

# CHROMOUS CAPACITIES OF FERROCHROMIUM AND MATTE SMELTING SLAGS

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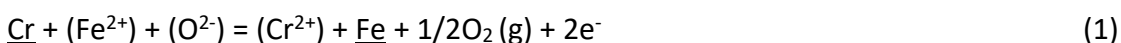
## Introduction

The concept of slag capacity has been well developed and utilised in high temperature metal processing operations. It has been principally used to describe the anionic species dissolving power of slags. The sulphide and phosphide capacities are the most frequently experimentally determined, modelled and used ones especially related to steel making. The aim of this paper is to extend the slag capacity concept to sparingly soluble cationic species encountered for example in matte smelting and ferrochromium processing in terms of chromous capacities. In this context in order to develop the chromous capacity the experimental data on slag-metal equilibrium for ferrochromium smelting and on chromium distribution between slag and matte phases encountered in sulphide smelting of PGM (Platinum Group Metals) and chromium containing copper nickel concentrates were used.

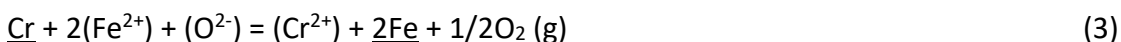
## Chromous capacity of ferrochromium smelting slags

The extensive slag-metal equilibrium data provided by Akyuzlu and Eric<sup>1</sup> were used to determine the chromous capacities of slags encountered in high carbon ferrochromium manufacturing. The data includes experimentally determined equilibrium compositions of both the carbon saturated ferrochromium metal phase and the silicate slag phase including the equilibrium partition values of chromium between both phases.

The dissolution of chromous  $\text{Cr}^{2+}$  ion in the slag can be expressed through the following equilibria:



The overall equilibrium being:



In these reactions, the bars under Cr and Fe indicate that they are in the metallic phase, lower case g refers to gas phase and obviously,  $\text{e}^-$  is an electron with negative charge.

In this slag capacity model approach, as it is clearly seen through reactions (1) and (2), the dissolution of chromium into the slag involves exchanges with any  $\text{Fe}^{2+}$  cations dissolved in the slag along with free  $\text{O}^{2-}$  anions of the slag. This exchange results in formation of metallic iron and release of electrons which are again consumed by  $\text{Fe}^{2+}$  cations producing more metallic iron. This is easily justified by the well-known fact that  $\text{Fe}^{2+}$  ions are relatively easier to reduce into metallic state than  $\text{Cr}^{2+}$  ions. Due to the highly reducing conditions prevailing in ferrochromium smelting the oxygen partial pressure in the system is very low and no three valent cations of both chromium and iron exist in the slag. This fact has also been confirmed by Akyuzlu and Eric<sup>1</sup>. Thus, the chromous capacity of ferrochromium smelting slags can be expressed as in Equation (4) below by making use of the overall reaction (3):

$$C_{\text{Cr}^{2+}} = [(\% \text{Cr})_{\text{slag}} (P_{\text{O}_2})^{1/2} (a_{\text{Fe}})^2] / a_{\text{Cr}} \quad (4)$$

In Equation (4)  $(\% \text{Cr})_{\text{slag}}$  is the chromium concentration in the slag assumed as divalent cation.  $P_{\text{O}_2}$  is the partial pressure of oxygen in the system governed by:



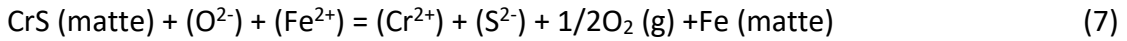
$$\Delta G^\circ = -111712.8 - 87.65T \text{ J/mole} \quad (6)$$

The equilibrium data in the Akyuzlu and Eric<sup>1</sup> study was generated at 1600°C under CO atmosphere ( $P_{\text{CO}} = 1.0 \text{ atm}$ ) and the use of graphite crucibles to contain the slag and metal phases together saturating the metal phase with carbon ( $a_{\text{C}} = 1.0$ ). Hence at 1600°C the  $P_{\text{O}_2}$  is  $4.09 \times 10^{-16} \text{ atm}$ . The activities of Cr and Fe in Equation (4) are their activities in the metal phase. They were calculated by use of the method reported by Healy<sup>2</sup> for the Fe-Cr-C system. The chromous capacities calculated at 1600°C for the ferrochromium smelting slags based on conditions, values and assumptions mentioned above are in the range of  $2.8 \times 10^{-8}$  to  $8.7 \times 10^{-8}$ . Another important feature is the fact that the chromous capacities of the slag decreases as the basicity of the slag increases. This is further proof of the depolymerisation of the melt with increasing basicity, resulting in an increase in the activity of free oxygen ions.

