

ISO-VISCOSITY CURVES FOR CAO-SiO₂-AL₂O₃-MgO STEELMAKING SLAGS AT HIGH TEMPERATURE *

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Abstract

A minor change in the chemical composition and temperature affects the slag viscosity, which has a great extent of the physical properties in regarding refining slags. Optimizing those parameters may affect the steel cleanliness. The viscosity measurement process is considered expensive, so the cost-effectiveness does not favor the measures at high-temperatures. Alternatively, it is possible to apply mathematical models or thermodynamic softwares to obtain viscosities for a given range of chemical composition and temperature of slags. The present work contemplates a validation of the experimental data, collected in the literature, with a calculated data and proposes an accurate representation of iso-viscosity curves applied for secondary steelmaking slags, covering the composition ranges: 0–100 wt.% CaO, 0–80 wt.% SiO₂, 0–77 wt.% Al₂O₃ and 0–15 wt.% MgO (CSAM) system at 1500°C. The viscosity representation fields include fully liquid and a partially liquid slags in the CSAM system and the viscosities were calculated using the *FactSage* 7.2 (for Liquid Phase) and the Roscoe-Einstein equation (for Phase mixture) for a total of 5976 slags. The preliminary results indicated that there is a great convergence between the calculated and experimental viscosities data, promoting an efficient approximation of the iso-viscosity curves for the CSAM slag system in the high-temperatures.

Keywords: *Viscosity; Steelmaking slags; Computational thermodynamics; FactSage 7.2.*

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1 INTRODUCTION

The viscous behavior of slags is of great concern to understand its physical-chemical properties, such as: gas permeability, heat transfer, reduction of FeO, the rate of desulphurization, etc [1]. Hence it is an essential factor to maximize productivity and ensure optimum operations. For these reasons, for six decades the slag viscosities are measured not only for the theoretical research, but also for the industrial application [1-12].

The steelmaking slags conventionally contains CaO, SiO₂, Al₂O₃, MgO, and the slags viscosity changes in wide range depending on the temperature and composition. This quaternary system represents the oxides commonly employed for steel refining at the secondary metallurgy. In this case, these slags must be designed to present a maximum refining capacity. The viscosity directly affects the main refining reactions of steel by slag. Including the removal of impurities such as sulfur [13] and nonmetallic inclusions [14]. However, it is well known that high temperature viscosity measurement is time consuming and costly, thus it is cost-effective to predict the viscosity behavior applying models which enable calculation of viscosity according to melt compositions and temperature.

As known, steelmaking slags presents two-phase melt, Phase Mixture, in which it contains a liquid fraction and a solid fraction. In view of the difficulties in the measure of two-phases viscosity, for more than a century, researchers have estimated the viscosities of solid-liquid mixtures using models. Einstein [15-16] derived a simple model to estimate the viscosities of two-phase melt and co-workers [17] improved the model, once Einstein developed a model that are applied exclusively to small fractions of solid particles. Nonetheless, Roscoe [17] has developed a new model based on the former to contemplate small and also large fractions of solid particles [18].

The aim of the present work is to apply a mathematical model to the Phase Mixture and thermodynamic software to the Liquid Phase, *FactSage 7.2*, to obtain the slags viscosities in this system, for a given temperature of 1500°C and within a range of chemical composition of slags. This study covers the composition by 0–100 wt.% CaO, 0–80 wt.% SiO₂, 0–77 wt.% Al₂O₃ and 0–15 wt.% MgO (CSAM) including the Liquid Phase and the Phase Mixture. Also, it is objective of this work to evaluate the iso-viscosity curves for different CSAM slag systems for the Liquid Phase and Mixture Phase. The representation of iso-curves of viscosity outside the liquid region of ternary diagrams at high temperature gaining greater application and arousing industrial steelmaking interest, since slag in the Mixture Phase being commonly used for the refining of special steels.

2 DEVELOPMENT

2.1 Experimental X calculated

In order to verify the accuracy of the *FactSage 7.2* software in the system CSAM, experimental viscosity data were collected through published works [1-12]. In this work, the viscosity data were obtained by different methods. Table 1 shows more detailed information about the experiments in the viscosity measurement from the literature adopted in this work and also the amount of the data collected.

Table 1. Reference sources of the experimental viscosity data.

