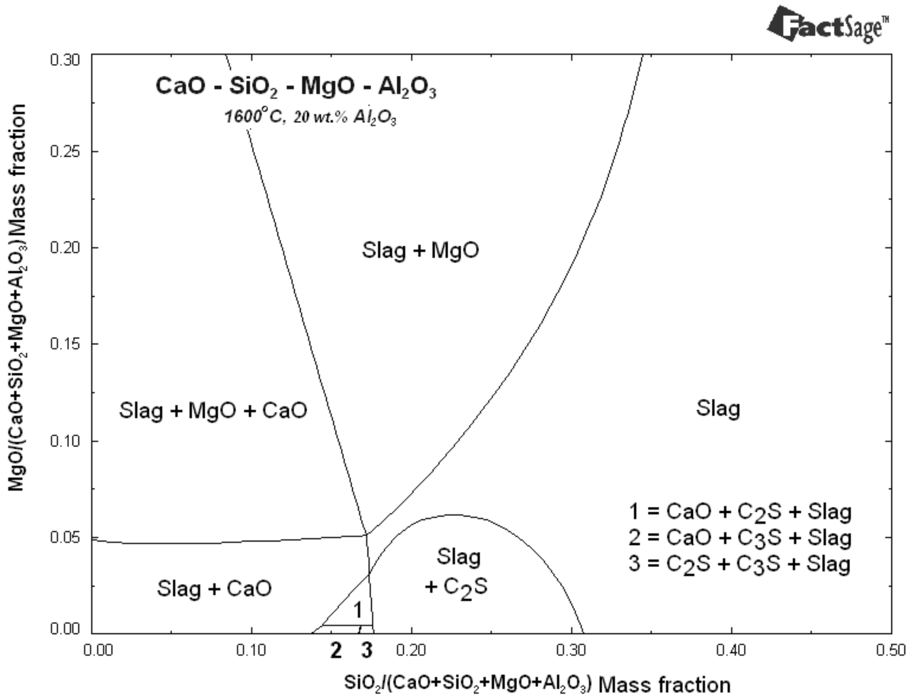

Figure 5. CaO-MgO-SiO$_2$ pseudo-ternary phase diagram depicting the CaO-rich corner (C-M-S-A system at 20 wt.% Al$_2$O$_3$) at the temperature of 1,600ºC.

The section at 1,500ºC (Figure 3) represents the most complex of them in terms of number of phases; in equilibrium, the Liquid (slag) phase takes part in all of the fields.

The field with Periclase saturation in slag is visible at the top-center portion of the figure; other binary phase fields are: Liquid (slag) + C_2S ($C_2S = 2CaO{\cdot}SiO_2$) and Melilite + Liquid (slag).

Between them, there are triple-saturated fields: MgO-C_2S-Slag and C_2S-Slag-Melilite for low to moderate MgO amounts; the fact that C_2S-phase is represented in the Fact-oxide database by a solid *solution* (dissolving up to ~5 wt.% MgO), instead of being a stoichiometric compound, is noteworthy.

At 1,550ºC (Figure 4), the phase diagram is much simpler; the Melilite phase is now of minor importance and can be disregarded.

At 1,600ºC (Figure 5), the phase diagram is the simplest; the influence of dicalcium silicate is now restricted to the neighborhood of its position in the CaO-SiO_2 axis and the area of phase field pure Liquid (slag) attains its maximum.

The phases Spinel ($MgO{\cdot}Al_2O_3$) and Forsterite ($2MgO{\cdot}SiO_2$) – because of their position in the C-M-S-A oxide system – were intentionally left out in this preliminary analysis. Their greatest influence would be on the cross section at the temperature of 1,500ºC.

3.2 Phase Amount for Binary Basicity B_2 Equal to 2

The same line of *binary basicity*, B_2, equal to 2 referred before would now connect (in the pseudo-ternary cross sections – Figures 3 to 5) the composition point 26.67 wt.% SiO_2 (at 0 wt.% MgO) with the composition point 16.67 wt.% SiO_2 (at 30 wt.% MgO). This unusual inclination is due to the false *right angle* between the composition axes SiO_2 and MgO.

