DETERMINATION OF SULFIDE CAPACITIES OF CAO-AL$_2$O$_3$ AND CAO-AL$_2$O$_3$-MGO SLAGS BY MEANS OF COMPUTATIONAL THERMODYNAMICS[1]

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Abstract

A comprehensive 'computational model' of a metallurgical reactor undergoing refining processes, which takes into account the fluid dynamics and the chemical thermodynamics, is currently under development. The main purpose of the present work is to evaluate the computational thermodynamic ability in dealing with the refining process of desulfurization – the first refinig process under consideration. Quantitative knowledge of the solubility of sulfur in slags is fundamental to an understanding of this refining process. To this purpose, sulphide capacity, C_s, of CaO-Al$_2$O$_3$ and CaO-Al$_2$O$_3$-MgO slags at steelmaking temperatures were determined by means of the computacional thermodynamics and compared with data from the literature.

Key words: Steel refining; Slag; Desulfurization; Sulfide capacity.

DETERMINAÇÃO DA CAPACIDADE DE SULFETOS DE ESCÓRIAS CAO-AL$_2$0$_3$ E CAO-AL$_2$0$_3$-MGO POR MEIO DA TERMODINÂMICA COMPUTACIONAL

Resumo

Um "modelo computacional" abrangente de um reator metalúrgico submetido a processos de refino, que leva em conta a dinâmica dos fluidos e a termodinâmica química, está atualmente em desenvolvimento. O principal objetivo do presente trabalho é avaliar a capacidade computacional termodinâmica em lidar com o processo de refino de dessulfuração - o primeiro processo de refino em análise. O conhecimento quantitativo da solubilidade do enxofre em escórias é fundamental para a compreensão deste processo de refino. Para este efeito, as capacidades de sulfeto, C_s, de escórias CaO-Al$_2$O$_3$ e CaO-Al$_2$O$_3$-MgO em temperaturas da produção de aços foram determinadas por meio da termodinâmica computacional e comparadas com os dados da literatura.

Palavras-chave: Refino de aços; Escória; Dessulfuração; Capacidade de sulfetos.

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1 INTRODUCTION

The studies of both chemical thermodynamics and fluid dynamics are necessary in order to obtain a complete understanding of the steel refining processes. For this reason, a comprehensive 'computational model' of a metallurgical ladle undergoing a refining process, which takes into account the two above mentioned disciplines, is currently under development.

The main purpose of the present work, considering the dual nature of the modeling, is to evaluate the computational thermodynamic software ability in dealing with the chemical refining process. This naturally leaves other assessments, including the 'fluid dynamic software' assessment as well as the complete model analysis to be completed somewhere else.

Due to its great importance, the first steel refining process selected for the 'computational model' was the desulfurization. Practically used slag in desulfurization is CaO-based slag. For the reason that steel is usually deoxidized with aluminum, a CaO-Al_2O_3 slag is formed in the process. This system, therefore, was chosen as the first subject to be investigated in this work. Since MgO from refractory dissolves in the CaO-Al_2O_3 slag at the steelmaking process, a second system, CaO-Al_2O_3-MgO, is also included in this study.

Needless to say, the model will be essentially affected by the thermodynamic *data*; however, the mathematical attributes of the thermodynamic software cannot be excluded and will be analyzed together. Even though not necessarily coupled, it is a common practice for software developer's to market both as a single 'product'. In order to evaluate the supplied *databases*, a comparison between experimental data from literature with calculated results will be made. For this purpose, determinations of the *sulfide capacity* and CaS *solubility* in the aforementioned slag systems were chosen as objectives for this investigation.

Concerning desulfurization under reducing conditions, where S dissolves in slag as sulfide (S^{2-}) rather than sulfate (SO_4^{2-}), the equilibrium between slag and the atmosphere can be written – using the ionic theory – as follows:

$$\tfrac{1}{2} S_2(g) + (O2^-) = \tfrac{1}{2} O_2(g) + (S2^-) \; . \qquad (1)$$

This reaction suggests that, at low pO_2, sulfur dissolves in slag by replacing the O^{2-} ion on the anion sublattice.