System	Author	Method	Crucible	Data
SiO ₂ -Al ₂ O ₃ -CaO Data: 90	Machin,1945	Oscillating	Pt	5
	Machin,1948	Oscillating	Pt	43
	Machin,1952	Oscillating	Pt	16
	Machin,1954	Oscillating	Pt	12
	Kozakevitch,1954	Rotating cylinder	Mo/W	12
	Pengcheng, 2016	Rotating cylinder	Mo	2
SiO ₂ -Al ₂ O ₃ -CaO-MgO Data:152	Machin,1945	Oscillating	Pt	15
	Machin,1952	Oscillating	Pt	48
	Machin,1954	Oscillating	Pt	32
	Hoffman,1959	-	-	10
	Kozakevitch,1966	Rotating cylinder	Mo/W	3
	Kowalski,1995	-	-	21
	Saito,2003	Rotating cylinder	Pt/Rh	3
	Kim,2010	Rotating cylinder	Pt/Rh	4
	Song,2011	Rotating cylinder	Mo	6
Pengcheng, 2016	Rotating cylinder	Mo	10	
Total Data				242

Collected experimental data from the literature.

It is possible to visualize that in some sources it does not present the method and the crucible used in the performance of the measurement of the viscosity. In total 242 data were collected to verify the convergence between the data that were calculated by the *FactSage 7.2* software and the experimental results provided by the references source. The composition ranges of the reference source data are presented in the Table 2 and illustrated in pseudoternary systems in the Figure 1.

Table 2. Composition ranges of slags of the reference sources by %mass.

System	MgO	SiO ₂	Al ₂ O ₃	CaO
SiO ₂ -Al ₂ O ₃ -CaO	0	0 - 70	0 - 54	10 - 55
SiO ₂ -Al ₂ O ₃ -CaO-MgO	0 -15	10 - 65	0 - 45	0 - 50

Collected data from the literature.