For this line, the amount of phases was determined (from 0 up to 35 wt.% MgO) for temperatures: 1,500°C, 1,550°C and 1,600ºC, and can be seen in Figures 6 to 8.

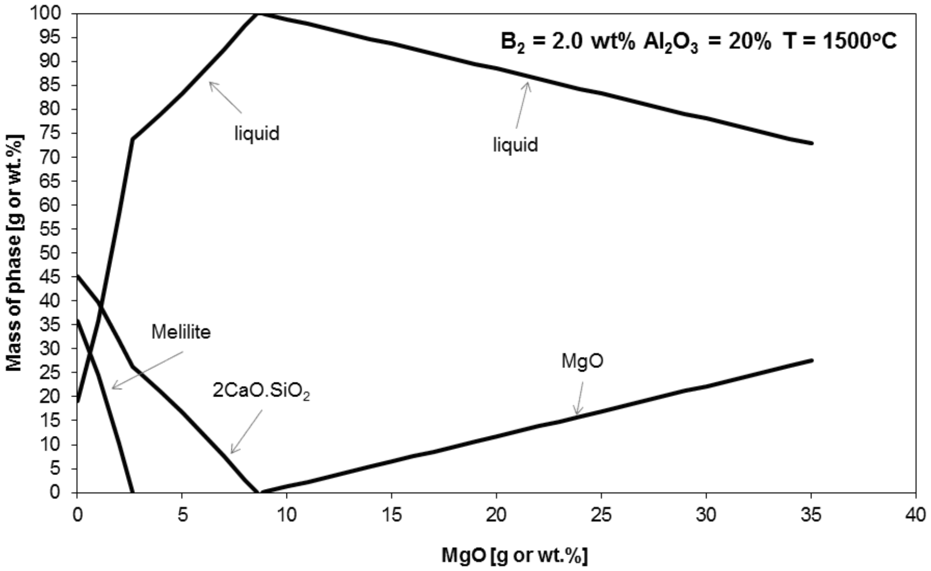

Figure 6. Mass of phases in the equilibrium state for wt.%CaO/wt.%SiO_2 = 2, Al_2O_3 = 20 wt.% and variable amount of MgO (0 to 35 wt.%); T = 1,500°C; FactSage.

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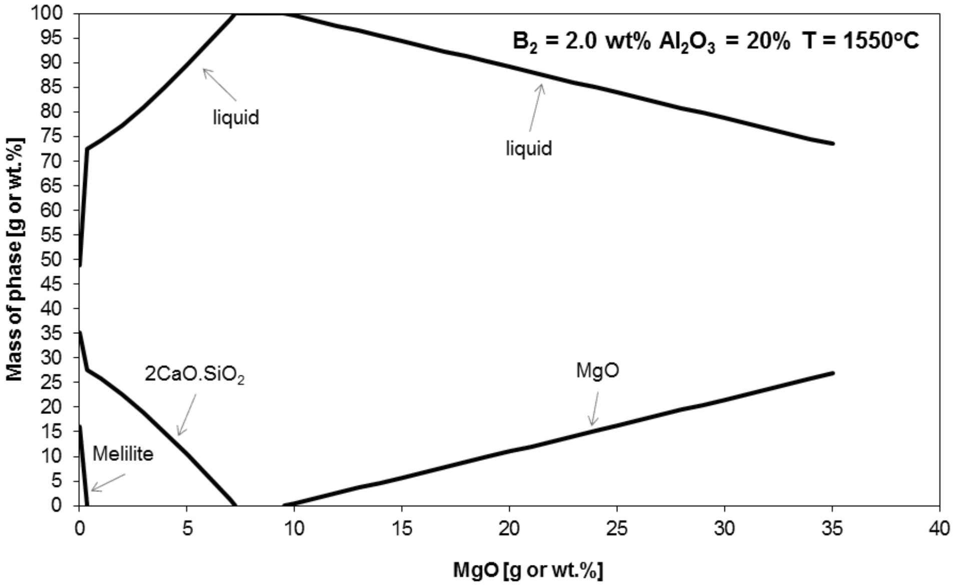

Figure 7. Mass of phases in the equilibrium state for wt.%CaO/wt.%SiO$_2$ = 2, Al$_2$O$_3$ = 20 wt.% and variable amount of MgO (0 to 35 wt.%); T = 1,550^{o}C; FactSage.