The corresponding expression for the equilibrium constant is

$$K_1 = \frac{a_{S^{2-}}}{a_{O^{2-}}} \cdot \sqrt{\frac{p_{O_2}}{p_{S_2}}} \; .$$

However, for the reason that the activities of S^{2-} and O^{2-} ions can not be measured alone in slags, the *equilibrium constant* remains unknown. In view of this, Fincham and Richardson$^{(1)}$ proposed, in a classic paper of 1954, a coefficient to evaluate the physico-chemical desulfurizing power of slags. These researchers based their concept in two assumptions: first, the number of O atoms in slags greatly exceeds the number of other potential anions, including S^{2-}, so that the concentration of O^{2-} is assumed to be roughly constant; second, the physico-chemical behavior of sulfur in slag satisfies Henry's law.

Hence, the *sulfide capacity*, C_s, was then defined as follows:

$$C_S = K_1 \frac{a_{O^{2-}}}{f_{S^{2-}}} = (S\%) \cdot \sqrt{\frac{p_{O_2}}{p_{S_2}}}$$

or

$$\log C_S = \log(S\%) + \log\sqrt{\frac{p_{O_2}}{p_{S_2}}}$$

as a result, the sulfide capacity depends only on the slag *composition* and *temperature* and is independent of *sulfur content* in slag. Nevertheless, for a particular temperature and slag composition, C_s coefficient only has a meaning while the concentration of sulfur (as S^{2-}) in the slag remains proportional to $(p_{S2}/p_{O2})^{0.5}$.

The oxygen ion activity in slags is often related to slag *basicity* – usually given as the mass or molar ratio of 'basic' (CaO, MnO, FeO, etc.) to 'acidic' *oxides* (SiO_2, Al_2O_3, etc.) – so that the higher the basicity, the greater the oxygen ion activity. For that reason, a high basicity slag is needed for the steel desulfurization.

A similar sulfide capacity can be defined, which uses the sulfur *molar fraction* of the slag and will be denoted as $C_{s'}$ in this work.

For the metallurgist, however, the knowledge of sulfur equilibrium between slag and steel melt is the *final* objective. For this case, a second reaction, which resembles the first, can be written:

$$[S] + ½\,O_2(g) = ½\,S_2(g) + [O] \quad , \qquad (2)$$

$$K_2 = \sqrt{\frac{p_{S_2}}{p_{O_2}}} \cdot \frac{a_O}{[S\%]\,f_S} \quad .$$

As a result, the sulfur *distribution coefficient*, L_s, is defined as the ratio of the concentrations of sulfur in each of the two phases (steel and liquid slag). When the square root of the pressure ratio (from the equilibrium constant expression K_2) is substituted in the C_s expression, L_s can be written:(2)

$$L_S = \frac{(S\%)}{[S\%]} = C_S \cdot \frac{K_2 \cdot f_S}{a_O} \quad .$$

The new coefficient, determined by the thermodynamic software, is needed as an input for the fluid dynamic software, in order to bring about the coupling of both of them in the ladle 'computational model'.

2 SOFTWARE AND DATABASES

'FToxid' thermodynamic databases from the canadian group FACT were used in his work. The FToxid *solution* database (FToxid53Soln.sda) contains oxide solutions and the FToxid *compound* database (FToxid53Base.cdb) contains all stoichiometric solid and liquid oxide compounds. Both are evaluated and, whenever possible, optimized by the FACT group and are said to be thermodynamically consistent with each other.

The most important phase of the 'solution database' is the slag solution FToxid-SLAGA. Major oxide components of this solution are the oxides of Al, Ca, Fe(II), Fe(III), Mg, and Si. and Data are said to have been fully optimized and evaluated together at all compositions by the FACT group – that is, all available data for binary, ternary and quaternary sub-systems.

For this slag, according to the FACT group: (i) sulfur contents (as sulfide) will be calculated 'reasonably well' for total sulfide contents up to about 12 weight %; (ii) even though the 'equilibrium computing-module' output gives sulfide grouped as the 'constituents' CaS, FeS, MgS, etc., this is only a formalism; the model actually treats sulfur as a dissolved sulfide *ion* which is not associated with any particular cation.

