AN ADVANCE MATHEMATICAL MODEL OF THE SLAG PHASE IN A GAS-STIRRED LADLE

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ABSTRACT

The slag thermo-physical properties play a major role in the refining process. Therefore, the slag composition used in the modern secondary steelmaking process must be designed carefully to provide the target thermo-physical properties required for a high quality refining process. Slag viscosity and sulphur capacity are essential in the desulphurization refining process.

A three phase (steel/gas/slag) mathematical model based on the fundamental transport Equations has been developed to study the refining process in the secondary steelmaking process. In this present work a combination of advance slag thermo-physical properties prediction correlations were set together to trace the slag system behavior. Successful implementation of the NPL slag viscosity model and the Nilsson slag capacity model was achieved. Therefore, it is possible to study the influence of the slag system composition variation during the refining process.

In this model the Ca^{++} *cation behavior in the multicomponent slag system* CaO-Al_2O_3-SiO_2-MgO *was monitored at the steel/slag interface during the desulphurization process. Also the precipitation of the CaS phase in molten slag was allowed when it reach the saturation limit. In this approach, a Computational Fluid Dynamics (CFD) analysis was used to predict the flow pattern of the gas-stirred ladle system. The thermodynamic analysis package MTDATA from the National Physical Laboratory (NPL) was linked to the model to predict the mass transaction at the steel/slag interface during the refining process. The model prediction results of the desulphurization rate during vacuum degassing process have been compared to the data from the literature, and good agreement has been found.*

INTRODUCTION

Today, the mass and heat transport in the metal and slag phases can be predicted by solving the fundamental transport Equations using Computational Fluid Dynamics (CFD) as a tool. In addition, developed at the National Physical Laboratory (NPL), the MTDATA thermodynamics package is capable of predicting the different phases formed at the metal/slag interface at a chemical equilibrium. Mazumdar and Guthrie [1] published a comprehensive review in the mid-nineties; this illustrated the great potential of mathematical modeling in metallurgical process enhancement. Jonsson *et al.* [2] established a new approach to steel refining simulation. The multi-phase steel/slag/gas model was linked with a thermodynamic model to simulate the desulphurization process

Herasymenko and Speight [3] established the ionic theory of slag-metal equilibrium. Silicate and phosphate glass structures are random networks in which the small atoms with a large positive oxidation number, called the *network formers*, such as Si^{+4} and P^{+5}, are tetrahedrally surrounded by oxygen ions (O^{-2}) that form bridges between positive ions. In pure silica, the SiO_4 tetrahedra, sharing with neighboring tetrahedra form complex networks, where the slag viscosity increases with the increase of silicate ion size. In steelmaking slag, the acid oxide network structure (SiO_4) is demolished due to the oxygen bridges being broken by the addition of basic oxides such as CaO. This addition of basic oxide provides free ionic oxygen that improves the engineering properties of the slag. An acid slag that contains a high concentration of network formers cannot be used to extract impurities such as sulphur from the melt. This is due to its low capacity for these impurities and due to the relatively high viscosity, which reduces the mass transfer rates. Therefore, secondary steelmaking slags tends have basic oxide additions [4, 5, 6].

In simulation of the role of the slag in the metallurgical process, usually a huge amount of data on slag thermal properties is required over a wide range of complex slag compositions and temperatures to run the model. Various workers show dramatic increases in slag viscosity with the content of network formers such as SiO_2 that come within the range (1-100 Ns/m^2) [7, 8, 9, 10]. Unfortunately the available experimental results do not provide enough data over this wide range of complex compositions and temperature to run very dynamic models. The need for mathematical models that enable the estimation of the viscosities of complex slags systems is noticeable.

A great effort has been made and a number of models have been developed [11]. Mills *et al.* [12] ran a *round robin* project to determine the accuracy of the prediction of the slag viscosities and the reliability of various sophisticated models. The different types of industrial slag were classified into various groups such as mould slag, ladle slag, and more. The model performance was described by the difference between the calculated and the measured slag viscosities.