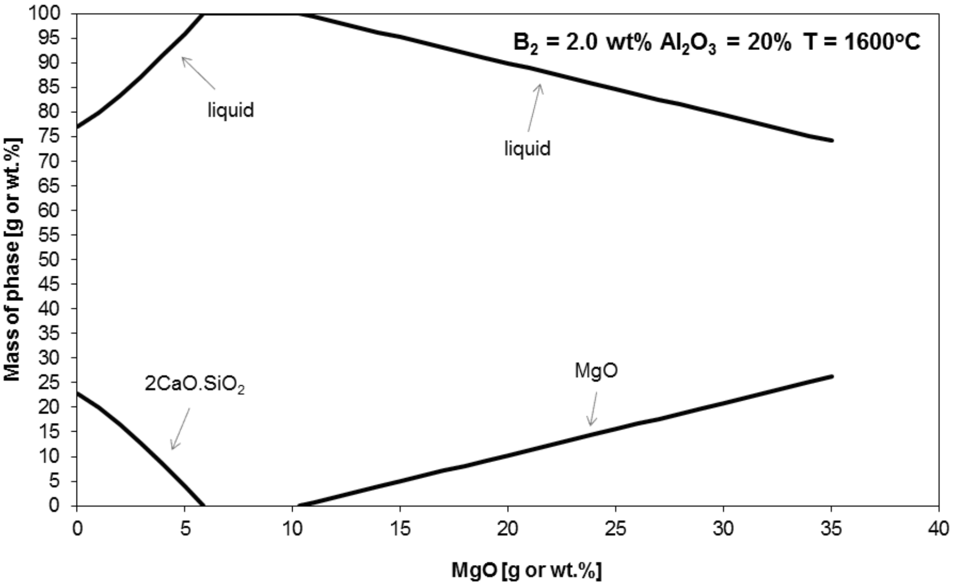

Figure 8. Mass of phases in the equilibrium state for wt.%CaO/wt.%SiO$_2$ = 2, Al$_2$O$_3$ = 20 wt.% and variable amount of MgO (0 to 35 wt.%); T = 1,600^{o}C; FactSage.

With reference to the diagram of Figure 1, a comparison can be made with Figures 6 to 8 in respect to the composition. Although the general behavior observed in both sources is the same, comparing in detail (i) the minimum MgO content required to form 100% Liquid phase and (ii) for Periclase saturation, from Slag Atlas diagram (Figure 1), and from the thermodynamic simulation *via* FactSage (Figures 6 to 8), some small differences can be cited; they are displayed in Table 1.

Table 1. Comparison of MgO wt.% values between Slag Atlas data (C-M-S-A system at 20 wt.% Al_2O_3) and simulation results (FactSage) to wt.%CaO/wt.%SiO_2 = 2.

	Slag Atlas [7] C-M-S phase diagram (20 wt.% Al_2O_3)			**FactSage**		
	1,500°C	1,550°C	1,600°C	1,500°C	1,550°C	1,600°C
100% Liquid	*	9.5	8.0	8.6	7.3	5.9
Periclase saturation	*	11.9	12.7	8.8	9.5	10.3
Δ wt.% MgO	-	2.4	4.7	0.2	2.2	4.4

** B_2 isobasicity line equal to 2 does not cross the Liquid slag phase field.*

It can be noticed by this comparison that regarding FactSage data the content of MgO for the two 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. As expected, the extension of liquid phase decreases with a lowering in the temperature.