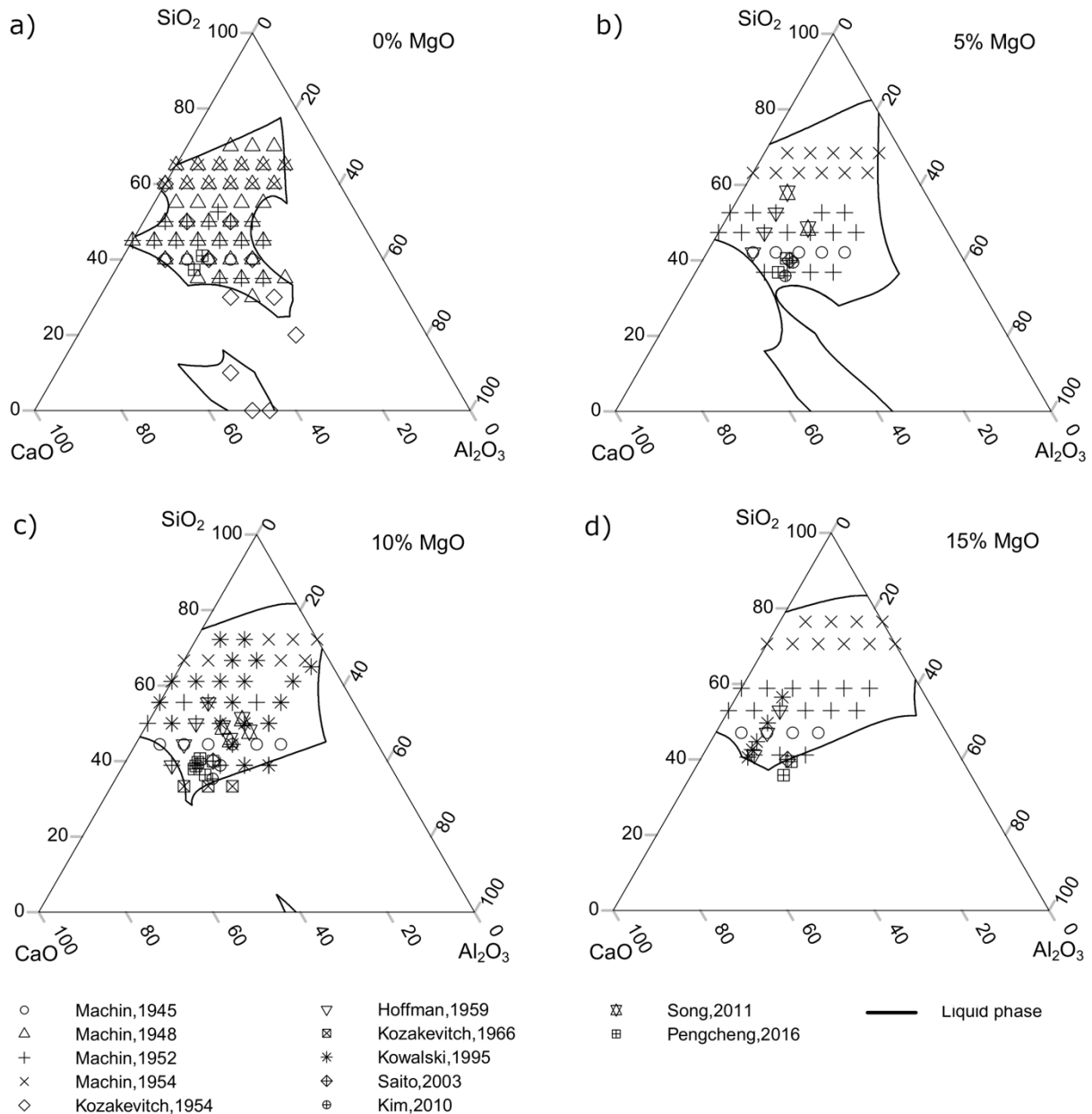


Figure 1. Composition ranges of slags of the sources expressed in form of: (a) CaO–SiO₂–Al₂O₃ system (%mass); (b) normalized CaO–SiO₂–Al₂O₃–(5%MgO) system (%mass); (c) normalized CaO–SiO₂–Al₂O₃–(10%MgO) system (%mass); and (d) normalized CaO–SiO₂–Al₂O₃–(15%MgO) (%mass), at 1500°C.

All the experimental data used in the present work are presented in Figure 1 and for each reference a different symbol was adopted.

2.2 Iso-viscosity curves

In order to observe the viscosity behavior of slags in high temperature, this work carried out a thermodynamic study with chemical compositions ranges covering Liquid Phase and certain zones of Phase Mixture. This thermodynamic analysis was based on software *FactSage* (version 7.2) to determine the values of effective viscosity solid fraction and composition of the liquid fraction. More information about the *FactSage* software and its databases can be found in the study of Bale *et al* [19].

The computational simulations were carried out through modules *Equilib* and *Viscosity*, both available in *FactSage 7.2*. In the *Equilib* module, the databases used were *FactPS* (stoichiometric pure substances) and *FToxid* (for oxides and sulfur) in order to obtain values for the solid fraction of slags. The *Viscosity* module uses *Melts* databases and provides the apparent viscosity (η) that was applied in the model proposed by Roscoe-Einstein [17] to calculate the effectivity viscosity (η_e) for the non-liquid phase, according to Equation 1.

$$\eta_e = \eta (1 - c)^{-2.5} \quad (1)$$

To calculate η_e , it is necessary to know the solid fraction of slag, defined as c in Equation 1 which is obtained using the *Equilib* module. Afterwards, an *MS Excel* spreadsheet was used to calculate the effective viscosity for the Phase Mixture.

Table 3 shows the chemical composition range for each phase adopted in the viscosity calculations considering all references sources as listed in Table 1.

Table 2. Composition ranges of calculated slags in the viscosity database (mass%).

System	Phase	MgO	SiO ₂	Al ₂ O ₃	CaO	Calculated Data
SiO ₂ -Al ₂ O ₃ -CaO-MgO Data: 5976	Liquid	0	0 - 76	0 - 54	6 - 60	535
	Mixture	0	0 - 43	0 - 77	23 - 100	902
	Liquid	5	0 - 78	0 - 60	0 - 54	814
	Mixture	5	0 - 42	0 - 65	29 - 95	666
	Liquid	10	0 - 80	0 - 58	0 - 52	632
	Mixture	10	0 - 46	0 - 67	12 - 90	1025
	Liquid	15	32 - 70	0 - 36	0 - 44	608
	Mixture	15	0 - 40	0 - 56	28 - 85	794

Calculated data from *FactSage 7.2* and Roscoe-Einstein equation.

Each chemical composition generates a certain viscosity. The chemical compositions adopted in the work covered all the Liquid Phase and some part of the Phase Mixture. The spacing between each composition calculated for both Phase Mixture and liquid phase is in the order of 1.6 to 2.5% mass, this variation is related to the size of the phase, for large phases a larger spacing was adopted and for smaller phases a smaller spacing was adopted. For simplification of data and to cover chemical compositions of interest by industry, the whole Phase Mixture was not covered. A total of 5976 data were used to generate representability for the production of the iso-viscosity curves.