More than ten models applicable for different slags were investigated in the *round robin* project. However, in this present work, the ladle slag system for the desulphurization process is of concern; this is a non-fluoride system. For such a non-fluoride slag system, the round *robin project* report a good slag viscosity estimation by Zhang and Jahanshahi [13], Royal Institute of Technology (KTH) [14] and the National Physical Laboratory (NPL) [15] models.

Mathematical Modeling

A 2D mathematical model of a gas-stirred ladle accounting for the steel, argon and slag phases was created and described elsewhere [16, 17]. The dissolved elements of interest such as Al, O, and S in addition to the species (Ca^{++} and CaS) were accounted. The Ca^{++}

mobility and the precipitation of CaS phase in the slag phase were accounted [18]. In this model the Ca^{++} cation behavior in the multicomponent slag system CaO-Al_2O_3-SiO_2-MgO was monitored at the steel/slag interface during the desulphurization process. A particularly novel aspect of this work is that the precipitation of the CaS is allowed to occur in the molten slag once the solubility limit is exceeded.

In the present work, the selected slag viscosity model must be integrated with the Fluent CFD package. Unfortunately, the KTH model cannot be integrated due to missing parameters covering the presence of Al_2O_3 in slag (in the present work the slag system includes 30 wt% Al_2O_3). This is essentially a copyright issue. The Zhang and Jahanshahi model cannot be implemented because model parameters have been developed specifically for a silicate slag system containing a minimum of 20 wt% SiO_2 (private communication with Dr. Ling Zhang). Therefore, the NPL model was employed in the present work. A comparison between the measures slag viscosity and the estimated one is illustrated in Figure 1.

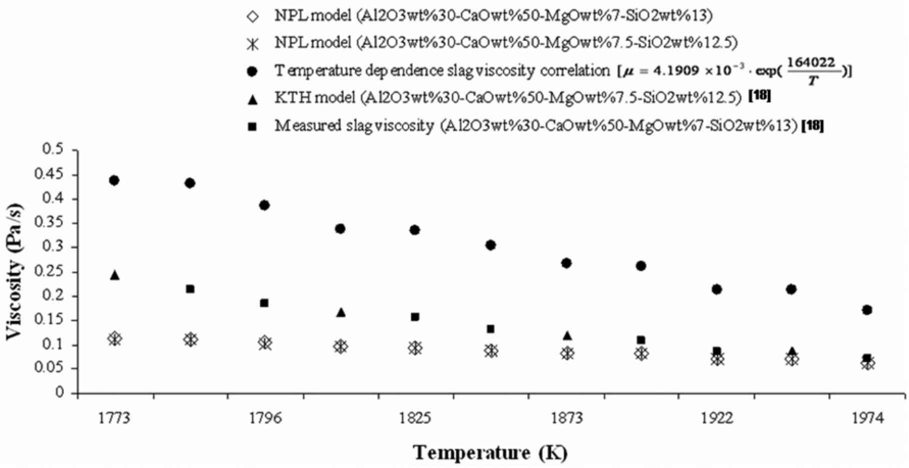

Figure 1: Estimated slag viscosity using various models

A particularly feature of this work is the implementation of the advance models estimating the slag behavior during the steel refining process. Nilsson *et al.* model was used to estimate the solubility limit, also the Mills and Sridhar [7] slag viscosity model was used to monitor the local slag viscosity changes due to the variation in CaO concentration.

NPL Slag Viscosity Model

Mills and Sridhar [7] in the NPL slag viscosity model, which is based on the corrected optical basicity, provide a reasonable estimation over a wide range of industrial slags. The model assumes Arrhenius behavior, as expressed by the following correlation:

$$ln\,\eta = ln\,A + B/T \tag{1}$$

where, T is the temperature, and A and B are parameters function of the corrected optical basicity (Λ^{corr}) as expressed below:

$$\frac{ln\,B}{1000} = -1.77 + \frac{2.88}{\Lambda^{corr}} \tag{2}$$

$$ln\ A = -232.69(\Lambda^{corr})^2 + 357.32 \cdot \Lambda^{corr} - 144.17 \tag{3}$$

$$\Lambda^{corr} = \frac{\sum x_i n_i \Lambda_i}{\sum x_i n_i} \tag{4}$$

where x_i and n_i are the component (*i*) mole fraction and the number of oxygen atoms in the molecule, e.g. one for CaO, respectively. Also, Λi is the optical basicity of component (i) as listed in Table 1.

