

# MOULD SLAG ALUMINA PICK-UP DUE TO CHEMICAL REACTIONS AT THE METAL-SLAG INTERFACE IN THE CONTINUOUS CASTING PROCESS<sup>1</sup>

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## Abstract

Mould powders are synthetic slags used during the continuous casting of steel. Their chemical composition can vary greatly because of the absorption of non-metallic inclusions from the liquid steel and also due to reactions at the metal-slag interface during continuous casting. It is known that even a low increase in alumina content can alter profoundly the viscosity of the mould slag, which is an important technological parameter. The objective of the present work is to quantify the alumina pick-up due to chemical reactions at the metal-slag interface, through computational thermodynamics. The calculations were executed considering simple slags systems and liquid iron containing Al and O as dissolved components. The method described in the present work has proven effective in evaluating the  $\text{Al}_2\text{O}_3$  pick-up during continuous casting.

**Keywords:** Mould powders; Alumina pick-up; Computational thermodynamics.

## AUMENTO DO TEOR DE ALUMINA DA ESCÓRIA DE MOLDE DEVIDO A REAÇÕES QUÍMICAS NA INTERFACE METAL-ESCÓRIA NO LINGOTAMENTO CONTÍNUO

### Resumo

Pós fluxantes são escórias sintéticas utilizadas durante o lingotamento contínuo de aços. Sua composição química pode variar muito, por causa da absorção de inclusões não-metálicas do aço e também devido a reações na interface metal-escória durante o lingotamento contínuo. Sabe-se que um pequeno aumento no alumina pode causar uma profunda alteração na escória, o que faz dele um importante parâmetro tecnológico. O objetivo do presente trabalho é quantificar o aumento do teor de alumina devido a reações químicas na interface metal-escória, através da termodinâmica computacional. Os cálculos foram executados considerando sistemas de escórias simples e ferro líquido contendo Al e O como componentes dissolvidos. O método descrito no presente trabalho mostrou que pode ser utilizado para se avaliar o aumento do teor de  $\text{Al}_2\text{O}_3$  da escória durante o lingotamento contínuo.

**Palavras-chave:** Pós fluxantes; Absorção de alumina; Termodinâmica computacional.

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## 1 INTRODUCTION

Mould powders are synthetic slags used during the continuous casting of steel, designed for specific steel grades and steel plant conditions. Their chemical composition varies greatly depending on the required properties. Typically, mould powders contain the following major constituents:  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-CaF}_2$ . The functions of the mould powders are the following: (i) to protect the steel meniscus from oxidation, (ii) to provide thermal insulation, (iii) to absorb inclusions, and (iv) to lubricate the strand and provide uniform heat transfer across the infiltrated slag layer between the steel strand and the mould.<sup>(1,2)</sup>

Once applied to the mould, the mould powder is heated up by the liquid steel. During heating, the decomposition of carbonates as well as the oxidation of carbonaceous materials (used to control the melting behaviour of the mould powder) take place. After melting, in contact with the molten steel, the liquid mould slag changes its chemical composition as a function of time, because of (i) absorption of non-metallic inclusions from the liquid steel and (ii) reactions between mould slag and liquid steel during continuous casting. Then, the modified liquid slag infiltrates into the gap between steel strand and mould wall and solidifies.<sup>(3,4)</sup>

The main concern regarding changes of chemical composition of the mould slag is the alumina pick-up while casting Al-killed steels, which can profoundly alter the viscosity of the mould slag. Depending on the effectiveness of protection against reoxidation and the cleanliness of the steel, the alumina in mould slag can rise up to 15 wt. percent.<sup>(2)</sup>

Change in mould slag composition should be minimized for the stable casting operation. Even a relatively small increase of the  $\text{Al}_2\text{O}_3$  content (2-4% in industrial practice for clean steel production) can increase viscosity significantly, the phenomenon being more prominent at lower temperatures. Such a relatively large increase in viscosity would affect the slag film thickness, hence the heat transfer, and the friction force acting on the solidified shell.<sup>(5)</sup> The dynamically changing chemistry of a mould slag leads to various casting problems: sticking of the mould slag to copper mould, increased crack frequency, nonuniform heat transfer across the mould slag, reduced mould heat transfer, reduced consumption of mould slag, and, hence, reduced lubrication, etc. The reasons for these casting problems are not yet completely understood.<sup>(6)</sup>

