Evaluating the Chemical Diffusion Coefficient of Sulfur in slag by metal analysis: Model Concept and Experiments

Luckman Muhmood[1] *Nurni N Viswanathan*[2] *and Seshadri Seetharaman*[3]
[1]*CSIRO, Process Science and Engineering, Australia*
[2]*Professor, Luleå Technical University, Sweden*
[3]*Professor, Royal Institute of Technology, Sweden*

Abstract: A novel technique was developed to evaluate the Chemical Diffusion Coefficient of sulfur using the fact that the diffusivity of sulfur in the slag is at least two orders of magnitude less than that in the metal. The methodology uses specially designed experimental setup supported by a model to evaluate the diffusion coefficient. A ternary slag of composition 51.5 % CaO-9.6 % SiO_2-38.9 % Al_2O_3 slag was chosen for the experiment. Experiments were conducted using a custom-made Armco Iron crucible. The crucible was specially designed to enable metal sampling without disturbing the slag-metal interface. CaS was used as the sulfur source. It was also ensured that the P_{S2} and P_{O2} pressures calculated from the equilibrium Gibbs energy of the reaction between CaO in the slag and solid CaS, was well within the limits to prevent any dissolution into the crucible material. Experiments were conducted at 1680 K, 1700 K, and 1723 K. The diffusion coefficient was back calculated such that a good fit is obtained between the experimental and model results. The diffusion coefficient was in the range of 3.98 - 4.14 x 10^{-6} cm^2/s for the temperature range 1680 – 1723 K, which is in good agreement with the results available in the literature.

Keywords: Diffusion Coefficient, Sulfur, Slag

1. Introduction

Chemical Diffusion Coefficients of species relevant to steelmaking are of immense importance as it provides a better understanding of the transport kinetics during refining. However, not much focus has been given to the diffusivity of species in the slag phase, especially sulfur. During refining of steel, in the event of the gas-slag-metal interfaces not being disturbed by external forces, the process time is limited by the diffusion of the species of interest through the molten metal and slag phases. A comparison between these diffusivities show that the diffusivity through molten metal is roughly two orders of magnitude greater than the corresponding diffusivity in the slag phase[1]. Hence the rate-determining step of such reactions would be the diffusion of the species through the slag phase. In this work sulfur has been used as the species of interest especially due to its critical importance in metal refining reactions.

Tracer diffusion has been a well established technique to find the diffusivity of the species of interest and has been practiced by many early researchers [2]. However, very little work has been carried out on chemical diffusivities. The only experimental study reported on the measurement of chemical diffusion coefficient of sulfur in slag was by Derge *et al.*[3] The experimental technique adopted by these authors was to keep a high sulfur slag in contact with a slag with a similar composition devoid of sulfur at high temperatures. The slag was analyzed after “quenching” the diffusion couple by shutting off the furnace power and rapidly cooling the bottom of the crucible in comparison to the top. The authors have claimed that such cooling reduces stirring and piping effects. However, it is well known that a temperature gradient in the crucible could result in stirring and would result in homogenizing the sulfur content in slag. Since the slags are fluids at the experimental temperatures, the diffusion of sulfur would be accompanied by convection effects due to minor temperature gradients and mixing or stirring effects could take place at the interface probably due to the enthalpies of the interfacial reactions. These phenomena would lead to an increase in the amount of sulfur transported through the interface. Thus a new method for the *in-situ* measurement of sulfur content in the system has been focused upon. This measurement technique uses metal sampling for sulfur analysis without disturbing the slag-metal interface.

A novel technique has been put forward for the evaluation of the chemical diffusivity of sulfur in the molten slag phase. A mathematical model [4] was formulated through which appropriate design parameters for the experimental setup was obtained. For this, the order of magnitude for the diffusion coefficient for sulfur was taken from the classic works of Saito and Kawai [2], the sulfide capacity and sulfur partition ratio were retrieved from the works of Taniguchi et al.[5], and the slag density was retrieved from earlier experimental results of the present authors [6]. The Henrian activity coefficients for the metallic solution were also retrieved from literature [7]. Using the model and experiments, the chemical diffusion coefficient of sulfur in the ternary slag of composition 51.5% CaO- 9.6% SiO_2- 38.9% Al_2O_3 slag was measured at 1680, 1700 and 1723 K [8].

