



# USING THERMOCHEMICAL EQUILIBRIA TO STUDY SLAGS OF THE CaO-SiO<sub>2</sub>-CrO<sub>x</sub>-MgO SYSTEM<sup>1</sup>

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#### Abstract

Metallurgical slags may be used – and studied – under greatly different conditions: from that of atmospheric air to the strongly reducing conditions of smelting furnaces. For chromium-containing slags, changes in oxygen pressure noticeably affect its composition, because of the multivalent oxidation states of the Cr-ions. Aim of the current paper is to evaluate the addition of periclase into slags of the system CaO-SiO<sub>2</sub>-CrO<sub>x</sub>. In order to carry out the investigation, slags of the Ca-O-Cr-Si-Mg quinary system were studied with the help of computational thermodynamics, at 1.2 binary basicity and temperature of 1600°C. Two conditions were especially motivating: chromium oxide-saturated and non-saturated slags.

Keywords: Slags; Stainless steel; Computational thermodynamics.

## USANDO EQUILÍBRIOS TERMOQUÍMICOS PARA ESTUDAR ESCÓRIAS DO SISTEMA CaO-SiO<sub>2</sub>-CrO<sub>x</sub>-MgO

#### Resumo

Escórias metalúrgicas podem ser utilizadas – e estudadas – sob condições muito diferentes: desde aquela ao ar, até as fortemente redutoras, utilizadas em fornos para redução de minérios. Para escórias contendo cromo, alterações na pressão de oxigênio afetam sensivelmente a sua composição, por causa dos múltiplos estados de oxidação dos íons do cromo. O objetivo do presente trabalho é avaliar a influência da adição de periclásio em escórias do sistema CaO-SiO<sub>2</sub>-CrO<sub>x</sub>. De ordem a executar esta investigação, escórias do sistema quinário Ca-O-Cr-Si-Mg foram estudadas com a ajuda da termodinâmica computacional, com basicidade binária 1,2 e temperatura de 1.600°C. Duas condições foram especialmente interessantes: escórias saturadas com óxido de cromo e escórias insaturadas.

Palavras-chave: Escórias; Aços inoxidáveis; Termodinâmica computacional.

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#### 1 INTRODUCTION

The word *slag* is used to describe the nonmetallic liquid solution consisting mainly of metal oxides, silicates, aluminates, etc. that floats on the top of molten metals, resulting from the smelting and refining operations. Even though it can be mixed with solid minerals, the word slag still applies.

Metallurgical slags are used basically to remove impurities, as a carrier (or source) for reactants, as shield against the oxygen from atmosphere and as thermal insulator.

From the point of view of chemical thermodynamics it is important to recognize that the *liquid* (more then one can exist, though) as well as each of the solid compounds and solutions is classified as a *phase*. In this work, the word *slag* will be used to designate the *liquid* phase only.

As pointed out by Rosenqvist,<sup>(1)</sup> slags may be used – and studied – under greatly different conditions: from that of atmospheric air to the strongly reducing conditions of smelting furnaces. For slags consisting only of "white" oxides SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO these changes in oxygen partial pressure do *not* noticeably affect the composition of the slag. This attribute can be primarily related to the absence of oxides of different valencies in these metal-oxide systems. For slags containing manganese, chromium, titanium, and iron oxides, however, considerable changes may occur.

Metal chromium is especially important for stainless steels. The conditions inside the metallurgical vessels used for the production of these steels – using either the AOD or the EAF route – can vary from oxidant to fairly or strongly reducing. And, in addition to those of Cr, at least oxides of the following atomic species: Ca, Si, Al, Mg, Mn can be found in the slag due to the charged materials,

As already cited, chromium is a multivalent metal and it was demonstrated experimentally that this metal can show *several* oxidation states.<sup>(2)</sup>

The most common oxidation state within a large temperature-composition range is the  $Cr^{3+}$ ; yet, several oxidation states are possible:  $Cr^{2+}$ ,  $Cr^{3+}$ ,  $Cr^{6+}$ , and probably  $Cr^{4+}$  and  $Cr^{5+}$  as well. Under strongly reducing conditions, and at high temperatures, however, substantial proportions of the chromium are present in the divalent state.<sup>(3)</sup>

In a series of three articles Degterov and Pelton<sup>(4-6)</sup> closely examine the inclusion of Cr-oxides in a wide database of optimized thermodynamic properties of oxide systems. The data are now part of the FactSage databases – the computational thermodynamic tool used in the present work.