To verify the convergence between the *FactSage* calculations and the reference viscosity data, for each slag composition, it was evaluated by the difference between measured and calculated viscosity value, which is expressed by Equation 2:

$$\delta_i = \frac{\eta_{Reference} - \eta_{FactSage}}{\eta_{Reference}} \quad (2)$$

A performance analysis of the reference source on viscosity (η) calculations through *FactSage* was evaluated by average relative error, Δ , for N measurements of viscosity (Equation 3).

$$\Delta = \frac{1}{N} \sum_{i=1}^N \delta_i \times 100\% \quad (3)$$

All data were plotted and analyzed by an open-source software [20].

4 RESULTS AND DISCUSSION

4.1 Convergence data

The comparison between experimental, from the reference sources as shown in Table 1, and calculated viscosities, by *FactSage*, is illustrated in Figures 2.

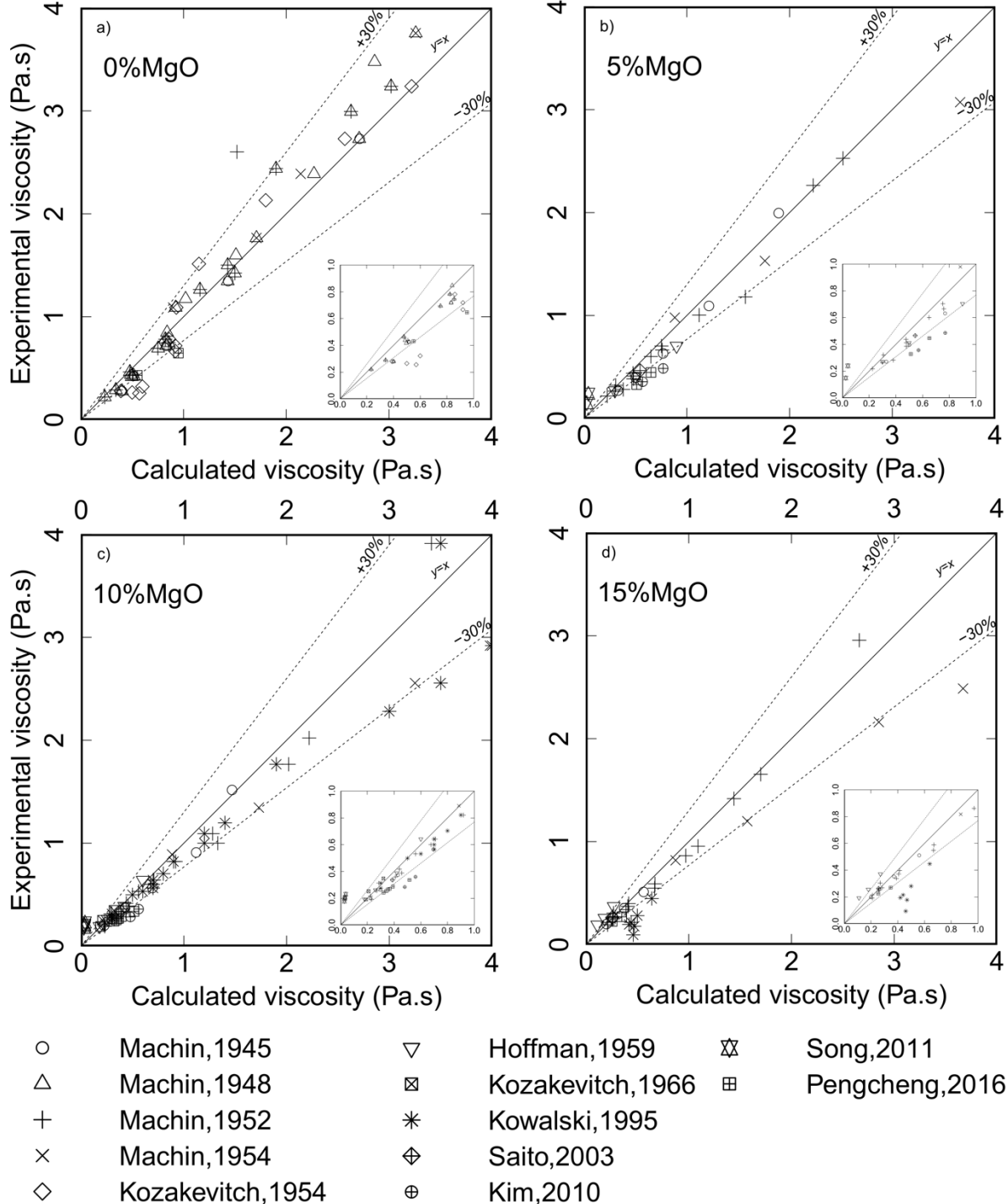


Figure 2: Calculated from *FactSage* 7.2 and measured viscosity comparison for (a) CaO–SiO₂–Al₂O₃ system; (b) CaO–SiO₂–Al₂O₃–5%MgO system (c) CaO–SiO₂–Al₂O₃–10%MgO system and (d) CaO–SiO₂–Al₂O₃–15%MgO, at 1500°C.

Regarding the comparative analysis shown in Figure 2, the possibility of errors and uncertainties in the experimental data will be taken into account in up to 30% as