2. The technique and the mathematical formulation

In the present paper, it is proposed to have slag-metal system wherein *in-situ* metal samples can be taken out and subsequently analyzed for sulfur to determine its diffusivity in the slag. For this purpose, a suitable metal phase has to be carefully chosen so that the diffusion coefficient of sulfur in the molten metal is much higher than that in the slag. In such a methodology, the whole system need not be disturbed through quenching.

A schematic of the proposed methodology for measuring slag diffusivity is illustrated in Figure 1. The system consists of liquid slag and metal with a known composition in a non-interacting crucible kept under isothermal condition. Considering sulfur transport, at the slag-gas interface, appropriate gaseous atmosphere could be maintained such that partial pressures of sulfur and oxygen are fixed. At steel refining temperatures, the intrinsic reaction rates are so fast that equilibrium can be achieved immediately at the slag-gas interface. Therefore, knowing the sulfide capacity of the slag, one can determine the sulfur composition at the gas-slag interface. Subsequently, sulfur will be transported through the slag phase governed by diffusion. At the slag-metal interface, the sulfur partition ratio based on equilibrium considerations could be calculated using the sulfide capacity as well as the solubility of sulfur in the molten metal. Later the sulfur diffuses through the metal phase.

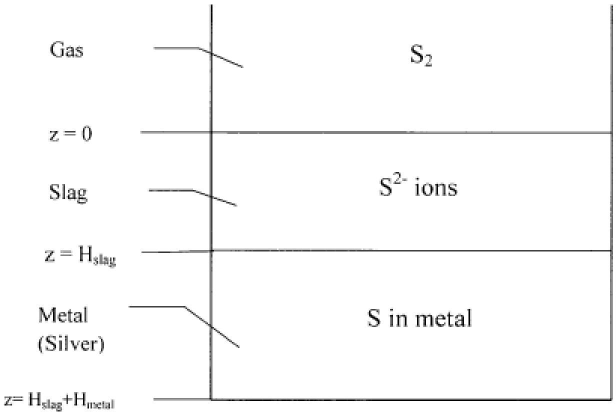

Figure 1: Schematic diagram showing the sulfur transport from the gas medium to the bulk metal through the slag.

According to the present proposed methodology, sampling from the molten metal will be carried out periodically. It is assumed that the composition of sulfur in the metal would be uniform. However, the uniformity of sulfur distribution in the metal phase will depend on the diffusivity of sulfur in metal relative to that in slag. Hence the selection of metal phase in the experiment is critical. The error involved in estimating the diffusivity of sulfur in the slag using the present proposed methodology will depend on the extent of uniformity of sulfur distribution in the metal phase. In order to compute this error, two cases were considered. In case I, for a given diffusivity of the species of interest in the slag phase, the composition in the metal phase was computed considering diffusion in the metal phase. Subsequently, using this composition in the metal phase at the top and bottom, diffusivity in slag phase was computed backwards using case II, wherein the composition of the species of interest in the metal was assumed to be spatially uniform. The governing equations for case I and case II are as follows.

Case I: Wherein the diffusion in both slag and metal phases were considered

For the diffusion through slag phase

$$\frac{\partial c_s^{slag}}{\partial t} = D_s^{slag} \frac{\partial^2 c_s^{slag}}{\partial z^2} \qquad 0 \le z \le H^{slag} \tag{1}$$

For the diffusion through metal phase

$$\frac{\partial c_s^{metal}}{\partial t} = D_s^{metal} \frac{\partial^2 c_s^{metal}}{\partial z^2} \qquad H^{slag} \le z \le H^{slag} + H^{metal} \tag{2}$$