Data for gases – CO, CO_2, SO_2, S_2, O_2 – are from FACT53 'compound database'. Gases used in computations were not limited to these five chemical species, but results showed no significant differences when more constituents were taken into account.

The German-Canadian 'FactSage' (version 5.5) software was used in all thermodynamic determinations.

3 RESULTS AND DISCUSSION

3.1 CaO-Al_2O_3 -slags

For the reason that oxygen level in steel melt is reduced with the use of aluminum following

$$2\,[Al] + 3\,[O] = (Al_2O_3)\ , \qquad (3)$$

and, considering – using the molecular theory – that a CaO-based slag reacts with sulfur in melt as

$$[S] + (CaO) = (CaS) + [O]\ , \qquad (4)$$

the global chemical reaction of steel desulfurization, is, therefore:

$$3\,(CaO) + 2\,[Al] + 3\,[S] = 3\,(CaS) + (Al_2O_3)\ , \qquad (5)$$

and, the resulting slag phase is mainly composed of CaO-Al_2O_3 constituents.

Regarding desulfurization *kinetics*, the most important factor is low viscosity – a property that can be achieved by keeping the slag free from *solid* phases. Consequently, the liquid slag ranges for CaO-Al_2O_3 binary system at different temperatures were determined first and can be seen in Figure 1. CaO (denoted as 'monoxide') and $CaAl_2O_4$ (or CaO.Al_2O_3) are well-known solid phases that can precipitate in CaO or Al_2O_3-rich liquid slags, respectively.

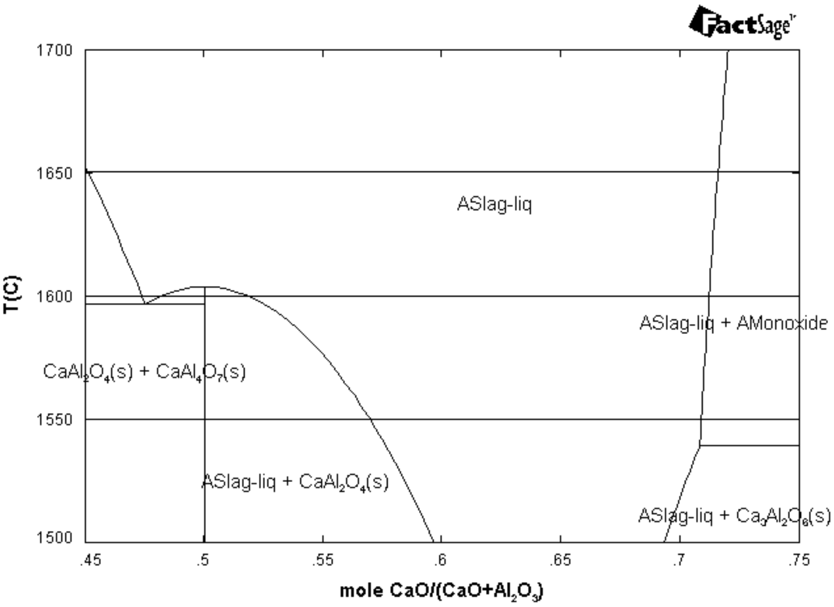

Figure 1. CaO-Al_2O_3 phase diagram

Figure 2 shows the logarithm of the molar sulfide capacities for homogeneous and CaO or $CaAl_2O_4$-saturated CaO-Al_2O_3 slags determined at 1550, 1600 and 1650ºC.

The value of log $C_{S'}$ determined for this slag increases at a fixed rate with the increasing concentration of CaO and temperature. These results suggest an oxygen ion activity increment with the rising of CaO molar fraction at constant temperature, and, for a fixed composition, an increase of K_1 values for higher temperatures.

