

# INVESTIGATION OF FLUORINE-FREE MOULD FLUXES PROPERTIES <sup>1</sup>

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## **Abstract**

Mould powders or mould fluxes are synthetic slags used to lubricate the mould during continuous casting of steel. Utilisation of fluorine-containing raw materials brings some advantages related to a stable continuous casting process and to production of clean steels. However, fluorine is undesirable from the environmental point of view due to the following reasons: (i) fluorides evolve easily from slags, producing health-injurious gaseous substances (such as fluoridric acid); (ii) corrosion of machinery; (iii) problems related to storage and utilisation of solid waste. In the present work, mould fluxes properties are investigated with the help of computational thermodynamics.

**Key words:** Continuous casting; Mould powders; Fluorine; Fluorspar.

## INVESTIGAÇÃO DAS PROPRIEDADES DE PÓS FLUXANTES LIVRES DE FLÚOR

## **Resumo**

Pós fluxantes são escórias sintéticas utilizadas para lubrificar o molde durante o lingotamento contínuo de aço. A utilização de matérias-primas contendo flúor traz diversas vantagens, relacionadas a um processo de lingotamento contínuo estável e à produção de aços limpos. No entanto, o elemento flúor é indesejável do ponto de vista ambiental devido às seguintes razões: (i) emissões de flúor acontecem facilmente a partir de escórias, produzindo substâncias gasosas prejudiciais à saúde (tais como ácido fluorídrico); (ii) corrosão da máquina de lingotamento contínuo; (iii) problemas de armazenamento de resíduos sólidos. No presente trabalho, a aplicação da termodinâmica computacional no desenvolvimento de pó fluxantes é analisada.

**Palavras-chave:** Lingotamento contínuo; Pós fluxantes; Flúor; Fluorita.

<sup>1</sup> *Technical contribution to 64<sup>th</sup> ABM Annual Congress, July, 13<sup>th</sup> to 17<sup>th</sup>, 2009, Belo Horizonte, MG, Brazil.*

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## 1 INTRODUCTION

Mould powders or mould fluxes are synthetic slags used to lubricate the mould during continuous casting of steel.<sup>(1)</sup> The chemical composition of industrial mould powders lies in the following ranges:<sup>(2)</sup> 35% – 45% SiO<sub>2</sub>; 25% – 35% CaO; 5% – 15% Al<sub>2</sub>O<sub>3</sub>; 2% – 7% MgO; 15% – 25% CaF<sub>2</sub>; 5% – 15% Na<sub>2</sub>O; 5% – 15% C.

At Figure 1<sup>(2)</sup> there is a schematic diagram of a copper mould containing mould powder and steel during solidification process. From this diagram the five basic functions of mould powders can be explained:

- lubrication at mould/strand interface, due to the fusion of mould powder;
- control of horizontal heat transfer, since a solid slag film is formed at mould/strand interface;
- thermal insulation, i.e. heat losses are avoided by mould powder layers above liquid steel;
- protection of liquid steel from atmosphere;
- inclusions absorption from liquid steel through liquid slag.

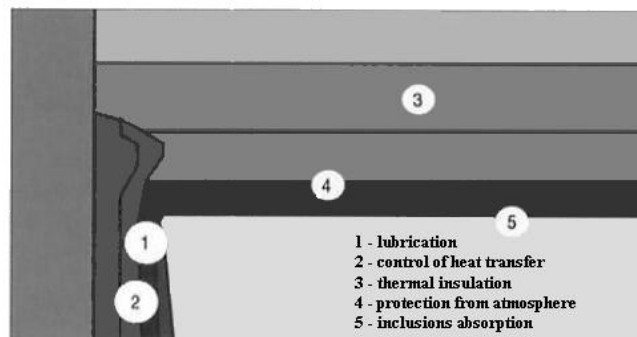


Figure 1 – Schematic drawing of the various layers formed in the mould.<sup>(2)</sup>

The main function of a mould powder is the creation of a lubricant film at interface mould/strand.<sup>(3)</sup> Lack of lubrication at this interface can cause sticker breakouts. Moreover, lubrication conditions explain the majority of ingots surface defects; mould powders must be selected considering this property.<sup>(4,5)</sup>