proposed by Suzuki *et al* [21], Mills [22] and Rocha *et al* [23]. The comparison is presented in 4 different systems, in which the MgO composition ranges between 0 to 15% mass.

In order to show a better presentation of the comparisons proposed in Figure 2, the range was reduced up to 4 Pa.s. Because about 80% of the all dates collected were present between 0 to 4 Pa.s.

Figure 3 shows the average relative error considering, as shown in Equation 2, for each reference source where the measured viscosity data was taken, in order to compare with the calculated values through *FactSage*. The average relative error between the measured and calculated viscosities is in the range of 10 to 38%. Considering all the references, the average relative error between measured and calculated viscosities is 21%. However, it is possible to analyze that in some references presented average relative error greater than 30%, in case of Kim [11] and Song [12].

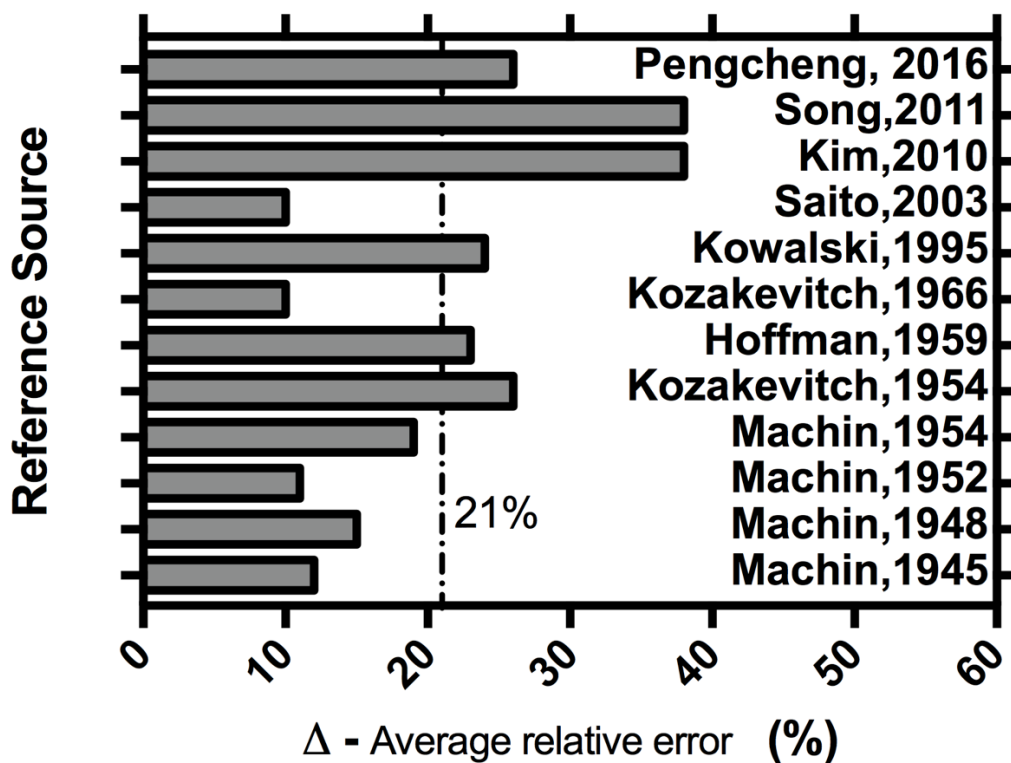


Figure 3: Average relative error between calculated from FactSage 7.2 and measured viscosity comparison for each reference.