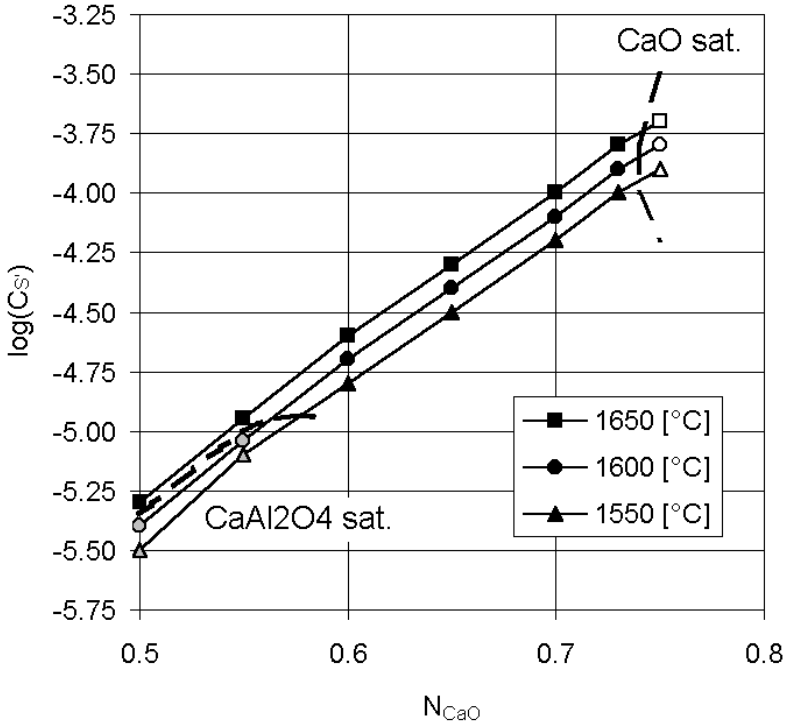

Figure 2. Logarithm of $C_{S'}$ values for CaO-Al_2O_3-slags

Comparison with previous work was done chiefly with the focus on the recent paper of Hino et al.(3) Figure 3. These researchers, from the Tohoku University, Japan, made an extensive literature review – along with their experimental work – what therefore turned their paper into a very important reference for the present investigation. The evaluation shows a fairly agreement between the reported values and those determined in the present work.

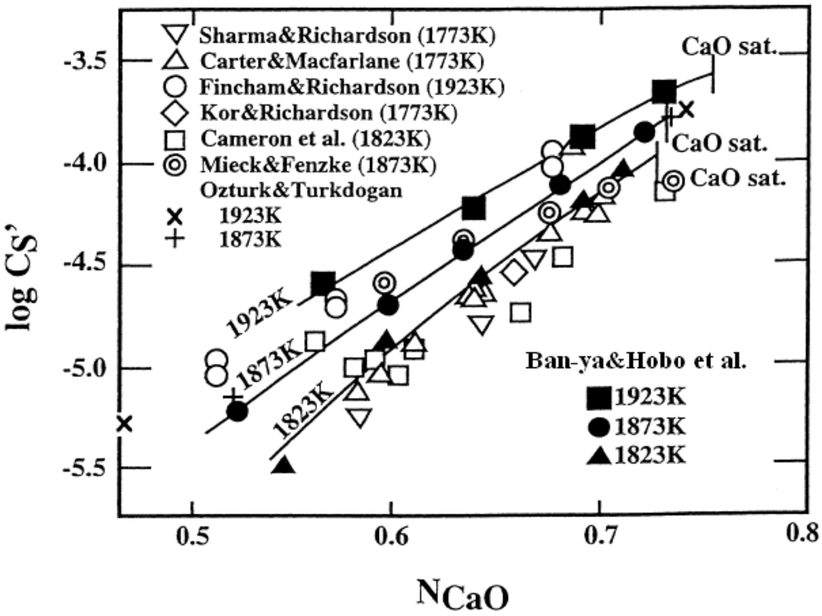

Figure 3. Logarithm of $C_{s'}$ values for CaO-Al_2O_3-slags.(3)

Logarithm of $C_{s'}$ values for CaO-Al_2O_3-slags were determined for 1600ºC at two fixed CaO to Al_2O_3 *molar* ratios – namely 2.2 and 1.4 (which corresponds to ~69% and ~58% molar CaO initial values, respectively) – as function of CaS molar fraction, Figure 4, and are comparable to the values reported by Hino *et al.*(3)