Some of the raw materials used in industrial mould powders production are: wollastonite, bauxite, fly ash, etc. Moreover, fluorspar (CaF<sub>2</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) are normally used to decrease viscosity and *liquidus* temperature.<sup>(2)</sup>

Utilisation of fluorine-containing raw materials brings some advantages related to a stable continuous casting process and to production of clean steels, such as:<sup>(2)</sup>

- the decrease (at *liquidus* temperature) of the slag viscosity (system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) – what promotes the necessary lubrication at mould/strand interface;
- the increase of the crystallization tendency (very important factor to peritectic steel slabs casting);
- the decrease of the driving force for redox reactions between liquid steel and liquid mould powder (slag).
- the positive behaviour regarding absorption of inclusions from steels, such as Al<sub>2</sub>O<sub>3</sub>(s).

However, fluorine is undesirable from the environmental and health points of view due to the following reasons:<sup>(6)</sup>

- it evolves easily from slags, producing health-injurious gaseous substances (such as fluoridric acid);
- it causes increased wear of refractories and corrosion of machinery;
- it creates problems for storage and utilisation of solid waste.

The high amount of fluorspar and sodium carbonate in industrial mould powders implies in an increase of fluoride content in water of the secondary cooling and at same time in the lowering of its pH value. Fluorides can be emitted into the gaseous phase above mould according to Equations 1 and 2.<sup>(2)</sup>



The weak bounds of gaseous fluorides – NaF(g), SiF<sub>4</sub>(g) – promote reactions with the residual moisture of mould powders, Equations 3 and 4. These reactions form HF(g).



Gaseous compounds which contain fluorine are formed when mould powder is heated by liquid steel. It is important to note the majority of gaseous compounds which contain fluorine are transported together with liquid slag at mould/strand gap. Then, at mould exit, these compounds react with the superheated steam of the secondary cooling; in this way, the formation of HF(g) according to Equations 3 and 4 is accelerated. NaF(g) formation starts at 456°C, and SiF<sub>4</sub>(g) formation starts at 857°C.<sup>(2)</sup>

#### *Possibilities to replace fluorine*

It is clear there is steady interest in fluorine content reduction methods. Naturally the good properties of a fluorine-containing mould powder must be maintained by its substitute.

To diminish the amount of fluorspar in mould powders, a possibility is to increase Al<sub>2</sub>O<sub>3</sub> content. At pseudo-ternary system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> it can be seen that, starting with wollastonite, Al<sub>2</sub>O<sub>3</sub> addition (e.g. bauxite addition) decreases *liquidus* temperature.<sup>(7)</sup>

A core result of the aforementioned European project<sup>(8)</sup> is that Li<sub>2</sub>O has a strong fluxing ability and can therefore be used as a fluorine substitute. However, the melting and solidification behaviour show differences with respect to the standard powders. This influences the performance of powders during continuous casting in terms of lubricating ability and steel solidification conditioning.

Schulz *et al.*<sup>(2)</sup> researched mixtures with lower fluorides emission potential, with the replacement of fluorine and/or sodium by lithium; the replacement of sodium is justified since in this case the formation of NaF(g) is avoided. Lithium utilisation in mould powders presents some advantages: (i) Li<sub>2</sub>O causes significant decrease of *liquidus* temperatures and of viscosity; (ii) with Li<sub>2</sub>O slags with better inclusions absorption potential can be produced; (iii) Li<sub>2</sub>O is thermodynamically more stable than other options, such as Na<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub>.

When using boron as substitute of fluorine, according to Schulz *et al.*<sup>(2)</sup> there is a risk of redox reactions involving dissolved elements in liquid steel – such as

aluminium and silicon –, what would cause boron pick-up. Furthermore,  $B_2O_3$  could cause a viscosity increase in mould fluxes.