The initial conditions are

$$For \quad t = 0 ; \; 0 \le z \le H^{slag} ; \; c_s^{slag} = 0$$

$$For \; t = 0 ; \; H^{slag} \le z \le H^{slag} + H^{metal} ; \; c_s^{metal} = 0 \tag{3}$$

and the boundary conditions are

$$z = 0 \; (Gas - Slag \; Interface) ; \; t > 0 ; c_s^{slag} = c_s^{slag,0} = C_s \sqrt{\frac{p_{s2}}{p_{02}}}$$

$$z = H^{slag} \; (Metal - Slag \; Interface); t > 0 ; \; -D_s^{slag} \left(\frac{\partial c_s^{slag}}{\partial z}\right) = -D_s^{metal} \left(\frac{\partial c_s^{metal}}{\partial z}\right)$$

$$c_s^{slag} = K^{slag/metal} c_s^{metal}$$

$$z = H^{\,slag} + H^{metal} \qquad \frac{\partial c_s^{metal}}{\partial z} = 0 \tag{4}$$

These equations were made dimensionless using the following.

$$c_*^{slag} = \frac{c_s^{slag}}{c_s^{slag,0}} \qquad c_*^{metal} = \frac{c_s^{metal}}{c_s^{slag,0}}$$

$$z^* = \frac{z}{H^{\,slag} + H^{metal}}$$

$$t^* = \frac{D_s^{slag}\, t}{(H^{\,slag} + H^{metal})^2}$$

and can arrive at

$$\frac{\partial c_*^{slag}}{\partial t^*} = \frac{\partial^2 c_*^{slag}}{\partial z^{*2}} \qquad 0 \le z^* \le \frac{H^{slag}}{H^{\,slag} + H^{metal}}$$

$$\frac{\partial c_*^{metal}}{\partial t^*} = \frac{D_s^{metal}}{D_s^{slag}} \frac{\partial^2 c_*^{metal}}{\partial z^{*2}} \; ; \quad \frac{H^{slag}}{H^{\,slag} + H^{metal}} \le z^* \le 1$$

$$For \quad t^* = 0\,;\; 0 \le z^* \le \frac{H^{slag}}{H^{\,slag} + H^{metal}} \; ; \; c_*^{slag} = 0$$

$$For \quad t^* = 0\,;\; \frac{H^{slag}}{H^{\,slag} + H^{metal}} \le z^* \le 1\,;\; c_*^{metal} = 0$$

$$z^* = 0 \; ; \; t^* > 0 \qquad c_*^{slag} = 1$$

$$z^* = \frac{H^{\,slag}}{H^{\,slag} + H^{metal}} \; ; \; t^* > 0 \; ; \; \left(\frac{\partial c_*^{slag}}{\partial z^*}\right) = \frac{D_s^{metal}}{D_s^{slag}} \left(\frac{\partial c_*^{metal}}{\partial z^*}\right)$$

$$c_*^{slag} = K^{slag/metal}\, c_*^{metal}$$

$$z^* = 1 \qquad \frac{\partial c_*^{metal}}{\partial z^*} = 0 \tag{5}$$

Please note that dimensionless equations help in a more general analysis independent of system components and dimensions.

Case II: Wherein the composition in metal phase is assumed to be spatially uniform

Considering spatially uniform composition in the metal phase, one needs to solve the diffusion equation in slag phase (Equation 1) along with the following equation

$$H^{metal} \frac{\partial c_s^{metal}}{\partial t} = -D_s^{slag} \left(\frac{\partial c_s^{slag}}{\partial z}\right)_{H^{slag}}$$

$$c_s^{slag} = K^{slag/metal}\, c_s^{metal} \tag{6}$$

In order to determine error involved in assuming uniform composition in metal phase, the normalized equations for case I were solved numerically, to obtain the dimenionsionless composition in the metal phase at the top (z = H^{slag}) and bottom (z = $H^{slag} + H^{metal}$). These compositions represent the maximum scatter in an experiment one can obtain if one takes sample from the metal phase. Therefore, the error in diffusivity will be corresponding to these top and bottom composition profiles in metal phase. The diffusivities in the slag phase corresponding to these composition profiles can be computed using case II wherein the composition in metal phase is assumed to be spatially uniform. For case II, the diffusivity in the slag phase were iteratively computed such that mean square deviation between the profiles obtained at the top or bottom using case I and that using case II were minimized.