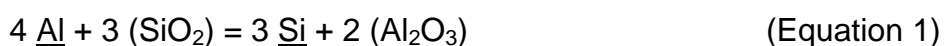
The assimilation of deoxidation products, *i.e.* oxide inclusions from the steel melt, is an important function of any slag. That function is desired to continue during casting, in tundish as well in *mould*. An opposite phenomenon, however, is also possible *i.e.* slag can be dispersed as droplets into the steel. In strong turbulent flow circumstances (without any gas bubbling), in tundish and mould during casting, slag can be dispersed into the steel as droplets. It is a well-known fact that when conditions for reactions between steel and slag are favourable, interfacial tension strongly decreases which can lead to an abundant mixing of slag and metal.<sup>(7)</sup>

Absorption of  $\text{Al}_2\text{O}_3$  is promoted by the use of mould slags with high basicity (V-ratio of around 2.0), low  $\text{Al}_2\text{O}_3$  contents, and high  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and F contents; the solubility in mould fluxes for  $\text{Al}_2\text{O}_3$  can be very high – up to 30%.<sup>(1)</sup>

$\text{Al}_2\text{O}_3$  pick-up during continuous casting of stainless steel 304 was studied by Hao *et al.*;<sup>(3)</sup> their research have showed that absorption of inclusions was not the main source for  $\text{Al}_2\text{O}_3$  entering into mould slag but interface reactions between slag and steel. A similar result was found for a titanium stabilized ultra low carbon steel grade.<sup>(8)</sup>

The  $\text{Al}_2\text{O}_3$  absorption was *quantified* by Nakano *et al.*<sup>(9)</sup> through a mass balance and the help of a rate per unit area coefficient,  $\beta$  ( $\text{g}/\text{cm}^2\cdot\text{s}$ ), which itself is a function of  $B_i$  – a basicity index which can encompass multicomponent mould powders.

The reaction between  $\underline{\text{Al}}$  and  $(\text{SiO}_2)$  leads to compositional changes in mould slags, decreasing  $(\text{SiO}_2)$  and increasing  $(\text{Al}_2\text{O}_3)$  contents – in a simple  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag system (the designations (X) and  $\underline{\text{X}}$  indicate the slag-phase and the metal-phase, respectively). This reaction can be seen in Eq. 1.



Some TRIP (Transformation-Induced-Plasticity) steels have significant quantities of aluminium in their chemistry – the composition of a typical Al-TRIP steel being 0.15C, 1.00Al, 0.30Si, 1.50Mn (wt.%). Thus, it is necessary to design special mould powders that are compatible with this steel chemistry and that allow sequence casting.<sup>(6,10)</sup> In a previous work the chemical interactions between a singular mould slag and particular TRIP steel were evaluated with the help of computational thermodynamics. It was suggested that the computational tool can be used to predict the complex chemical interactions of mould slags when in contact with liquid steel.<sup>(11)</sup>

In order to estimate the mould slag change in composition due to the reaction with molten steel during the continuous casting of steels and to design an optimum slag composition, a mathematical model was described in the literature. Change in composition of mould slag was calculated by taking into account the mass transfer between mould slag and molten steel and the mass balance of some components in both phases.<sup>(12)</sup>

The melting and crystallization behaviour of mould slags in the presence of alumina pick-up can be modelled through computational thermodynamics. Phase diagrams showing directly the effect of alumina pick-up on the melting behaviour as well as on the precipitating oxides were generated. Such type of information can be useful as a design tool in order to develop mould powders.<sup>(13)</sup>

The objective of the present work is the quantification of the *potential*  $\text{Al}_2\text{O}_3$  pick-up due to chemical reactions at metal-slag interface. All the considerations are limited to the thermochemical equilibrium aspects – in spite of the recognition that kinetic aspects can be equally important. The motivation for using the thermodynamic approach is the fact that the direction of the reactions and the limiting conditions can be firmly established with this tool.

## 2 METHODOLOGY

In the following paragraphs, a method to quantify the potential  $\text{Al}_2\text{O}_3$  pick-up due to *chemical reactions* at the metal-slag interface will be presented.