## Chromous capacity of matte smelting slags

In South Africa, the PGM (Platinum Group Metals) processing industry is based on copper-nickel-iron sulphide concentrates which also contain a few percent of chromium oxide as an unwanted impurity. These concentrates are smelted usually in six electrodes in line electric slag resistance furnaces to separate the slag forming oxides from the matte forming sulphide constituents. The matte (which virtually contains all the PGMs) is then oxidised in a converter operation to remove the iron sulphide as iron oxide in a silicate slag phase and the remaining copper nickel matte is further processed to produce metallic copper and nickel and to recover the PGMs. The chromium oxide impurity has the potential to create severe problems for the matte smelting operation due to its high melting point and its tendency to form solid spinels

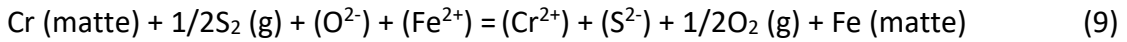
affecting the slag-matte equilibrium as well as viscosity and conductivity of the slag. It is then imperative to dissolve the chromium in the slag completely. The industry tries to render the chromium soluble by imposing reducing conditions in the furnace as well as increasing temperature to around 1450-1500°C. Recently Eric<sup>3</sup> reported results of carefully conducted experiments on chromium partition between matte and slag phases at 1450°C by varying the oxygen and sulphur partial pressures pertinent to PGM processing. Based on this experimental work chromous capacity of PGM matte smelting slags are derived assuming that the chromium exists as CrS in the matte phase and as chromous ion in the slag phase due to the highly reducing conditions imparted and employing the approach summarised below.



The CrS in the matte is related to sulphur of the gas phase (which can also be a variable) through the following reaction;



Then the overall equilibrium reaction for derivation of the chromous capacity is obtained by adding reactions (7) and (8):



In all the reactions shown above the round brackets around ionic species indicate the slag phase, “g” refers to gas phase. The chromous capacity is then defined by the following equation:

$$\text{C}_{\text{Cr}^{2+}} = [(\% \text{Cr})_{\text{slag}} (\text{P}_{\text{O}_2})^{1/2} (a_{\text{Fe}})] / [(a_{\text{Cr}}) (\text{P}_{\text{S}_2})^{1/2}] \quad (10)$$

Chromous capacities of matte smelting slags were calculated using Equation (10) and the slag-metal equilibrium composition values as well as the partition data on chromium provided by Eric<sup>3</sup> under varying oxygen and sulphur partial pressures at 1450°C. The iron and chromium activities in the matte phase were estimated using dilute solution interaction parameter formalism. The chromous capacities of matte smelting slags varied in the range  $1.19 \times 10^{-4}$  and  $7.75 \times 10^{-4}$ . They increased with decreasing basicity of the slags and displayed a moderate increase under decreasing partial pressure of oxygen. The effect of sulphur partial pressure was not clear.

## Conclusions

The experimental data on slag-metal equilibrium for ferrochromium smelting and on chromium distribution between slag and matte phases encountered in sulphide smelting of PGM (Platinum Group Metals) and chromium containing copper nickel concentrates were used to develop chromous capacities of slags. Due to highly reducing conditions in ferrochromium smelting and the imposed low oxygen partial

pressures in sulphide smelting of chromium and PGM containing concentrates chromium in the slag was assumed to be in its divalent state. The slag-metal/matte reaction for dissolution of chromium into the slag as a cation under reducing conditions -in contrast to reactions for dissolution of species such as sulphur and phosphorus into the slag as anions under oxidising conditions- required the release of electrons. Thus, to maintain charge neutrality the dissolution of chromium from the metal or the matte phases into the slag as  $\text{Cr}^{2+}$  ions was accompanied by consumption of these electrons by reduction of  $\text{Fe}^{2+}$  ions in the slag into metallic Fe which dissolved in the metal/matte phase. This was supported by the experimental equilibrium data. Hence the slag-metal/matte reaction defining the chromous capacity involved both  $\text{O}^{2-}$  and  $\text{Fe}^{2+}$  ions of the slag phase. The calculated chromous capacities were in the  $10^{-8}$  range for ferrochrome smelting slags and  $10^{-4}$  range for matte smelting slags.

## References

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2. G. W. Healy, "Activities in the liquid Cr-Fe-C system above 1600° C", in *Proceedings of the Reinhardt Schuhmann International Symposium on Innovative Technology and Reactor Design In Extractive Metallurgy*, Edited by D. R. Gaskell, J. P. Hager, J. E. Hoffmann and P. J. Mackey. TMS-Metallurgical Society, USA, 1986, 667-679.
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