3. Realization of the experiments

The physical translation of the model to experiments is of utmost importance for the success of the concept. In this regard, proper experimental planning in terms of the material of the crucible, the composition of the slag and metal, the source for sulfur, working temperature, sampling time and technique, etc. needs to be addressed. The following sections explain the methodology used to tackle these hurdles.

Sulfur transport through different metal phases

The model was used to find out the sulfur movement through the same slag with identical conditions but different metal phases. The exercise was to estimate the effect of the solubility of sulfur in various metal phases and its effect on the sulfur transport in the slag phase. Iron and silver were used as the metal phases individually. The solubility of sulfur in molten iron and silver could be calculated from the data given in Table I. It was found that, under identical conditions, the solubility of sulfur in molten iron was more than that in molten silver. Where $\Delta\hat{H}_{X_2}$ is the partial molar enthalpy and $\Delta\hat{S}^{E}{}_{X_2}$ is the partial molar entropy of the solubility of the diatomic gaseous sulfur gas in molten metal in atomic form.

Table I: Henrian (Sievert’s) constants for sulfur diatomic gas dissolved as atomic S in silver and iron.[7]

X= Sulfur in liquid metals	$\Delta\hat{H}_{X_2}$ (kJ/mol)	$\Delta\hat{S}^{E}{}_{X_2}$ (J/K/mol)
Ag	137.3	72.4
Fe	251.2	61.6

Figure 2 shows the sulfur transport in the slag phase with identical conditions but with different metal phases. The right extreme in the figure represents the slag-metal interface. The higher sulfur concentration at the slag-metal interface in the case of silver is due to the lower solubility of sulfur in molten silver in comparison to molten iron.

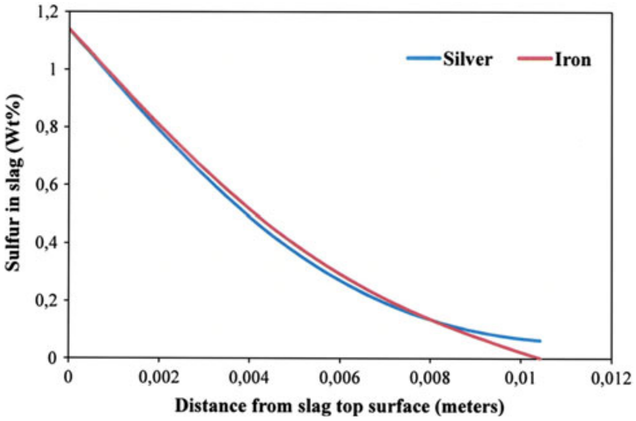

Figure 2: Sulfur concentration variation in the slag phase when using silver and iron metal phases independently. The right extreme represents the slag-metal interface.

The ultimate driving force for the movement of sulfur from the gas phase to the liquid metal would be the chemical potential difference of sulfur between the gas and the metal phases. In case of iron, the potential is much higher owing to the higher solubility of sulfur in iron. Despite this, there is no significant variation in the sulfur transport through slag. Thus it could be concluded that the thermodynamic relationships between the metal phase and sulfur do not have a significant impact on the sulfur movement in the slag.

Sampling technique and crucible design

The diffusivity of sulfur in slag depends on the slag composition. However, the analysis of the slag in comparison to the metal involves larger errors due to unreliable measurement techniques. Hence it was decided to analyze the metal sample instead of slag. The problem of taking out metal samples without slag inclusion posed another difficulty. In order to overcome this, a special crucible structure was designed as shown in Figure 3. Material selection to fabricate this complex crucible was another hurdle. Using of ceramics for crucible manufacture posed a great problem due to its difficulty in machining and delicacy. Also it would lead to a change in the composition of the slag due to dissolution in slag. Boron Nitride crucibles would lead to the introduction of surface active species at the slag-metal interface, which would again lead to faulty experimental results. Hence; it was decided to use pure Armco iron as the crucible material. Accordingly, silver was chosen as the metal phase since its melting point was lower than that of iron and its negligible solubility with respect to iron.