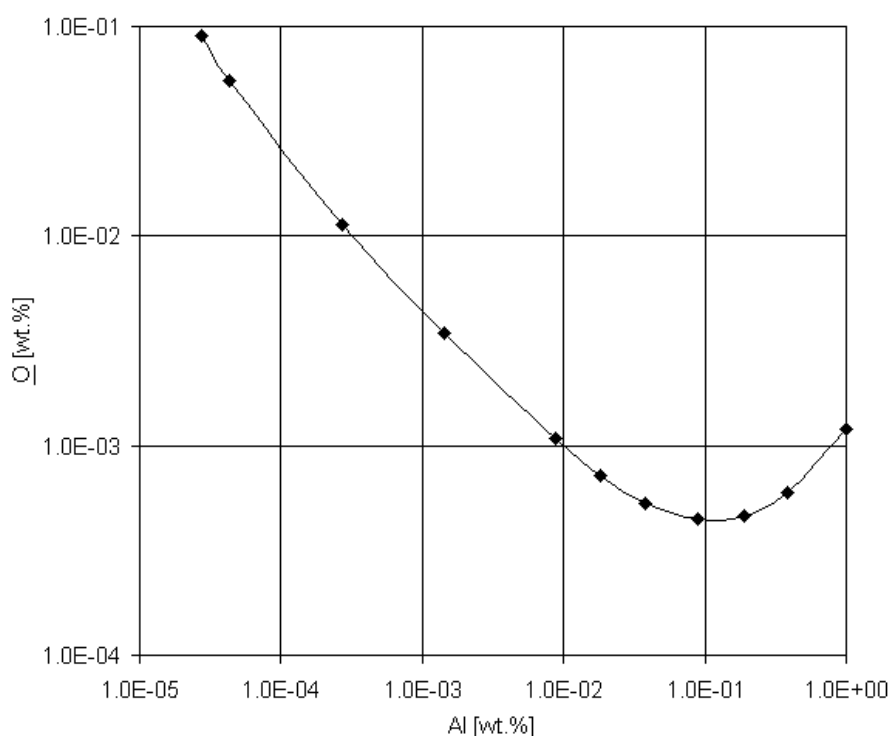
Reddy and Sankaranarayanan<sup>(13)</sup> suggested it is possible to approximate a mould slag composition using  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  after recognizing that these oxides account for 70-95 % mass content of the oxides present in the commercial mould powders. For that reason the  $\text{Al}_2\text{O}_3$  pick-up will first be determined here for a simple slag of the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system. Determinations for liquid slags containing  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and other constituents are currently being considered.

As a computational thermodynamic tool it was employed the *Equilib* module of the commercial software package FactSage v. 5.5.<sup>(14)</sup> This module calculates the concentrations of all chemical species at the state of thermodynamic equilibrium,

from elements or compounds selected as input, using the Gibbs energy minimization method. The following databases were used: FToxid solution (FToxid53Soln.sda) – which contains the liquid slag phase (slagA) –, FSstel (FSstel53base.cdb) – for the liquid Fe-alloy phase – and FACT53 (FS53Base.cdb) – containing gases and minerals.

The equilibrium state due to interactions between mould slag and liquid metal, at 1600°C, was determined for a particular slag with composition: 15%  $\text{Al}_2\text{O}_3$ , 35% CaO and 50%  $\text{SiO}_2$  (binary basicity 0.7). A proprietary mould powder composition optimized for billet casting was used as basis for this formulation. The liquid iron contained only Al and O as dissolved constituents (Fe balance). Fe-Al-O alloys with three Al (and correspondingly O) values, i.e. 0.1, 0.01 and 0.001 (wt.%), were used.

The oxygen values that match the selected aluminium contents in iron were found with the help of an equilibrium determination and are equivalent to those of an Al-killed steel (without  $\text{Al}_2\text{O}_3$ ). The resulting pairs (along with other values) were plotted in a diagram O versus, Al, Figure 1. They emphasize the complexity of the data / steel mathematical model of the database used, and are very far from those of the simple linear relationship given by a single equilibrium constant.



**Figure 1** – Oxygen versus aluminium dissolved in liquid iron, in equilibrium with solid alumina, at 1600°C, calculated through computational thermodynamics and used as input for all determinations

For the reason that a slag/metal *mass balance* is involved, it is necessary to establish the relative mass amounts of both liquids – what can be seen as the ‘powder consumption’ in real process. The *nominal* powder consumption is a measure of the amount of liquid slag infiltrating the mould/strand channel in some useful unity e.g. kilograms of powder per tonne of steel. This is an adequate way to monitor the cost and can be converted to kilograms of powder per square metre of mould, which is a measure of the liquid *lubrication power* – a valuable process control parameter. Nevertheless, for the simulation the first of these variables would be adequate. However, since not all slag nor the whole steel mass take part of the reactions, it is



necessary to establish an *effective* slag/metal mass ratio, S/M. Nakano *et al.* [9] cited the value 0.45 (kg/t) but, since numeric values are quite seldom in the literature, this causes a simulation difficulty. In order to overcome successfully this inconvenience, equilibrium states were determined to S/M ranging from 0.1 to 10 (kg/t).