Table 1: Slag oxides optical basicity [7]

CaO	Al_2O_3	SiO_2	MgO	MnO	P_2O_5
1.0	0.60	0.48	0.78	1.0	0.40

Slag Sulphur Capacity

Richardson and Fincham [19] and Richardson [20] have shown that the sulphur is held in the slag totally in the form of sulphide at oxygen partial pressures less than 10^{-5}-10^{-6} atm. Its concentration is controlled by the equilibrium:

$$\frac{1}{2}S_2(gas) + O^{-2}(slag) = \frac{1}{2}O_2(gas) + S^{-2}(slag) \tag{5}$$

Furthermore [19, 21], sulphide capacity (Cs) is shown to be constant for a given temperature and composition for oxygen partial pressures less than 10^{-5}-10^{-6} atm. In the steelmaking industry, the oxygen partial pressure is within the range of 10^{-8}-$10^{-9.2}$ atm. Therefore, the sulphur tends to be present as sulphide rather than sulphate.

The solubility of CaS in calcium aluminate melts (mass ratio CaO/Al_2O_3 ≈1.55) at 1600°C and lime saturation is ≈ 4.77 wt% CaS (≡ 2.12wt% S) [22]. During the desulphurization process, if an insufficient amount of ladle slag is used or the molten steel has particularly high sulphur content, the excess precipitated CaS which is formed can result in a decrease in the dissolved CaO content of the slag. This then results in a low rate of desulphurization. However, the local accumulation of sulphide in slag beyond the solubility limit could result in the precipitation of CaS phase [23]. Nzotta *et al.* [24] report the dramatic effect of CaO concentration changes on sulphur capacity in a slag system containing about 50%wt CaO. Generally, slag sulphur capacity is sensitive to temperature and composition variation [25, 26, 27].

Slag Sulphur Capacity Model

A model suggested by Nilsson *et al.* [26] is described briefly below to predict slag sulphur capacity as a function of temperature and slag composition. According to Nilsson *et al.* the sulphur capacity equilibrium constant can be expressed as follows:

$$K = exp\left(\frac{-\Delta G^{\theta}}{RT}\right) \tag{6}$$

where, ΔG^{θ} is the standard Gibbs free energy change for reaction (5). The Gibbs function difference is the driving force for phase change, just as the temperature difference is the driving force for heat transfer [27]. R and T are the gas constant and absolute temperature respectively. Furthermore the authors provide a new expression for the $(a_{o^{2-}} / \gamma_{s^{2-}})$ ratio.

$$\left(\frac{a_{o^{2-}}}{\gamma_{s^{2-}}}\right) = exp\left(-\frac{\xi}{RT}\right) \tag{7}$$

By combining Equations 6 and 7, the sulphide capacity, Cs, can be expressed as follows:

$$C_s = exp\left(-\frac{\Delta G^{\theta}}{RT}\right) exp\left(-\frac{\xi}{RT}\right) \tag{8}$$

The ξ parameter is a polynomial function of both temperature and composition for a multi-component system and is expressed as:

$$\xi = \sum x_i \xi_i + \xi_{mix} \tag{9}$$

where the subscript *i* denotes component *i*, and x_i is the mole fraction of this component in the system. The model parameters for various slag systems can be found in [24, 25, 26, 27].

Cations Diffusion In Slag

Slag is ionic in nature consisting of positively and negatively charged ions called cations and anions respectively. Cations are mobile species in slag and show much higher diffusivity rate than anions [28]. In addition the diffusivity coefficient of an element is of an order of magnitude greater in a liquid metal than molten slag [29, 30]. The diffusion coefficients are influenced by species concentrations in slag. Variations of the species concentration result in composition and viscosity changes of the slag, which in turn alters the coefficient of diffusion. Silicon concentration gradient has a significant influence on species diffusivity in silicate slags [29]. Also, calcium cation diffusivity coefficient in lime-alumina slag is about four times the value in silicate slag for the same temperature. In ternary silicate slag the diffusivity for some cations are in the following order [$D_{Fe}>D_{Na}>D_{Ca}>D_{Al}>D_{Si}$] [25]. In addition diffusivity coefficient variation with temperature gradient is not great [31]. Some of the interesting cation diffusivity coefficient values are given in Table 2.