Regarding sodium-containing raw materials, it is an interesting material to substitute fluorspar, since  $Na_2O$  decreases viscosity, liquidus temperature and it also promotes inclusions absorption (though inclusions absorption when using  $Li_2O$  is better). It is important to observe that increasing  $Na_2O$  content to compensate for fluorine content diminution is possible up to 20% only, due to precipitation of the solid phase nefeline ( $Na_2O \cdot Al_2O_3 \cdot 2 SiO_2$ ). Frequently  $Na_2O$  content in industrial mould powders is high ( $>10\%$ ).<sup>(2)</sup>

Wen *et al.*<sup>(9)</sup> developed fluorine-free mould powders for peritectic steel slab casting. Regarding conventional mould powders, horizontal heat transfer control is obtained by control of crystallization of the solid phase cuspidine. To produce fluorine-free mould powders, it is necessary to develop a composition which simultaneously diminishes viscosity and crystallizes in a way that control of heat transfer is obtained. The raw material used to substitute fluorine was ferrovanadium production slag, a material which presents a high content of  $TiO_2$  and a high tendency to crystallize. Thus, the proposal of Wen *et al.* was to use slags of the system  $CaO-SiO_2-TiO_2$ , since in this way there is precipitation of solid phases containing titanium. It was showed titanium effect is similar to fluorine effect, to certain compositions ranges, since crystallization is also promoted at solid slag film.

### Objective

The objective of the present work is to evaluate computational thermodynamics utilisation as a tool for the development of fluorine-free mould powders.

## 2 METHODOLOGY

Regarding development of fluorine-free mould powders, three problems which involve thermodynamics were studied in the present work:

- *liquidus* temperature reduction with increase of  $Al_2O_3$  content;
- mould fluxes melting behaviour;
- chemical interactions between molten mould powder and liquid steel.

The problems of the present work were dealt with the help of the computational thermodynamics commercial package *FactSage* version 5.5. This software contains the module *Equilib*, which is the Gibbs energy minimization workhorse of *FactSage*.<sup>(10)</sup> This module calculates the concentrations of chemical species at the state of thermodynamic equilibrium from elements or compounds selected as input. The following databases were used in the present work:<sup>(11)</sup> FToxid solution database (FToxid53Soln.sda), FSstel (FSstel53Base.cdb) and FACT53 (FS53Base.cdb). Beside module *Equilib* it was also used the module *Phase Diagram*, to construte equilibrium diagrams.

## 3 RESULTS AND DISCUSSION

### 3.1 *Liquidus* Temperature Reduction with Increase of $Al_2O_3$ Content

One way to reduce  $CaF_2$  amount in mould powders compositions is to increase  $Al_2O_3$  content, to obtain lower *liquidus* temperatures.

In a research project involving different European institutions<sup>(8)</sup> a good surface quality of as-cast strands (billet casting) with spring and bearing steels was

accomplished during experiments using mould powders or granules with a composition located closely to the eutectic of the pseudo-ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ , at  $1.266^\circ\text{C}$ , combined with a more glassy solidification. When the composition of the powder is moved towards the wollastonite precipitation, the grinding index deteriorates due to a higher viscosity and a more crystalline solidification of the molten mould powder.

Starting from pseudowollastonite, which is the synthetic correspondent of wollastonite  $\text{CaO}\cdot\text{SiO}_2$  (one of the main raw materials for the industrial production of mould powders), with  $\text{Al}_2\text{O}_3$  addition to the system  $\text{CaO-SiO}_2$  it is possible to obtain *liquidus* temperature reduction, according to Figure 2.<sup>(7)</sup> The melting temperature of pure wollastonite is  $1.548^\circ\text{C}$ ; with  $\text{Al}_2\text{O}_3$  addition the liquidus temperature decreases up to  $1.265^\circ\text{C}$ , at the region near grossularite ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{SiO}_2$ ).<sup>(2)</sup>