According with Mills [22], the viscosity measurements were subject to experimental uncertainties from the possible arise of problems, such as temperature difference from thermocouple measurement and actual temperature of the melt. In view of this, the viscosity measurements differ from recommended values by an average of $\pm 30\%$, and in some cases more than 50%. In this context, it can be said that the obtained results in terms of relative deviation have shown reasonable results.

4.2 Iso-viscosity curves

The iso-viscosity curves for the system CSAM are present at various content of MgO in Figure 4.

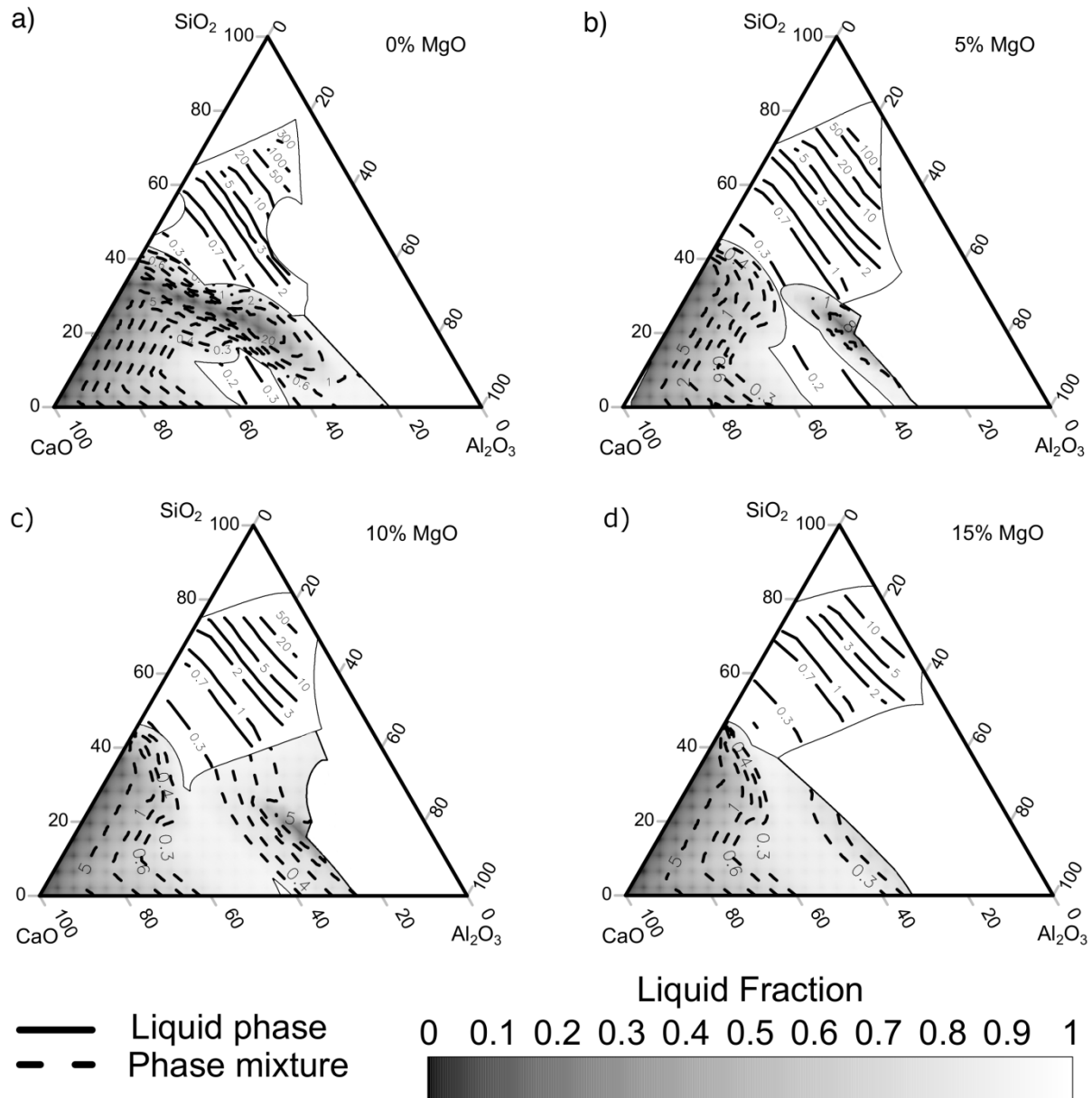


Figure 4. iso-viscosity [Pa.s] curves of slags in Liquid and Phase Mixtures: (a) CaO–SiO₂–Al₂O₃ system (%mass); (b) normalized CaO–SiO₂–Al₂O₃–(5%MgO) system (%mass); (c) normalized CaO–SiO₂–Al₂O₃–(10%MgO) system (%mass); and (d) normalized CaO–SiO₂–Al₂O₃–(15%MgO) (%mass), at 1500°C.