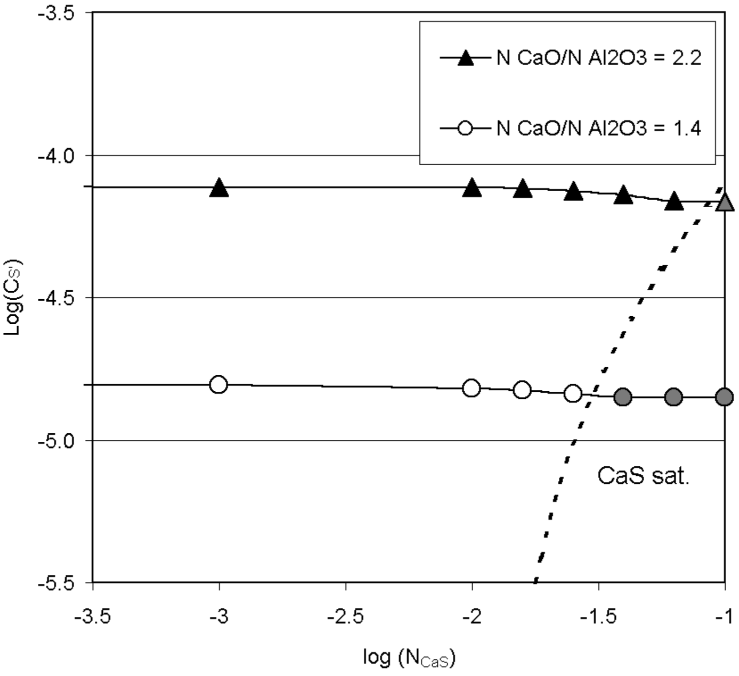

Figure 4. Logarithm of $C_{s'}$ values for CaO-Al_2O_3-slags at 1600ºC, for two CaO/Al_2O_3 molar ratios, as a function of CaS molar fraction

Limiting CaS saturation values, when plotted in a ternary phase diagram CaO-Al_2O_3-CaS, at 1600ºC isotherm, Figure 5, show some similar values (boundary) – but a somewhat different trend – when compared with the data measured by several authors (some at different temperatures), Figure 6.