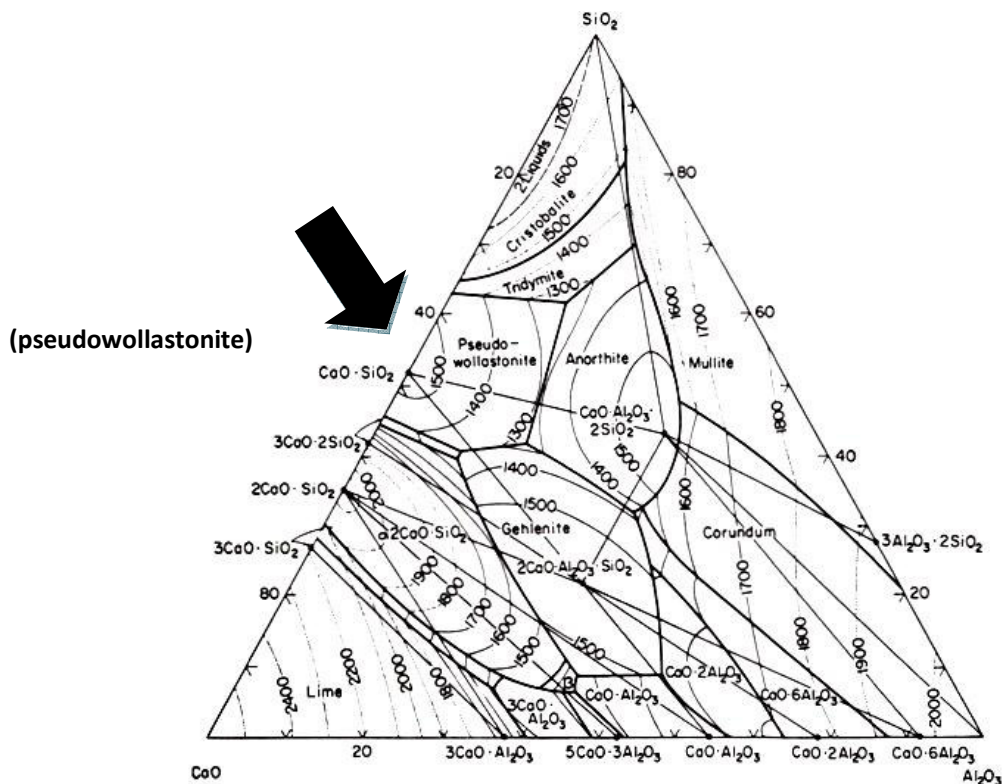


Figure 2 -  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  system.<sup>(7)</sup>

At  $1.300^\circ\text{C}$  it can be seen at Figure 3, calculated through *FactSage*, the pseudo-ternary system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ . Starting from pseudowollastonite and adding  $\text{Al}_2\text{O}_3$ , the slag liquid proportion increases up to 100% (liquid slag region is represented as "s"). However, when  $\%\text{Al}_2\text{O}_3$  is higher than  $\sim 14\%$  (considering the molar ratio  $\text{CaO/SiO}_2 = 1$ ) occurs the precipitation of the solid phases anorthite and gehlenite. Thus, the precipitation of these phases imposes a limit to  $\text{Al}_2\text{O}_3$  addition.

Evidently this kind of analysis is simplified, since it considers only three components ( $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ). Mould powders are complex slags; in this context, computational thermodynamics could be useful, as is showed in the following.