3.3 Pure Liquid Slag Viscosity

The viscosity of the pure Liquid slag was calculated *via* FactSage (using *melts* database). The description of the models used in FactSage can be seen in.(11,12)

The composition for the determination of viscosity at the three temperatures studied (1,500°C; 1,550°C and 1,600°C) was: 8.7 wt.% MgO; 20 wt.% Al_2O_3; 47.5 wt.% CaO e 23.8 wt.% SiO_2. This composition was chosen with basis on the values given in Table 1 (with 8.7 wt.% MgO there is only Liquid at all three temperatures) and for the reason it shows binary basicity equal to 2. The viscosity values obtained are 1.6, 1.2 and 1.0 Poise for 1,500°C, 1,550°C and 1,600ºC, respectively.

The Slag Atlas does not give viscosity values for a slag of this composition. Still five partial pseudo-ternary diagrams are given which show composition ranges in close proximity; all for the temperature of 1500 ºC though. They consist of cross-sections of the C-M-S-A system at 35, 40, 45 and 50 wt.% SiO_2 and also at 10 wt.% MgO.

Table 2. Viscosity (Poise) values comparison between Slag Atlas data and simulation results (FactSage), (C-M-S-A system at 10 wt.% MgO and 20 wt.% Al_2O_3, variable 35-50 wt.% SiO_2).

	wt.% SiO_2				
	35	40	45	50	T [ºC]
Slag Atlas	**4**	**7**	**11**	**22**	1,500
FactSage	**3.1**	**4.9**	**8.9**	**19.0**	1,500
	2.4	**3.6**	**6.4**	**13.2**	1,550
	1.8	**2.8**	**4.7**	**9.3**	1,600

In order to verify the results from FactSage model against the Slag Atlas experimental and modeled viscosity data, the viscosity for a slag composition of 10 wt.% MgO; 20 wt.% Al_2O_3; 30-50 wt.% SiO_2, was calculated using FactSage. For the temperature of 1500 ºC they show results quite comparable with those in Slag Atlas (Table 2). Viscosity values for the other temperatures are given in spite of the lack of data from Slag Atlas.

3.4 Solid-Liquid Slag Viscosity

Most slag models are conceived for fully molten slags since their theoretical basis is not applicable to solid–liquid mixtures. The presence of solid phases in the slag will affect viscosity in two ways. First, the components which form the solids are no longer part of the liquid phase. This changes the liquid phase composition and hence its viscosity. Second, the interaction of solid particles with each other and the liquid phase will affect the bulk slag viscosity. This effect will vary with the size, shape, orientation and mass fraction of the particles.(13)

Pretorius e Carlisle(14) provided the concept of *effective viscosity*, which was defined to relate viscosity to the amount of second phase particles. It is based of Roscoe-Einstein model, as follows:

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

Where:

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

The Figure 9 shows the solid fraction calculated for the slags shown in Figures 6 to 8: $B_2 = 2.0$; $Al_2O_3 = 20$ wt.% and MgO content from 0 to 35 wt.%.

With the calculated solid fraction, bearing in mind that the solids are making an emulsion with the Liquid slag, the effective viscosity can be determined.