Aim of the present work is to evaluate theoretically the addition of periclase into slags of the system CaO-SiO<sub>2</sub>-CrO<sub>x</sub>.

In order to carry out the investigation, slags of the Ca-O-Cr-Si-Mg quinary system will be studied with the help of computational thermodynamics, at 1.2 binary basicity and temperature of 1600°C. Two conditions are especially motivating: chromium oxide-saturated and non-saturated slags.

Some (binary to quaternary) subsystems are mentioned or analyzed first, in order to clarify some significant aspects of the investigation.

It must be kept in mind, however, that all considerations presented here will be limited to the thermodynamic equilibrium aspects. While recognizing that kinetics may be equally important, the thermodynamic approach does, however, establish the direction and the *limiting* conditions for the reactions.

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## **2 SOFTWARE AND THERMODYNAMIC DATA**

The equilibrium state for every system under study in the present work was determined by the Gibbs energy minimization method using the *Equilib* module of the *FactSage* software (version 5.5) – software is described elsewhere by Bale *et al.*<sup>(7)</sup>

The following databases were employed:

- FToxid solution database (FToxid53Soln.sda): contains oxide solutions evaluated and optimized by the FACT group; one of these is the molten slag phase (SLAGA), which contains the fully optimized CaO-SiO<sub>2</sub>-CrO-Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system. The molten slag phase is represented correspondingly to the modified quasichemical model, which is described in the literature by Pelton and Degterov.<sup>(4)</sup>
- FToxid compound database (FToxid53Base.cdb): contains 247 stoichiometric solid and liquid oxide compounds evaluated and optimized by the FACT group to be thermodynamically consistent with the FToxid solution database.
- FACT53 (FS53Base.cdb): contains data for over 4500 compounds (pure substances) and is the updated version of the old FACT general compound database. It contains data from standard compilations as well as most of the data for those compounds which have been evaluated and optimized to be thermodynamically consistent with the FACT FToxid solution database.

The CaO-rich part of the system CaO-CrO-Cr<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (*i.e.*, compositions in the CaO-Ca<sub>2</sub>SiO<sub>4</sub>-CaCr<sub>2</sub>O<sub>4</sub> 'triangle') in air was not considered in the optimization of the FactSage databases.<sup>(6)</sup> Bearing in mind the conditions of the present work, this fact has no significance.

Caution is needed when selecting candidate phases for participating of the equilibrium state. The application may suggest phases which are inadequate. One example is the phase  $CrO_2(s)$  contained in the database FACT53; if this phase is selected, results are inconsistent. This phase can participate of the equilibrium state only where pressure is higher than that of atmospheric pressure.<sup>(8)</sup>

Some problems were experienced with the 'phase diagram' module of the used software; they seemed to be related with some equilibrium conditions or with the chosen phases.

## **3THERMODYNAMIC ANALYSIS RESULTS AND DISCUSSION**

The present computational thermodynamic analysis will be restricted to the system with Cr-Ca-O-Si-Mg atomic species as components. In some points, however, for the sake of clearness, the analysis will take into consideration only some of them at a time.

Due to industrial relevance, emphasis will be given to the conditions corresponding approximately to those existing close to the interface molten steel-slag -i.e., moderately reducing conditions.

## 3.1 CaO-SiO<sub>2</sub>-CrO<sub>x</sub> System

To the steel maker, the relatively simple  $CrO-Cr_2O_3$ -CaO slag could be the first of concern due to the fact that EAF stainless steel production practice usually starts with the use of lime.

Existing slags, however, are far more complex than those described by the Cr-Ca-O atomic components alone. Therefore, in order to get closer to reality, the



composition variable of the system under simulation must be expanded to include other elements.

Among the candidate atomic species, the ubiquitous Si should be the first to be considered. The existence of  $SiO_2$  in the slag – related both to the oxidation of Si present in the scrap and to the use of ferrosilicon as deoxidant for stainless steels – firmly justifies the choice.