The reoxidation of Al by the atmosphere is not possible here due to the simple fact that there is no oxygen outside the slag or liquid metal initially in the simulation; therefore, even the O<sub>2</sub> of the atmosphere is coming from the slag or the melt.

The mass percentage increase of the Al<sub>2</sub>O<sub>3</sub> content of the slag potentially attainable is named here  $\Delta\text{Al}_2\text{O}_3$ . The  $\Delta\text{Al}_2\text{O}_3$  was calculated for different liquid slag/metal ratio, S/M, and Al contents by means of:

$$\Delta\text{Al}_2\text{O}_3 = \% \text{Al}_2\text{O}_3_{\text{ final}} - \% \text{Al}_2\text{O}_3_{\text{ initial}} \quad (\text{Equation 2})$$

Since this  $\Delta\text{Al}_2\text{O}_3$  is the pick-up value due to *chemical* interactions at the metal-slag interface, it will be reached only under favorable kinetic conditions. They can be related to e.g. interface reactions *rate*, *diffusion* boundary layers at the interface and slag and metal *convection*.

There is a theoretical *maximum* value for  $\Delta\text{Al}_2\text{O}_3$ . This limiting value, according to Equation 1, and, for this particular slag, is attained when there is no more SiO<sub>2</sub> to be consumed.

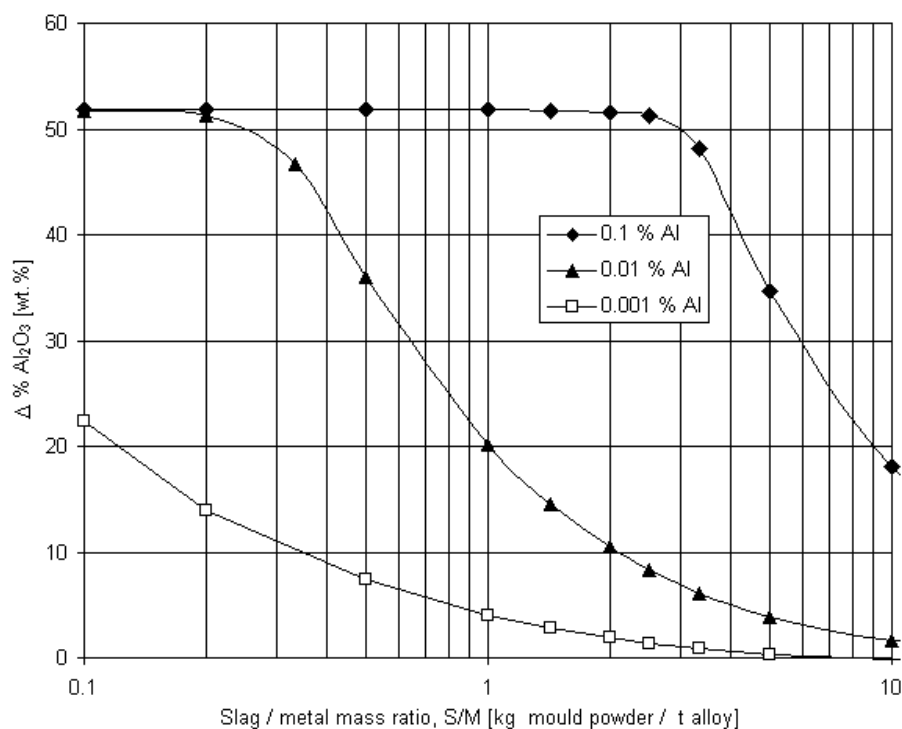
### 3 RESULTS AND DISCUSSION

At Figure 2 it can be seen that the  $\Delta\text{Al}_2\text{O}_3$  increases when slag/metal ratio decreases, for all Al contents. The limiting  $\Delta\text{Al}_2\text{O}_3$  value – around 50% for these conditions – tends to be reached more easily for decreasing slag/metal ratio and liquid metal of higher Al content. Taking the range 0.01%-0.1% Al (i.e. 100 ppm-1000 ppm Al) as embracing the possible aluminium contents of most commercial carbon steels, it can be seen that the possible  $\Delta\text{Al}_2\text{O}_3$  values will be limited between these two lines.