Table 2: Diffusion coefficients for some cations of interest in molten slag

Slag composition Wt%	Cation	Diffusivity (x10-6).cm2.s-1	Temperature ºC	Ref
$38CaO.20Al_2O_3.42SiO_3$	Ca	4.5	1450	[24]
	Si	0.047	1365	[25]
	Si	0.105	1430	[25]
$50.1CaO.49.9Al_2O_3$	Ca^{+2}	19	1450	[24]
$40CaO.20Al_2O_3.40SiO_3$	Ca^{+2}	0.2-0.45	1350	[25]
$40CaO.20Al_2O_3.40SiO_3$	Ca^{+2}	1.5-4.0	1500	[25]

RESULTS AND DISCUSSION

In this present work two cases were run to make a comparison to study the influence of CaS precipitation on the desulphurization rate. Figure (2) presents the desulphurization rate over time for two cases where the CaS precipitation and Ca^{++} mobility were allowed in comparison with a standard case where the slag compositions are assumed to be constant. The desulphurization rate during the refining process is shown in Figure (2) and is in good agreement with [2].

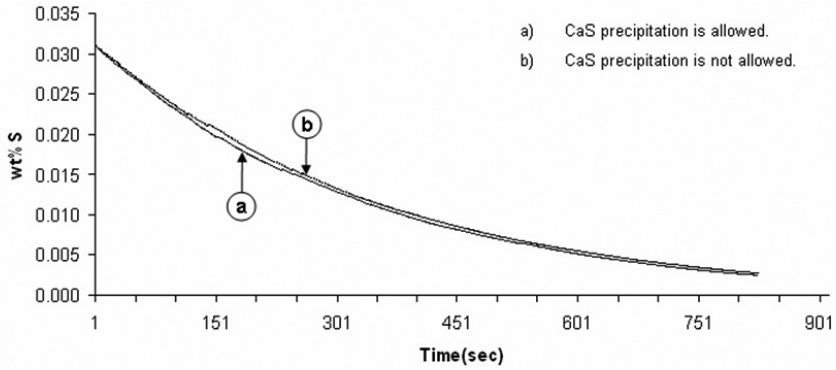

Figure 2: The predicted desulphurization rate during the refining process

Initially, the precipitated CaS is higher at the bubble slag zone where the gas break the slag layer and create a three phase (steel/slag/gas) mixing zone that enhance the desulphurization rate [31]. However, the concentrations in the slag phase rapidly homogenize. This could be due to the fact that the precipitated CaS, in these calculations, has been defined as a species of the slag system, and therefore can move quite rapidly. It would be desirable to treat it as a fourth phase (after steel, slag, and gas) but when this approach was attempted the solution become unstable. This requires more attention. Looking to the data in Table 2, the significant influence of the presence of the network former SiO_2 on the restriction of the Ca^{++} mobility is noticeable. In this present work the influence of SiO_2 present in the slag was neglected due to the lack of information about the cation diffusivity in slag. Therefore, a high value of the Ca^{++} diffusivity rate ($19x10^{-6}.cm^2.s^{-1}$) used in this present work.

CONCLUSIONS

A combination of slag properties models set together to develop an advance gas-stirred ladle system model was demonstrated. Successful implementation of the NPL slag viscosity model and the Nilsson slag capacity model was achieved. Also, it was possible to allowed the Ca^{++} mobility and CaS precipitation in the slag phase. Therefore, it is possible to study the influence of the slag system composition variation during the refining process.

A particularly novel aspect of this work is that the precipitation of the CaS is allowed to occur in the molten slag once the solubility limit is exceeded. A particularly feature of this work is the implementation of the advance models estimating the slag behavior during the steel refining process.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the project sponsor the Saudi Basic Industries Corporation (SABIC), Saudi Arabia.

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