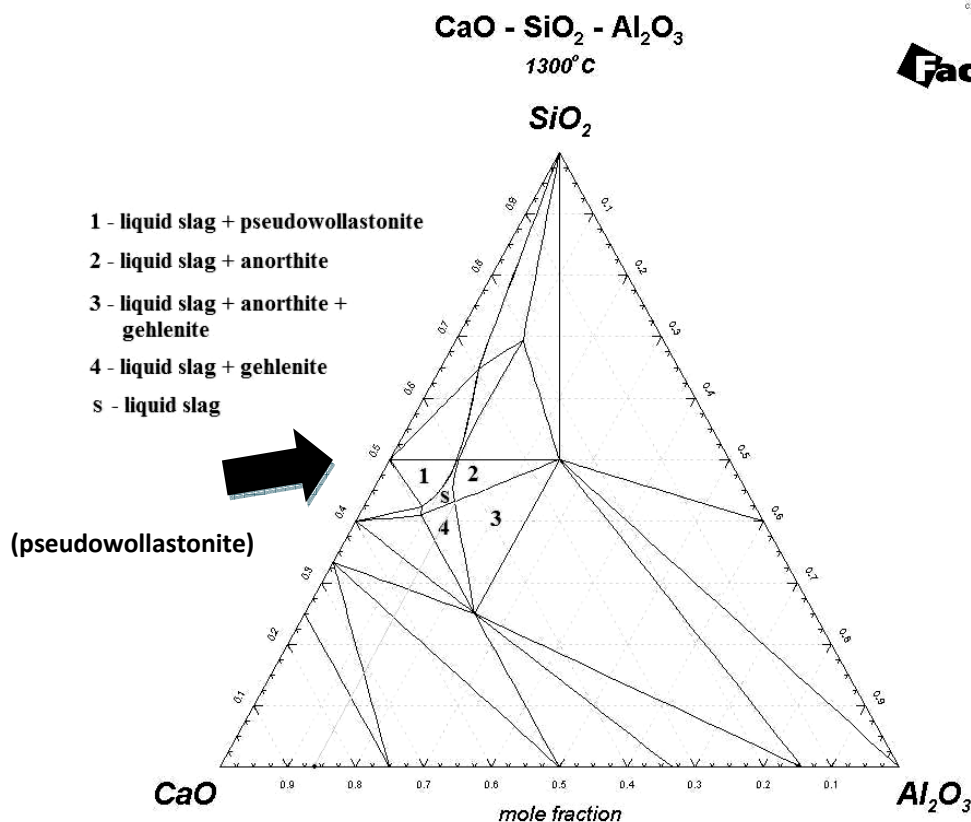


Figure 3 - CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> calculated by FactSage, at 1300 °C.

### 3.2 Mould Fluxes Melting Behaviour

The recipe (mixture of raw materials) named in the following as “Standard” is the mould powder Accutherm ST-SP/512SV-DS, produced by Stollberg do Brasil and used in steelworks plants. Derived from “Standard” three new recipes which do not contain fluorspar (R1, R2 and R3), using Brazilian raw materials, were elaborated at Stollberg do Brasil, as described in the work of Klug *et al.*<sup>(12)</sup>.

Table 1 – Chemical compositions of the recipes analysed in the present work

Mixture	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	F	Li <sub>2</sub> O
Standard	35.43	25.30	2.95	12.27	0.51	2.57	3.84	1.55	3.87	-
R1	33.80	22.78	4.75	10.79	0.35	1.91	7.99	1.59	0.48	-
R2	35.61	24.03	4.42	9.48	0.32	1.54	6.91	1.13	0.51	0.33
R3	38.39	25.44	4.46	7.85	0.23	0.96	6.38	0.73	0.62	0.36

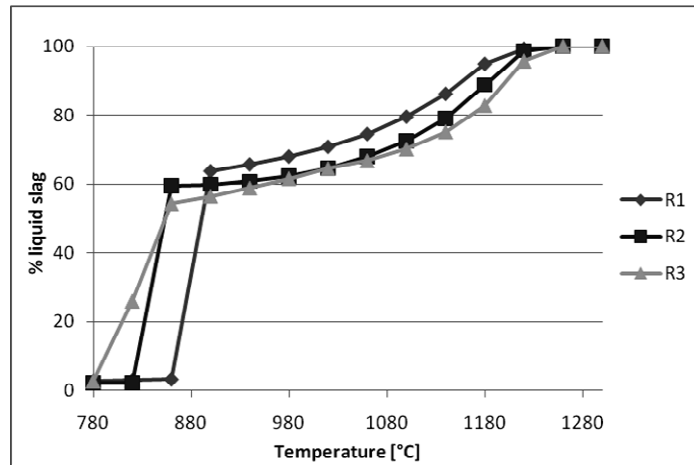
Regarding melting behaviour of mould powders, it has a major impact on the casting conditions stability and strand surface quality.<sup>(13)</sup>

The melting behaviour of a synthetic slag, such as a mould powder, can be evaluated through a heating microscope and also by computational thermodynamics.

In a recent work<sup>(14)</sup> experimental data from a heating microscope were correlated with results obtained by the commercial package *FactSage 5.5*; work main objective was to evaluate the behaviour of ashes generated after the injection of pulverized coal (PCI technique) inside a blast furnace.