In connection with slags, an important parameter in the steel industry is the known *slag binary basicity index* (or V-ratio), wt.% CaO / wt.% SiO<sub>2</sub>. Bearing in mind some aspects that will become clear later, from now on, a fixed value of 1.2 will be considered for all simulations.

Figure 1 shows an isothermal phase diagram for this system, with total (actually oxygen) pressure ranging from  $1 \times 10^{-14}$  to  $1 \times 10^{-9}$  [atm], at 1600°C, and binary basicity 1.2. Diagrams of this type are quite seldom but show, with great emphasis, the impact of the oxygen potential on the equilibrium state of the system (note: the 'compound' Cr<sub>1.29</sub>O<sub>3.29</sub>Si was made up in order to satisfy both software and basicity requirements).

It is apparent from the diagram that a  $(CaO-SiO_2-CrO-Cr_2O_3)$  slag phase will always be present in the equilibrium state when basicity is equal to 1.2. Nevertheless a slag phase can be found in thermodynamic equilibrium with *metallic* Cr only for pressures *lower* than approximately  $9x10^{-13}$ ; otherwise it will stay in equilibrium with *eskolaite* (also known as *chromia*), Cr<sub>2</sub>O<sub>3</sub>.

The meaning of this information, for the steel producer, is threefold:

- a plain CaO-SiO<sub>2</sub> slag in contact with Cr (or an alloy containing Cr, like Fe-Cr) will absorb this costly metal from the melt until saturation;
- more important, at 1600°C, a Cr-saturated slag will oxidize metallic chromium to eskolaite for oxygen pressures higher than ~9x10<sup>-13</sup> (in addition to the detrimental effect of chromium *instability*, the solid mineral will stiffen the slag); and,
- the lower the pressure (up to the threshold value) the greater the *solubility* of chromium oxides in the liquid slag phase.

Pretorius and Muan<sup>(9)</sup> while studying the same system under strongly reducing conditions at 1500°C also concluded that the lowering of  $pO_2$  causes a significant increase in the solubility of chromium oxide in the liquid phase.

Nevertheless, kinetics – as always – plays an important role and may set the rate for chromium transfer from *e.g.* the Fe-Cr melt.

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**Figure 1**.  $Ca_{1.29}O_{3.29}Si-Cr_2O_3$  phase diagram for system (oxygen) pressures ranging from  $1 \times 10^{-14}$  to  $1 \times 10^{-9}$  [atm], 1600°C, binary basicity = 1.2

# 3.2 CaO-SiO<sub>2</sub>-CrO<sub>x</sub>-MgO System

In this work on slags, the second element of concern should be Mg.

The presence of magnesium can be related to the large use of MgO-based refractory materials for inner walls and linings of metallurgical vessels or ladles – e.g. EAF and LF.

Other source of magnesium is the dolomite – a calcium magnesium carbonate – which can be added with the charge at some point during the production of stainless steels.

Related to the Mg atomic species, the simplest system of relevance is the ternary CaO-SiO<sub>2</sub>-MgO.

Starting with the binary system CaO-SiO<sub>2</sub>, for a fixed binary basicity of 1.2 and temperature of 1600°C, the sole condensed phase will be the liquid slag. When certain amount of MgO is added to 100g of CaO-SiO<sub>2</sub>, *two* new phases will precipitate: first C<sub>2</sub>S (dicalciumsilicate) followed by MgO (periclase) (Figure 2).





**Figure 2**. Amount of phases as a function of MgO addition to 100g of CaO-SiO<sub>2</sub> system; pressure:  $1 \times 10^{-10}$  [atm], 1600°C, binary basicity = 1.2

The attainment of the *dual saturated slag* ( $C_2S$  and MgO) is suggested by Pretorius and Nunnington as the ideal aim during the production of stainless steels.<sup>(10)</sup> For basicities higher then 1.2, liquid slag tends to vanish and, in the opposite direction, dual saturation will be unfeasible (this can be checked very quickly with the help of a simple pseudoternary phase diagram of the system CaO, SiO<sub>2</sub> and MgO at 1600°C isotherm).