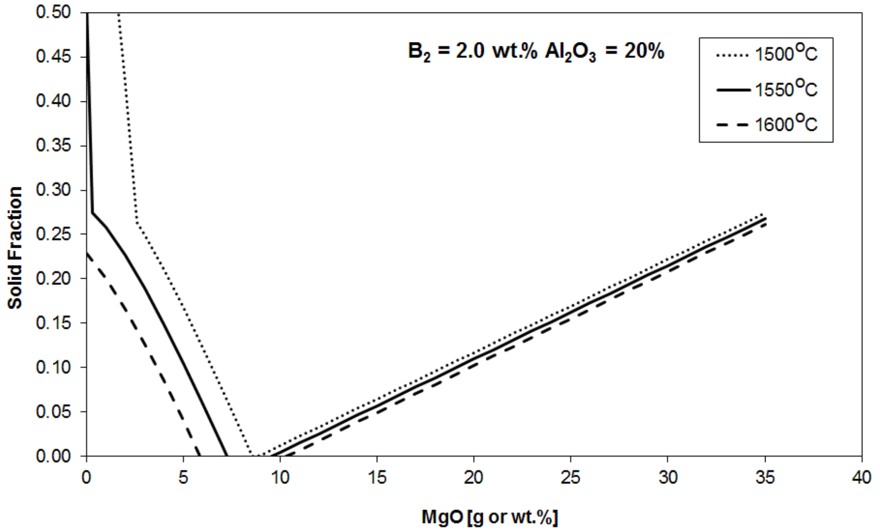

Figure 9. Solid fraction for slags in Figures 6 to 8 at 1,500°C, 1,550°C and 1,600ºC.

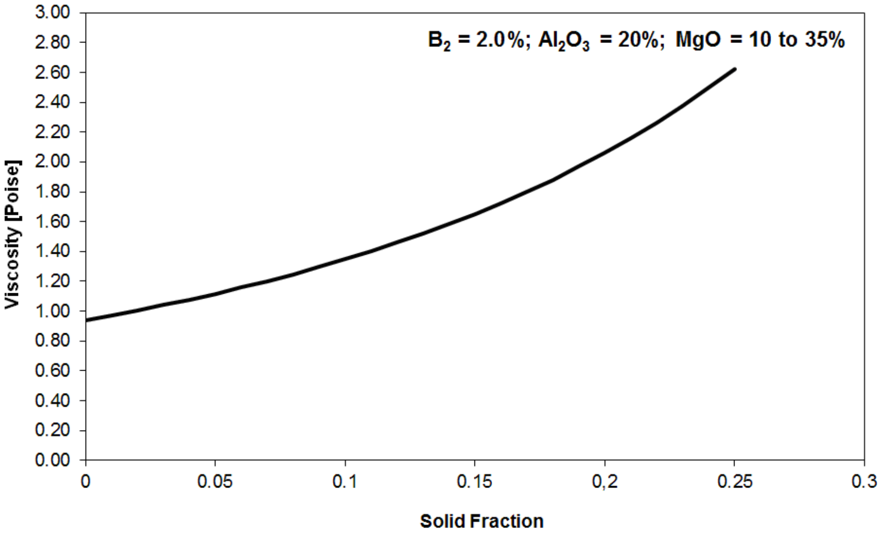

Figure 10. Effective viscosity determined for the Liquid Slag: 10.3 wt.% MgO; 20 wt.% Al_2O_3; 46.5 wt.% CaO e 23.3 wt.% SiO_2 at 1,600ºC.

The composition of the pure liquid in the beginning of Periclase saturation at the temperature of 1,600ºC: 10.3 wt.% MgO; 20 wt.% Al_2O_3; 46.5 wt.% CaO and 23.3 wt.% SiO_2 (B_2 = 2) was used as a basis. The viscosity value for this slag, obtained at 1600ºC, was 0.931 Poise. Then, the effective viscosity could be determined for this Liquid slag using Equation 1. The results can be seen in Figure 10.

One can observe that in the presence of 25% solid fraction in the slag, the resulting viscosity is almost 2.5 times greater than the viscosity of the simple Liquid slag.

4 CONCLUSIONS

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

Comparing the line for the 1600 ºC isotherm in Figure 1 (C-M-S-A system at 20 wt.% Al_2O_3) with that of corresponding phase diagram from FactSage, it can be said that there is an acceptable similarity between them. However, it can be noted also that MgO content for some Periclase saturation points determined with the help of FactSage software, in comparison with Slag Atlas data, are somewhat smaller.

The Slag Atlas does not give viscosity values for slags of binary basicity equal to 2; nevertheless, for some compositions at 1,500ºC, it shows some consistencies with FactSage calculated values for the C-M-S-A system.

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