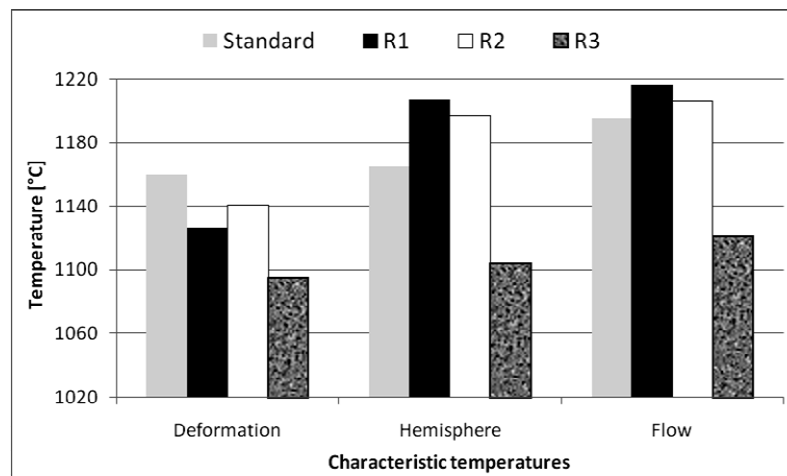
Computational thermodynamics was applied in the present work to evaluate melting behaviour of the recipes without fluorspar (R1, R2 and R3). The chemical equilibrium was calculated by *FactSage 5.5* at several temperatures (and  $pO_2 = 0.21$  atm). In this way, the phases and their proportions at each temperature were determined. At Figure 4 recipes R1, R2 and R3 liquid slag fractions, as function of temperature, are showed.

As it can be seen in Figure 4, R3 has a higher amount of liquid slag at lower temperatures ( $T < 850^\circ\text{C}$ ). On the other hand, R1 gets a significant amount of liquid slag only when temperature is above  $850^\circ\text{C}$ . R2 presents an intermediate behaviour.



**Figure 4** – Liquid slag percentage as function of temperature. Recipes R1, R2 and R3 (computational thermodynamics results).

At Figure 5 it can be seen heating microscope results, extracted of the work of Klug *et al.*<sup>(12)</sup>



**Figure 5** – Characteristic temperatures. Recipes Standard, R1, R2 and R3 (heating microscope results).

Despite timeless nature of a thermodynamic analysis, some correlations can be established between *FactSage* results and heating microscope characteristic temperatures.

Eccentric behaviour of the mixture R3 can be explained by the existence of different solid phases (which in turn present different refractorinesses). Depending on the chemical composition, there are different phases and proportions of phases. For example, R3 has higher SiO<sub>2</sub> content and lower Al<sub>2</sub>O<sub>3</sub> content than Standard, R1 and R2. This fact could explain the easier fusion of the mixture R3.

For example, considering 100 g of mould powder at 780 °C (~ 100% solid, see Figure 4) the three main solid phases according to *FactSage* are (there are others in lower amounts):

- R1: Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (45.43 g), Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> (10.81 g), CaMg<sub>2</sub>Al<sub>16</sub>O<sub>27</sub> (10.6 g);
- R2: Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (39.49 g), Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> (17.66 g), Mg<sub>4</sub>Al<sub>10</sub>Si<sub>2</sub>O<sub>23</sub> (7.65 g);
- R3: Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (36.47 g), Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (15.63 g), CaMgSi<sub>2</sub>O<sub>6</sub> (10.7 g).

At 780 °C it can be seen the main phase is Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (NC<sub>2</sub>S<sub>3</sub>) for all the analysed mixtures. The high quantity of NC<sub>2</sub>S<sub>3</sub> can be explained by the relatively high sodium content of the studied mould powders.

It is interesting to note the second main phase of R3 at 780 °C is the solid phase grossularite (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>). In a pseudo-ternary CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram,<sup>(7)</sup> grossularite has a lower melting point (1.265 °C). However, a computational thermodynamics analysis is more appropriate than an analysis which uses only a pseudo-ternary phase diagram, since a mould powder has several components (CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, etc.). In this way, the interactions of all components of the mixture can be simultaneously determined.

Starting from ambient temperature, when the temperature is raised several chemical transformations take place, since the phases originally present at mould powders raw materials suffer transformations depending on temperature.