In the analysis of the systems proposed (Figure 4) it is possible to visualize the trend of composition dependence, as increases the MgO content conversely the viscosity decreases. The MgO typically as a network “modifier”, and thus decreases the viscosity [24]. The Liquid Phase are gradually reduced, with increases of the MgO content, as seen in past work [9]. Additionally, it is also revealed in the Figure 4 that the low viscosity area (0 ~ 1Pa.s) is much larger in compositions with higher MgO

contents. In view of the Phase Mixture it is not possible to see a large effect on viscosity reduction in regarding the increases of the MgO content as seen in the Liquid Phase. However, there is a reduction in its viscosity with the increase of the liquid fraction as shown in Figure 4 between the 40 ~ 60 CaO regions. The Phase Mixture in Figure 4a in the area of 40 ~ 70% CaO, 20 ~ 40% SiO₂ and 0 ~ 40% Al₂O₃, a rich solid fraction was found to be considerable which resulted in an increase in viscosity.

In order to explain this effect, the Figure 5 shows the equilibrium phases in the Liquid Phase and Phase Mixture approached in this paper.

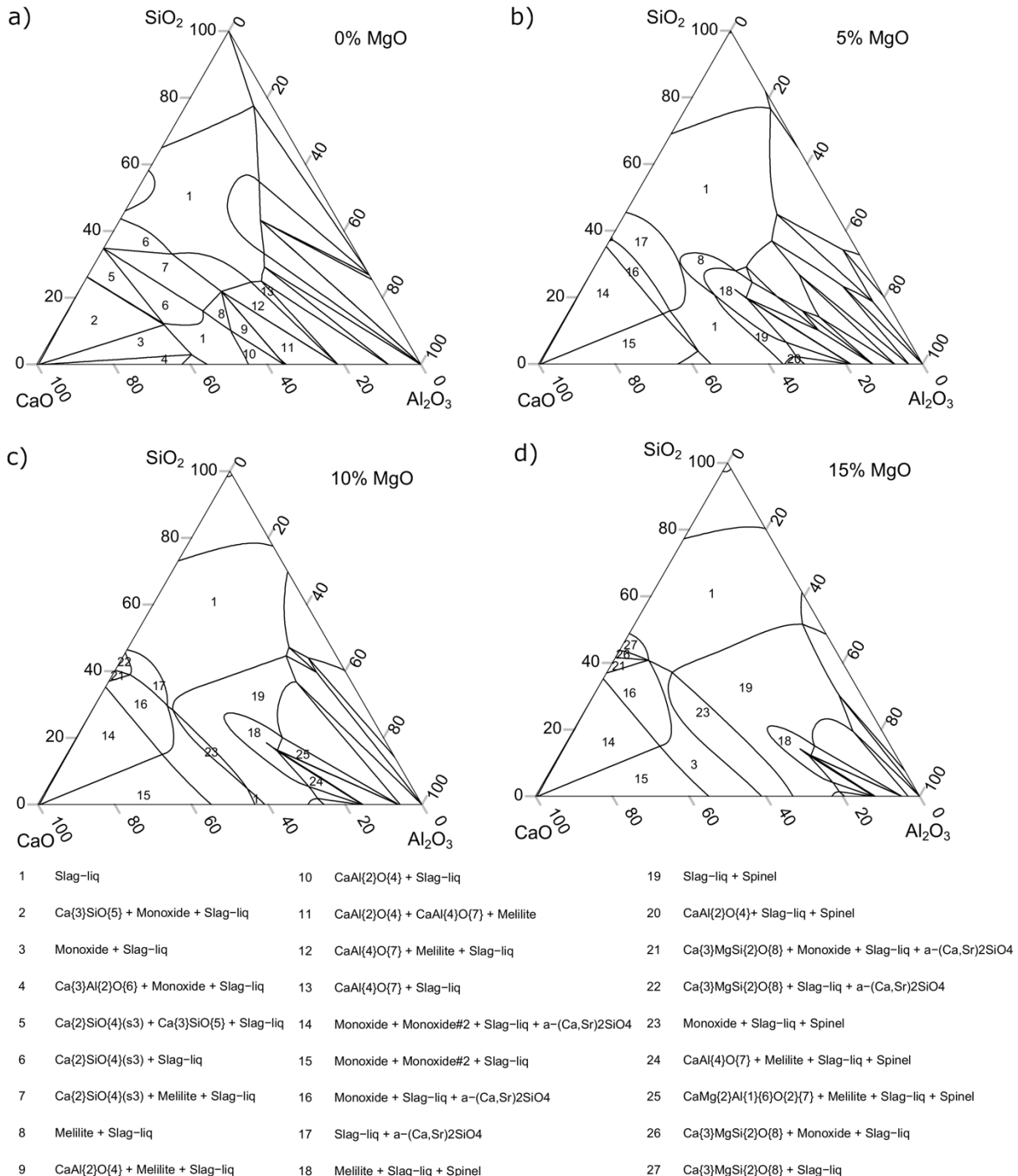


Figure 5. Equilibrium phases presents in the Liquid and Phase Mixtures: (a) CaO–SiO₂–Al₂O₃ system (%mass); (b) normalized CaO–SiO₂–Al₂O₃–(5%MgO) system (%mass); (c) normalized CaO–SiO₂–

Al₂O₃–(10%MgO) system (%mass); and (d) normalized CaO–SiO₂–Al₂O₃–(15%MgO) (%mass), at 1500°C.

The slag-liq represents the Liquid Phase and the remainders of the phases are classified in Phase Mixture. Regarding the Figure 5, the Melilite ((Ca₂(Al,Mg,Fe²⁺)(Si,Al)₂O₇) phase is present (7, 8, 9, 11, 12, 18, 24, 25) in the compositions where there were an increase of the solid fraction, as seen in Figure 4. Correlating the Figure 4 with Figure 5 it is possible to see that the increase of the solid fraction is connected to the presence of the Melilite phase. The increases of MgO guide the Melilite phase to lower CaO, SiO₂ and higher Al₂O₃ contents until disappeared from the Phase Mixtures that was calculated in this paper as shown in Figure 4.

Comparing the specific effect of the Liquid phase and Mixture Phase (Figure 4), for the remaining oxides, the CaO effect for the Liquid Phase shows a progressive reduction in the viscosity whereas for the Phase Mixture it has a double effect: initially a reduction in viscosity up to 50% mass of CaO and subsequently with higher mass contents of 50% tends to increase viscosity. The increase of the viscosity is governed by the greater amount of CaO over the saturation point, therefore precipitating solid particles.