As already seen, a CaO-SiO<sub>2</sub> binary slag will dissolve chromium (metallic or from a Cr-alloy) in contact with it. Therefore, it is interesting to observe the effect of MgO addition to this system taking into consideration the presence of  $CrO_x$ . Since pressure matters, a total pressure of  $1 \times 10^{-10}$  [atm] will be fixed for all the remaining simulations.

Using the same basicity as above – in order to secure dual saturation – and fixing  $Cr_2O_3$  contents of 5% and 15%, the effect of the MgO addition to the Cr-containing system can be seen in Figures 3 and 4.

A marked feature is that  $MgO \cdot Cr_2O_3$ -Spinel (picrochromite or magnesiochromite) is now present in both equilibrium states and precipitates very early.

For the last composition, eskolaite is present since the beginning along with the slag (denotes a chromium oxide-*saturated* slag), but gives way very soon to picrochromite precipitation.

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**Figure 3**. Amount of phases as a function of MgO addition to 100g of CaO-SiO<sub>2</sub>-CrO<sub>x</sub> system, 5% Cr<sub>2</sub>O<sub>3</sub>; pressure:  $1 \times 10^{-10}$  [atm], 1600°C, binary basicity = 1.2



**Figure 4**. Amount of phases as a function of MgO addition to 100g of CaO-SiO<sub>2</sub>-CrO<sub>x</sub> system, 15%  $Cr_2O_3$ ; pressure: 1x10<sup>-10</sup> [atm], 1600°C, binary basicity = 1.2



Slag composition evolution for 5%  $Cr_2O_3$  content can be seen in Figure 5(a). Due to the rise of MgO participation, alumina and silica contents show a slight decrease. Content of the chromium oxides, on the other hand, shows a peculiar tendency up to 6 g added MgO: near constant for CrO or growing for  $Cr_2O_3$ ; from then on there is for both a steady decrease. Due to the moderately reducing conditions, the  $Cr^{2+}$  content shows a higher share. Toward bigger amounts of MgO these contents decrease at different rates and cross each other at the end, where the  $Cr^{3+}$  content becomes a little larger.

At 21 g MgO the system composition reaches a field where *all* phases show constant composition. Only the amount of some *individual* phases is changing, as a consequence of the MgO addition (this, of course, is the phenomenon analyzed before, with the pseudoternary system CaO-SiO<sub>2</sub>-MgO).



**Figure 5(a)**. Slag constituents content as a function of MgO addition to 100g of CaO-SiO<sub>2</sub>-CrO<sub>x</sub> system, 5% Cr<sub>2</sub>O<sub>3</sub>; pressure:  $1 \times 10^{-10}$  [atm], 1600°C, binary basicity = 1.2

**Figure 5(b).** Activities of the chromium oxides in slag as a function of MgO addition to 100g of CaO-SiO<sub>2</sub>-CrO<sub>x</sub> system, 5% Cr<sub>2</sub>O<sub>3</sub>; pressure:  $1 \times 10^{-10}$  [atm], 1600°C, binary basicity = 1.2

Activities of the chromium ions (reference state: pure liquid) where determined at the same time and can be seen in Figure 5(b). CrO activity is bigger and does not show the same tendency of the CrO *content* to cross, remaining always greater than the  $Cr^{3+}$  activity.

## **4 CONCLUSION**

Slags of the Ca-O-Cr-Si-Mg quinary system were studied with the help of computational thermodynamics, at 1.2 binary basicity and temperature of 1600°C.

The quaternary Ca-O-Cr-Si subsystem was analyzed first and, from the observed results, the behavior is twofold, depending on the system pressure. For oxygen pressures higher than  $\sim 9 \times 10^{-13}$ , chromium shows *instability* in contact with a CaO-SiO<sub>2</sub> slag and, after slag saturation, will *oxidize* to eskolaite. For lower pressures metallic chromium will stay in equilibrium with the slag. Near the transition pressure, however, the Cr-saturation content is high.

When periclase (MgO) is added to the (now quinary) system (at a fixed pressure of  $1 \times 10^{-10}$ ), precipitation of MgO·Cr<sub>2</sub>O<sub>3</sub>-Spinel (picrochromite or magnesiochromite) is observed without delay for eskolaite saturated system

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(containing 15%  $Cr_2O_3$ ). For the unsaturated system (5%  $Cr_2O_3$ ) the added MgO amount should be *circa* 6 times greater.

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