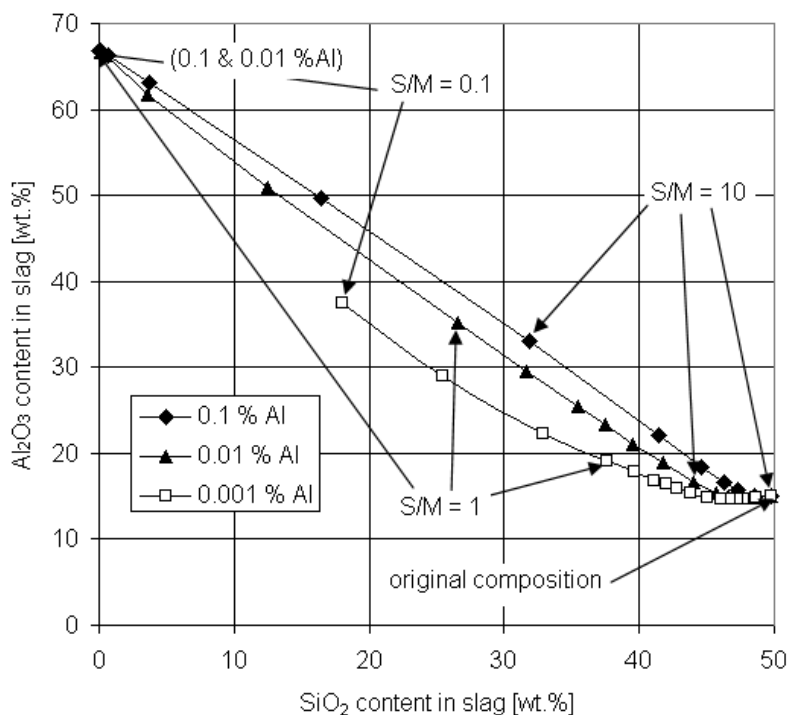
The decreasing of (SiO<sub>2</sub>) content (for simultaneous S/M decrease and Al increase) was foreseen by thermodynamics, according to Equation 1. Moreover, the slag/metal ratio and the Al content influence the *minimum* attainable (SiO<sub>2</sub>) content (at equilibrium), according to Figure 3.

It was observed that (CaO) content remains almost constant in the slag; as a consequence, the chemical interaction takes place solely between (SiO<sub>2</sub>) and (Al<sub>2</sub>O<sub>3</sub>). As an end result, the binary basicity increases significantly. On the other hand, the determined ternary basicity stays at an almost fixed value.

The higher the alumina content, the higher the viscosity of the liquid slag. Moreover, the increase in alumina content tends to cause solid phases precipitation – which by the way determines a further increase in viscosity. To the simulations conditions of the present work the precipitation of solid compound CaAl<sub>4</sub>O<sub>7</sub> was observed. For simple systems like this, solid compounds which precipitate when alumina content increases can be determined also by CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagrams.



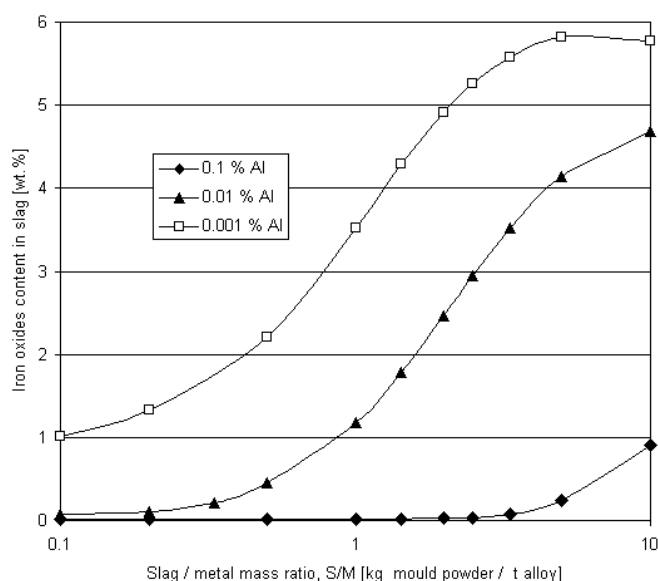
**Figure 2.** Potential alumina pick-up determined through computational thermodynamics for different slag/metal ratios and initial Al contents, at 1600°C