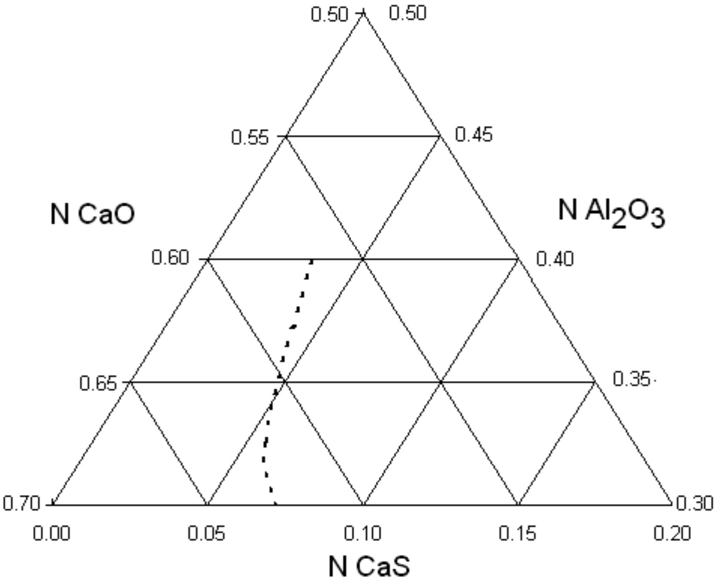

Figure 5. CaS saturation boundary, 1600ºC

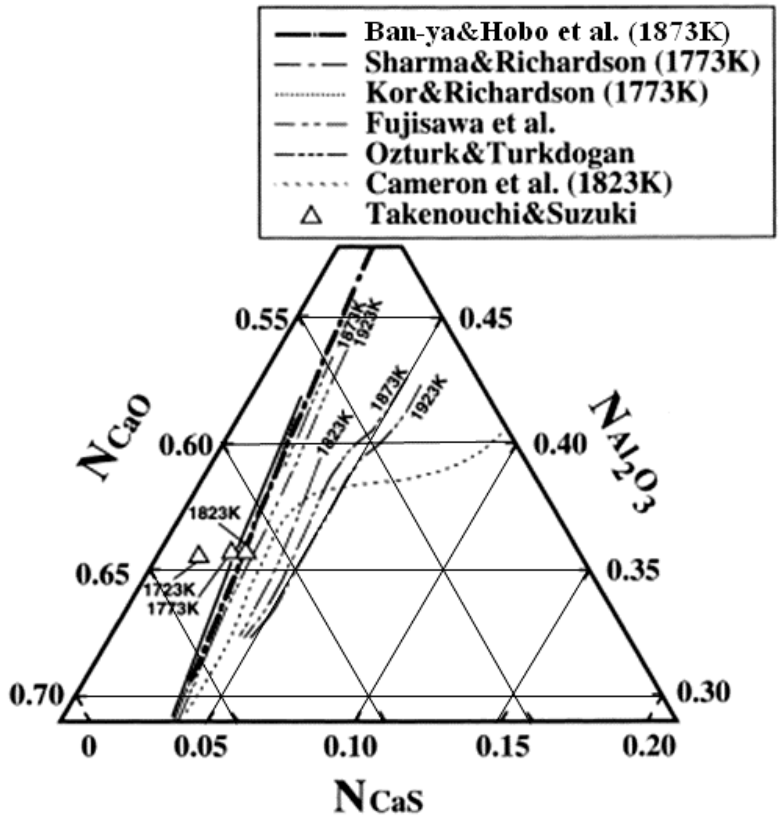

Figure 6. CaS saturation boundaries from the literature at several temperatures.(3)

3.2 CaO-Al_2O_3-MgO -slags

For desulfurization, a slag with a high basicity index is wanted and, in order to cope with this property, a basic refractory is needed at the slag 'line'. For this reason, in spite of being expensive, a MgO-based lining is often used. The ideal desulfurizing *fluid* and *turbulent* slag, however, is aggressive to the refractories. As a result of the strong slag action, MgO may be incorporated into the initially binary slag.

The liquid slag range regarding the CaO-Al_20_3-MgO ternary system at 1600ºC – significant for the reasons already mentioned – was determined and can be seen in Figure 7. The calculated boundaries are in good approximation to the data reported in the literature.(4)

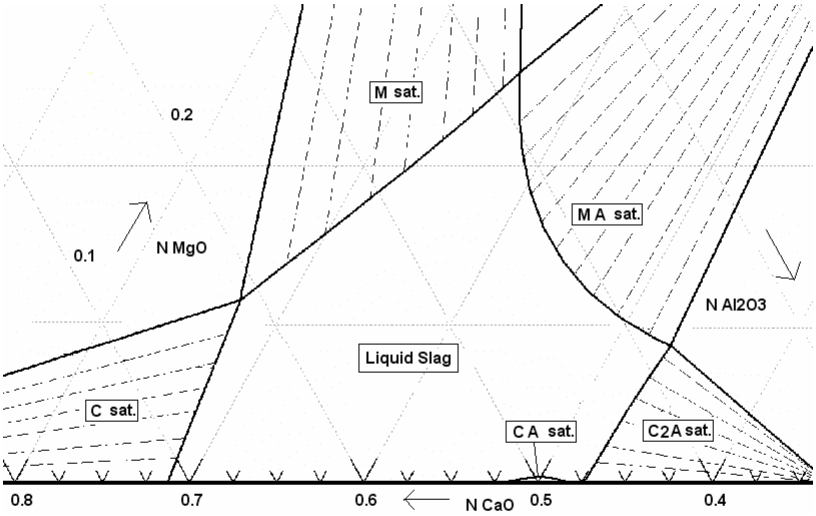

Figure 7. CaO-Al_2O_3-MgO phase diagram, at 1600ºC, emphasizing the liquid slag zone; M=MgO, A= Al2O3, C= CaO