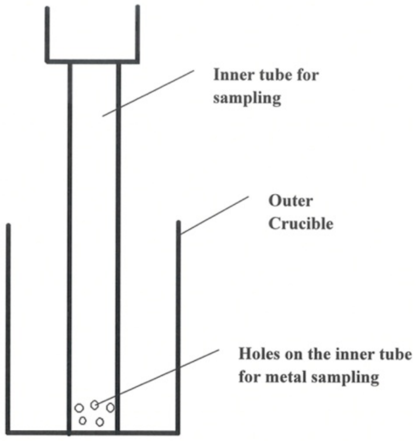

Figure 3: Crucible design for experiment.

Iron has a good solubility for sulfur in comparison to silver[7]. However since iron is solid at the working temperature and the diffusion of sulfur in solid iron is too low, practically no sulfur was absorbed by the iron crucible [8]. The use of a gas cleaning system was mandatory as the presence of oxygen in the system would lower the melting point of iron and hence lead to crucible puncture. Also using an iron crucible limited the experimental temperature range to be in between 1673 – 1723 K. The upper limit for the experimental temperature was determined by the melting point of iron while the lower limit was decided by the melting point of the slag used.

Slag composition and working temperatures

After selecting the material for the crucible and metal phase, the next step was to find a suitable slag composition that would give a reasonable working temperature. Further, a knowledge about the various slag properties was required especially density. Since the authors had carried out density measurements in the low silica $CaO-Al_2O_3-SiO_2$ ternary slag system[6], a slag of composition CaO = 51.5 %, Al_2O_3 = 38.9% and SiO_2 = 9.6% by mass was chosen. This gave a reasonable working temperature between 1673K and 1723K.

Source for sulfur

Probably the most difficult task of all was to select a suitable source for sulfur. Since pure iron was used as the crucible material, the partial pressures of oxygen and sulfur had to be accurately controlled in order to prevent any formation of FeO and FeS. The desired values of p_{O2} and p_{S2} were 10^{-7} and 10^{-1} Pa respectively. For achieving this, combinations of $CO-SO_2-Ar$, $CO-CO_2-SO_2-Ar$ and H_2S-Ar were computed using Thermocalc[9]. However, the extremely low flow rates of gases for achieving these partial pressures would introduce errors in the measurements. Thus, it was found that gas mixtures mentioned above were unsuitable for the present measurements. Another idea used was to pass argon gas, which was maintained at 400K by a heating sheath, through a sulfur bath maintained at 393K, so that the argon gas would carry sulfur gas along with it. Later it was found theoretically, that it was difficult to maintain a constant p_{S2} by this technique. Finally, it was decided to use CaS pellets as the source of sulfur. Since the density of CaS was lower than that of the slag and also due to its very high melting point (2800K) [10], it would act as a perfect source for sulfur. Further, thermodynamically, at the temperature of interest, CaS provided the required sulfur partial pressure as calculated from the reaction

$$CaS_{(s)} + 1/2O_2 \leftrightarrow CaO_{(slag)} + 1/2S_2 \qquad (7)$$

4. Results and Discussion

The experimental set up and method are discussed in details elsewhere[8]. Metal samples were taken at regular intervals and these samples were then analyzed for sulfur. The samples taken at 1723 K (first trial) were sent to NILAB AB for sulfur analysis. While the later samples (1680, 1700 and 1723 K) was analyzed using the in-house EDS system. The concentration profile of sulfur in the metal obtained by sampling was compared with that obtained by the model under the assumption of uniform composition. Table II shows the comparison between the sulfur concentrations measured by both methods. To calculate the diffusion coefficient of sulfur, the model mentioned earlier was used. In the model, the only term assumed was the diffusion coefficient; hence fitting the concentration curve to the experimental concentration profile would help in back calculating the diffusion coefficient. Figures 4, 5 and 6 show the comparison of the model and experimental concentration profiles of sulfur and the corresponding diffusion coefficient values obtained at 1680, 1700 and 1723 K respectively.