The increase of SiO₂ and decrease of Al₂O₃ content in Liquid Phase showed an expressive increase in the slag viscosity. Nonetheless, in Phase Mixture this effect of these elements did not appear as expressive in relation to the CaO oxide effect, as previously mentioned.

5 CONCLUSIONS

In summary, *FactSage 7.2* was employed to calculate the behavior of slags in the Liquid and the Roscoe-Einstein model to the Phase Mixture for the CSAM systems at 1500°C. The calculated data were compared with experimental data that were collected by the references cited in this paper. About 240 experimental data were collected to verify the convergence of the data between the calculated and experimental data, to propose an accurate representation of iso-viscosity curves applied for secondary steelmaking slags.

The following main conclusions can be drawn from this work:

- The obtained results in terms of average relative error of the calculated viscosity have shown reasonable results compared to the experimental data.
- The viscosities calculated through chemical compositions of the literature were generally within the acceptable range of relative error compared to the literature (up to 30%).
- By the analysis proposed it is possible to visualize that the effect of the MgO content decreases the viscosity in the Liquid Phase. However, the Liquid Phase area decreases as the MgO content increases.
- The effect of the CaO oxide for the Phase Mixture showed a double effect. Initially a reduction in viscosity up to 50% mass of CaO and, subsequently, with higher mass contents of 50%, tends to increase viscosity.
- The *FactSage 7.2* showed to be very promising for the creation of pseudoternary systems with iso-viscosity curves. This is a very useful representation for the steelmaker, considering the slag designing process, aiming at obtaining the best conditions of steel refining.

It is not known by the literature of iso-curves of viscosity inside the Phase Mixture of ternary diagrams of slags at high temperature. For this reason, the present work will be continued in order to gather new results, considering different compositions and different temperatures for new slag systems.

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