The negative logarithm of C_s values for CaO-Al_2O_3-MgO-slags were calculated for 1600ºC for this system, at two fixed CaO to MgO *ponderal* ratios – namely 9/1 and 8/2 – and are plotted in the Figure 8. Results are roughly comparable to the values reported by Hino, Kitagawa e Ban-Ya.(4)

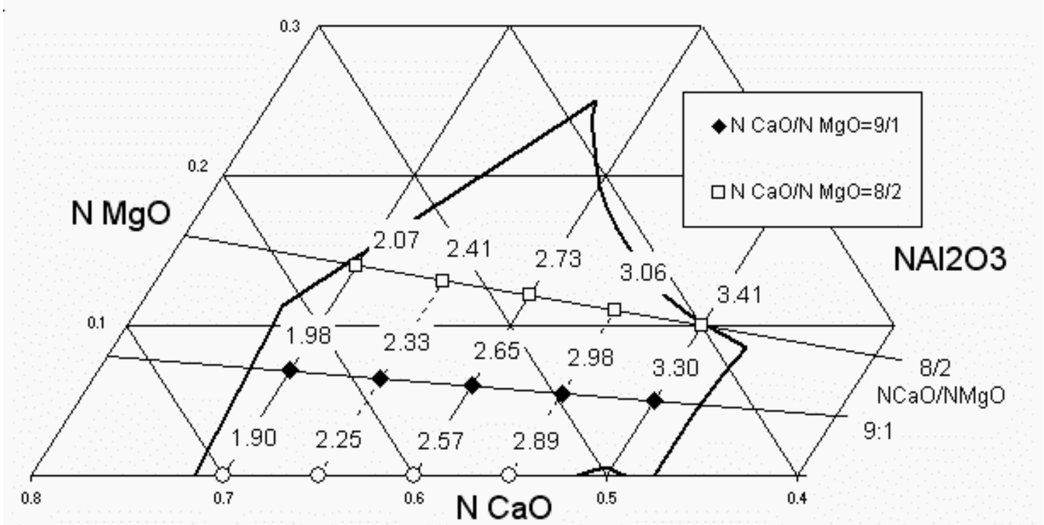

Figure 7. CaO-Al_2O_3-MgO phase diagram, at 1600ºC, showing –log C_s values

4 CONCLUSIONS

Sulphide capacity, C_s, at 1550, 1600 and 1650ºC and the solubility of CaS in the CaO–Al_2O_3 slags at 1600ºC, and also the sulphide capacity in the CaO–Al_2O_3–MgO slags at 1600ºC were determined by means of the computacional thermodynamics.

Logarithm of $C_{s'}$ values for CaO-Al_2O_3-slags are comparable to the values in the literature reported by Hino et al.(3)

Limiting CaS saturation values, showed some similar values (boundary) – but a somewhat different trend – when compared with the data measured by several authors.

Boundaries for the liquid slag range regarding the CaO-Al_2O_3-MgO ternary system at 1600ºC are in good approximation to the data reported in the literature, but C_s values do not show a very good agreement.

As pointed out by the data producers, sulfur contents (as sulfide) will be calculated ‘reasonably well’ (computed S levels are within bounds).

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REFERENCES

1 FINCHAM, C. J. B.; RICHARDSON, F. D. The behavior of sulphur in silicate and aluminate melts. **Proceedings of the Royal Society of London**, Serie A 223, p.40–62,1954.
2 ROSENQVIST, T. **Principles of Extractive Metalurgy**. McGraw-Hill, Tokyo, 1974.
3 BAN-YA, S; HOBO, M; KAJI, T.; ITOH T.; HINO, M. Sulphide Capacity and Sulphur Solubility in CaO-Al_2O_3 and CaO-Al_2O_3-CaF_2 Slags. **ISIJ International**, v. 44, n. 11, p. 1810-1816, 2004.
4 HINO, M.; KITAGAWA, S.; BAN-YA, S. Sulphide Capacities of CaO-Al_2O_3-MgO and CaO-Al_2O_3-SiO_2 Slags. **ISIJ International**. v. 33, n. 1, p. 36-42,1993.