Table II. Sulfur concentration in silver metal during the diffusion experiments repeated at 1723 K. Sampling time is from the time CaS was introduced into the system.

Sampling time (seconds)	Concentration of sulfur in silver metal (ppm)	
	First trial	Second trial
18600	9.7	-
20100	16	15.6
21600	20.2	19.9

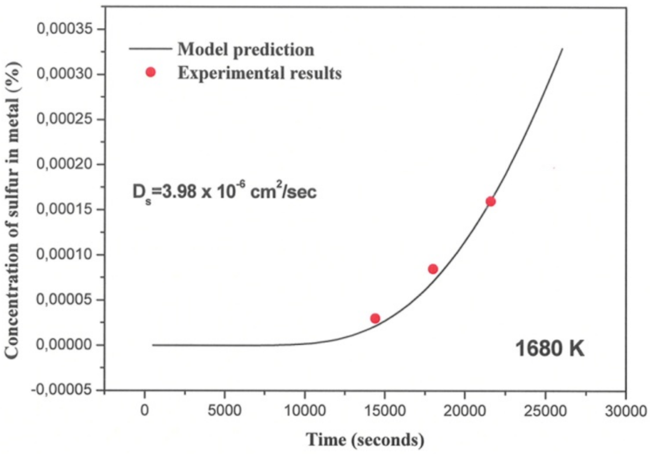

Figure 4: Comparison of Experimental results with model prediction at 1680 K. The diffusivity of sulfur through slag is estimated to be 3.98 x 10^{-6} cm^2/s.

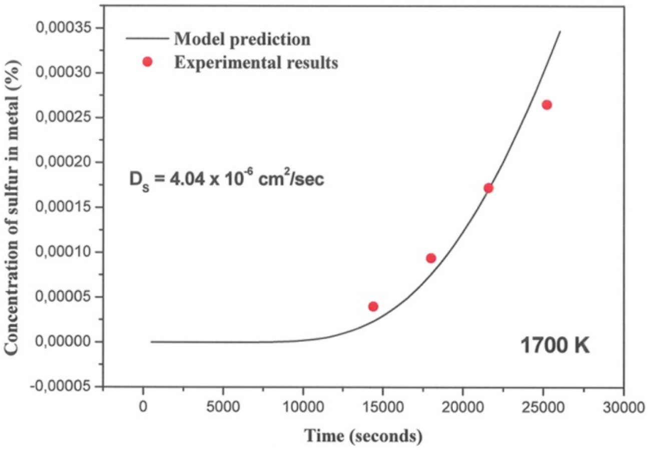

Figure 5: Comparison of Experimental results with model prediction at 1700 K. The diffusivity of sulfur through slag is estimated to be 4.04 x 10^{-6} cm^2/s.

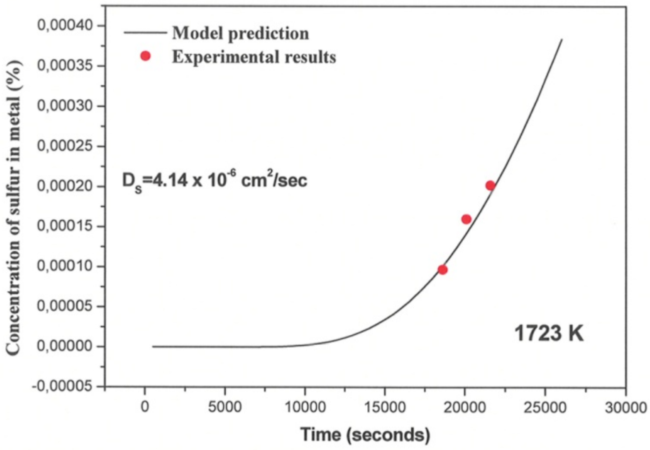

Figure 6: Comparison of Experimental results with model prediction at 1723 K. The diffusivity of sulfur through slag is estimated to be 4.14 x 10^{-6} cm^2/s. The experimental points are average of the values obtained by experiments.