According to Marschall *et al.*<sup>[13]</sup> sodium calcium silicates such as Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (NC<sub>2</sub>S<sub>3</sub>) are formed during the heating process of mould powders. These crystals are developed by reactions of sodium and calcium containing phases. The conclusions of these researchers were based on a series of experimental investigations, such as DTA including thermogravimetry, x-ray diffraction of annealed samples, reflected light microscopy, scanned electron microscopy, and hot stage microscope.

When the temperature is further raised to 980 °C the liquid slag fraction is higher than 60% (see Figure 4) and there is no more NC<sub>2</sub>S<sub>3</sub>. At this temperature the three main solid phases are:

- R1: Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> (21.36 g), Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub> (2.51 g), Fe<sub>2</sub>O<sub>3</sub> (1.9 g);
- R2: Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> (27.61 g), Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (2.66 g), Fe<sub>2</sub>O<sub>3</sub> (0.69 g);
- R3: Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> (28.61 g), Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (3.03 g), CaSiO<sub>3</sub> (1.47 g).

According to literature several minerals can be formed during heating of mould powders:<sup>(13)</sup> cuspidine Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>, wollastonite CaSiO<sub>3</sub>, anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, gehlenite CaAl<sub>2</sub>SiO<sub>7</sub>, carnegieite NaAlSiO<sub>4</sub>, pectolite NaCa<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>(OH), Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> (NC<sub>2</sub>S<sub>3</sub>), akermanite Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> and villiaumite NaF. Cuspidine is the most important phase (in the case of mould powders which contain usual fluorine contents).

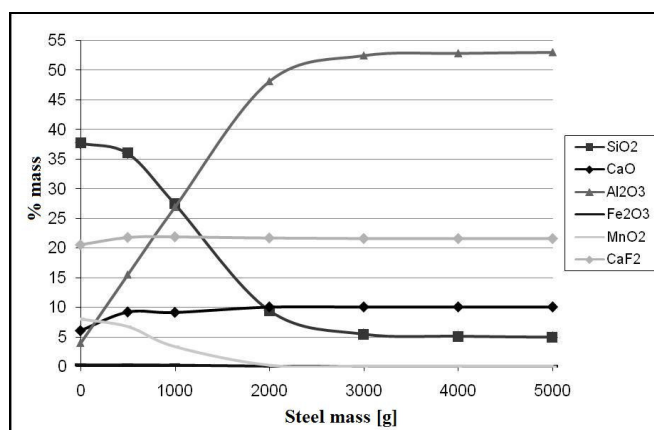
### 3.3 Chemical Interactions Between Molten Mould Powder and Liquid Steel

Besides melting behaviour, computational thermodynamics can also be applied to determine chemical interactions between liquid slag and liquid steel.<sup>(15)</sup>



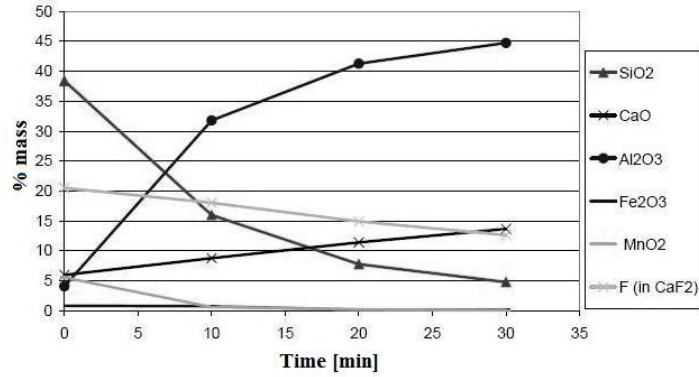
After melting, in contact with the molten steel, the mold powder forms a slag which changes its chemical composition as function of time. Because of these changes some slag properties are altered, *e. g.* viscosity. These chemical transformations, which occur at the liquid slag / liquid metal interface, have also implications on the friction force between solidified shell and the copper mold [3]. Frictional forces were measured at plant [5] and it was concluded that alumina absorption by mold flux slags had an important effect on the frictional forces, since the mineralogical constitution of the analyzed plant slags was a function of their alumina content.