**Figure 3.**  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  relationship in the liquid slag as a function of initial Al and slag/metal ratio (S/M), at 1600°C

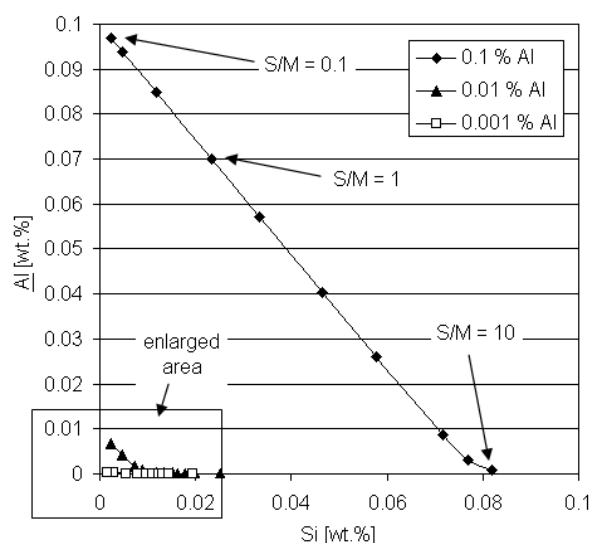
The analysed slag also shows that iron oxides  $\text{Fe}_2\text{O}_3$  and (mainly)  $\text{FeO}$  as slag constituents appear when the Al content decreases, Figure 4. This is especially true for higher S/M ratios. The increase in the total iron oxides content in slag was found

to be clearly connected to an increase in the  $\underline{Q}$  level. The oxidation power of the slag is therefore mainly a function of the S/M ratio.

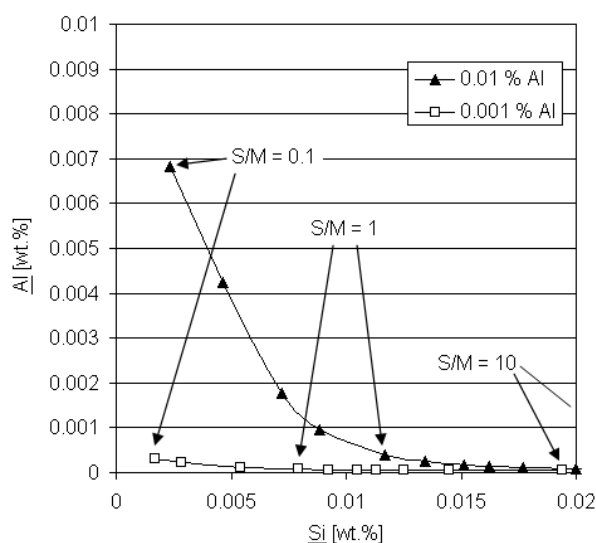


**Figure 4.** Iron oxides content in slag as a function of slag/metal ratio and initial  $\underline{Al}$ , at 1600°C

The interrelationship between  $\underline{Si}$  and  $\underline{Al}$  can be seen at Figure 5 as a function of slag/metal ratio and  $\underline{Al}$ . It will be accurate for the case of reactions being the sole responsible for the increase in  $(Al_2O_3)$  – provided a favourable kinetics is there.



**Figure 5(a).**  $\underline{Al}$ - $\underline{Si}$  relationship in liquid metal as a function of initial  $\underline{Al}$  and S/M, at 1600°C.



**Figure 5(b).** Enlarged area marked on Figure 5(a).

## 4 CONCLUSIONS

Mould powder chemical composition varies greatly as a result of alumina absorption and steel/liquid mould slag interfacial chemical reactions. Considering that even a low increase in the alumina content can alter profoundly the viscosity of the mould slag, it is important to forecast such observable fact.

The method described in the present work can be used to evaluate, through computational thermodynamics, the simultaneous effects of  $Al$  and liquid slag/metal ratio, S/M, on the  $Al_2O_3$  pick-up by slag/metal chemical interactions during the continuous casting process.

For the particular mould powder composition of this work the chemical interaction can be of considerable extent when the combination low S/M with high aluminium content in the liquid metal are combined in the continuous casting operation.

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