The value for the diffusion coefficient of sulfur in the slag was in good agreement with the trend of the values obtained by Saito and Kawai[2] and with that of Derge et al[3]. The slag used in the current work was below the orthosilicate region while that used by Saito and Kawai had more than 33% silica content. Derge et al. used a quaternary slag composition 45.3% CaO – 14.1% Al_2O_3 – 37.1% SiO_2 – 3.5% MgO and the diffusion coefficient of sulfur in slag varied from $9x10^{-7}$- $6x10^{-6}$ cm^2/sec.

The compositions of the slags used in the current work and that used in the classic works of Saito and Kawai are compared in Table III. Other thermophysical properties are also been compared. The values for the sulfide capacity have been obtained from the works of Taniguchi et al.[5]. The viscosities are taken from the classic works of Kozakevitch[11].

Table III: Comparison between the slags used by Saito and Kawai[2] and the current work.

	Slag used by Saito and Kawai	Slag for current work
Composition (mass %)		
CaO	50.3	51.5
Al_2O_3	10.4	38.9
SiO_2	39.3	9.6
Diffusion Coefficient of sulfur (cm^2/sec)	$0.89x10^{-6}$ (at 1718 K)	$4.14x10^{-6}$ (at 1723 K)
Sulfide Capacity	$0.49x10^{-4}$	$0.447x10^{-3}$
Viscosity (Pa.s)	0.530	0.77

As seen from the table, the slag used by Saito and Kawai had a lower sulfide capacity, which resulted in a lower sulfur diffusivity in the slag media. Further, the basicity of the slag was lower compared to the slag used in the current work. The viscosity of the slag used in the current work was higher in comparison to that used by Saito and Kawai; however the higher sulfide capacity would lead to a higher value of diffusivity.

The effect of silica content present in the slag also affects the diffusivity. In the current slag compositions studied, the mole percent of SiO_2 was well-below 33% required for the orthosilicate composition. This would correspond to the existence of discrete SiO_4^{4-} tetrahedral units along with O^{2-} in the silicate melt and thus ruling out the possibility of the impact of silicate polymerization. In the absence of polymerization, the melt system would consist of Ca^{2+}, AlO_4^{-5}, SiO_4^{4-} and O^{2-} ions, which would result in a fast sulfur movement through the slag and thus a higher diffusion coefficient. It is also well known that the tracer, chemical and impurity diffusion coefficients decrease with increasing SiO_2 content in the slag.

Viscosity and diffusivity are interrelated by the Eyring relationship [12]

$$D_S = {}^{k_B T}/_{\eta}\, \lambda \qquad (8)$$

Where
k_B is the Boltzmans constant
η is the viscosity of the slag at temperature T K and
λ is the mean interatomic distance which is equal to twice the ionic radius.

The viscosity of the slag could be obtained from the classic works of Kozakevitch[11] for a composition of 10% SiO_2 – 40% Al_2O_3 – 50% CaO as 0.77 Pa.s at 1723 K. The value of the ionic radius of S^{2-} is 170 x 10^{-12} m [13]. From equation 2 we get the value of the diffusion coefficient as $1x10^{-6}$ cm^2/sec at 1723 K. The variation of the diffusivity value from the experimental results could be due to the approximation on the interatomic distance.