Thermodynamic simulations were done considering the composition of the proprietary mold flux Accutherm Al4D, from Stollberg, in contact with a TRIP steel. Several thermodynamic equilibria were calculated for a fixed amount (100 grams) of the mold flux and increasing amount of the TRIP steel. The slag composition as “oxides”, as a function of steel amount, can be seen at Figure 6. All the calculations were done at 1.530 °C. The zero value for steel mass means the original composition of the mold flux. No oxygen was added to the system, *i. e.* the simulations were done under severely reducing conditions. This consideration makes sense since the carbon content of the mold fluxes creates a reducing atmosphere on the top of the steel pool.



**Figure 6** - Variation in liquid slag chemical composition calculated with FactSage software at 1.530°C.

Results from an experimental analysis done to assess the kinetic behavior of reactions between the same mold powder Accutherm Al4D and the TRIP steel used in the aforementioned simulation are shown in the literature<sup>(1)</sup> (Figure 7). The experiments – at laboratory scale – were done in the temperature range of 1525-1.535°C. Samples were taken at time intervals starting from the point where the mold flux was put in contact with the molten steel (time zero). The evolution of the slag composition as a function of time was evaluated through chemical analysis. The great increase in alumina content of the slag – with the simultaneously diminishing amount of silica – can be clearly seen.

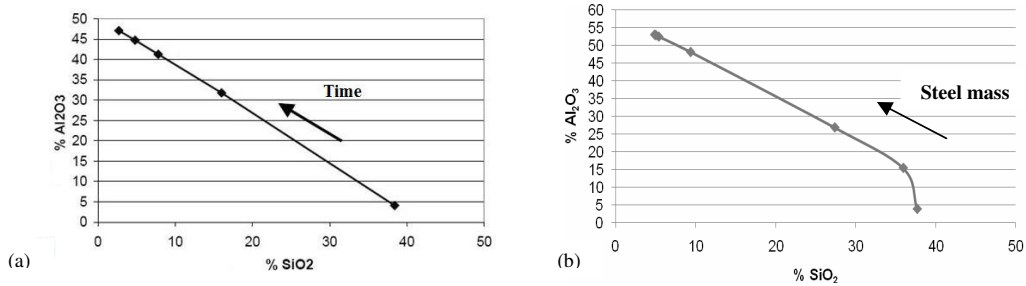


**Figure 7** - Variation in liquid slag chemical composition with time (experimental work).<sup>(3)</sup>

From a comparison of the theoretical with the experimental results, a good correspondence is found. This is actually an astonishing conclusion, since results shown in Figure 1 are from a thermodynamic (timeless) analysis, while Figure 2 displays experimental results, directly coupled with the velocity of reactions (rate phenomena). Thus, they are of an absolutely different nature.

The following Figure 8 is a compilation of data from Figures 1 and 2. Figure 3(a) contains the results of the aforementioned experimental work<sup>(3)</sup> and Figure 3(b) displays the seven points showed at Figure 6 (calculated by *FactSage*).

Given a certain allowance, these results suggest that computational thermodynamics can be used to evaluate the chemical interactions between mold flux and steel as a function of time.



**Figure 8** - %Al<sub>2</sub>O<sub>3</sub> versus % SiO<sub>2</sub> content: (a) results of an experimental work;<sup>(1)</sup> (b) results from a thermodynamic determination (present work).

## 4 CONCLUSIONS

Computational thermodynamics can be used as a tool to the development of fluorine-free mould powders. The phases of some recipes which do not contain fluorspar (R1, R2 and R3 in the present work) and their proportions at different temperatures were determined through *FactSage* commercial package. Results obtained from thermodynamics were correlated with heating microscope results and others experimental results from literature.

The chemical interactions between a proprietary mold flux in contact with a TRIP steel were evaluated, with the help of the computational thermodynamics. The results and discussions of the present paper suggest that computational thermodynamics can be used to predict the complex chemical interactions of mold fluxes when in contact with liquid steel.

## Acknowledgements

The authors Jeferson Leandro Klug and Aline Lima da Silva wish to express their gratitude to the Brazilian Science and Technology National Council (CNPq) for the granted scholarships.

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