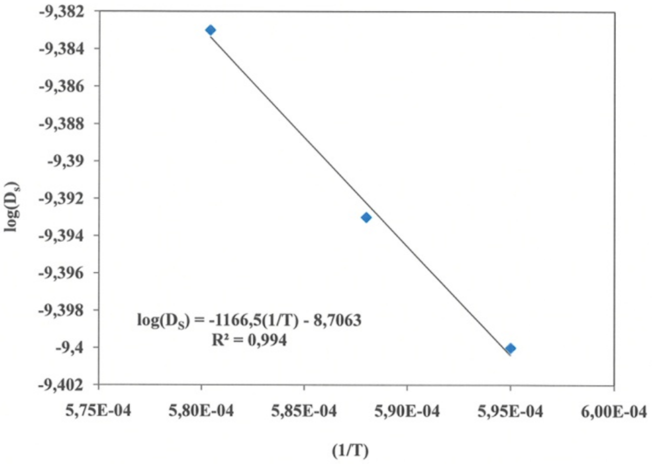

Figure 7: Temperature dependence of Diffusion coefficient of sulfur in 51.5% CaO- 9.6% SiO_2- 38.9% Al_2O_3 slag.

Figure 7 shows the temperature dependence of the diffusion coefficient of sulfur in CaO-Al_2O_3-SiO_2 slag. The activation energy calculated from the slope, *viz,* $\log(D_S)=-1166{,}5(1/T)-8.7063$ is lower than the value reported by Saito and Kawai. This is attributed to the fact that the temperature range used in the current work is rather narrow.

5. Conclusions

A new method for estimating the diffusivity of species in slag was designed taking into consideration the real parameters like diffusion coefficient, sulfide capacity, sulfur partition ratio and density of the slag. This method incorporated a model and corresponding experiments. The method was verified by evaluating the diffusion coefficient of sulfur in the ternary slag of composition 51.5% CaO- 9.6% SiO_2- 38.9% Al_2O_3 slag at temperatures 1680, 1700 and 1723 K by chemical diffusion from the variation of concentration of sulfur in silver metal, kept in contact with the slag. The order of the diffusion coefficient of sulfur in 51.5% CaO- 9.6% SiO_2- 38.9% Al_2O_3 slag was estimated to be 10^{-6} cm^2/sec which is in good agreement with the results available in literature.

Acknowledgements

The authors would like to thank the Swedish Research Council (Project No: H 6971) for the financial support. Also L. Muhmood would like to thank CSIRO for the financial support to attend MOLTEN 2012.

References

[1] M.D. Dolan , R.F Johnston. Met. and Mat. Trans. B, 2004, vol. 35B, p. 675.
[2] T. Saitô , Y. Kawai. Japan J. Inst. Metals, 1953, vol. 17, p. 434.
[3] G. Derge, W.O. Philbrook , K.M. Goldman. Trans. AIME, 1950, vol.188, p. 1111.
[4] L. Muhmood, N. N Viswanathan, S Seetharaman . Met. and Mat. Trans. B, Vol 42(2), 2011, p. 460-470.
[5] Y. Taniguchi, L. Wang, N. Sano, S. Seetharaman. Met. and Mat. Trans. B, Available online, 2012, DOI: 10.1007/s11663-011-9621-3.
[6] L. Muhmood, S. Seetharaman. Met. and Mat. Trans. B, 2010, vol. 41B, p. 833.
[7] O. Kubaschewski , C.B. Alcock. Metallurgical Thermochemistry, 5th Edition, Pergamon press, 1979, p. 47.

[8] L. Muhmood, N. N Viswanathan, M. Iwase, S Seetharaman . Met. and Mat. Trans. B, Vol 42(2), 2011, p. 274.

[9] Thermocalc®: Royal Institute of Technology, Stockholm, Sweden.

[10] M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald , A.N. Syverud (Ed.). JANAF Thermochemical Tables, The American Chemical Society and the american Institute of Physics , 3rd Edition, Part 1, 1985, p. 715.

[11] P. Kozakevitch. Rev. Metallurg., 1960, vol.57, p. 149.

[12] Slag Atlas. Ed: Verein Deutscher Eisenhűttenleute, Verlag Stahleisen m.b.h, 1995, p. 545.

[13] R.D. Shannon. Acta Cryst, 1976, A32, p.751.