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SULFIDE CAPACITIES OF SILICATE SLAGS

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Synopsis: In this paper, a new model has been developed to predict the sulfide capacities in acidic silicate melts based on the Reddy and Blander silicate slag model [1]. An expression for volume fraction of monomer(ϕ_s) in the range of $0.33< X_{SiO2} <1.0$ was developed. The expression for mean polymer chain length (m) and the volume fraction of polymer site(ϕ_p) in polymer solution as a function of X_{SiO2} and a_{MO} was developed. Calculations of C_s for MnO-SiO$_2$ slags, using this model at 1773 and 1923 K was made, and our predictions are in excellent agreement with available experimental data.

Key Words: Sulfide Capacity, Silicate Slag, Volume Fraction of Monomer, Mean Polymer Chain Length, Volume Fraction of Polymer Site.

1. Introduction:

Recently, we showed that C_s, the sulfide capacity can be calculated "a priori", based on a simple solution model and on a knowledge of the chemical and solution properties of sulfide and oxides [1,2]. The method of calculating sulfide capacity (practical definition was first given by Fincham and Richardson [3]) for basic melts in the composition range $0 \leq X_{SiO2} \leq 0.33$ SiO$_2$ and $0.33 \leq X_{SiO2} \leq 0.50$ SiO$_2$ in the binary silicate slag systems has been fully discussed [2].

2. Theoretical Consideration:

For basic melts in the composition range $0 \leq X_{SiO2} \leq 0.33$ SiO$_2$ in the MO-SiO$_2$ binary system, the composition is considered to be a ternary mixture of MO-M$_2$SiO$_4$ and MS. The equation for sulfide capacity of slags, C_s, is written as

$$C_s = 100\ W_s\ K_m\ a_{MO}\ \left(\frac{1-2X_{SiO2}}{\hat{W}}\right) \qquad (1)$$

where $\hat{W}$ is the average weight of the solution, w_s is the molecular weight of the solution, a_{MO} is the activity of MO in MO-SiO$_2$ melts and K_M is the equilibrium constant for the sulfur reaction $MO_{(l)} + \frac{1}{2}S_{2(g)} \rightleftharpoons MS_{(l)} + \frac{1}{2}O_{2(g)}$.

For the composition range $0.33<X_{SiO2}<1.00$ SiO_2 in the $MO-SiO_2$ system, the solution is a mixture of sulfide anions with silicate polymer anions. Using polymer solution theory, we obtain an equation for C_s, written as

$$C_s = 100\ w_s\ K_M\ a_{MO} \frac{X_{SiO2}}{\hat{w}} \left(\frac{\phi_s}{a_{MS}}\right) \qquad (2)$$

where ϕ_s is the volume fraction of S^{2-} sites. The partial molar free energy of a monomer for dilute solutions i.e. neglecting the higher order terms is given by

$$\Delta G_{MS} = RT[\ln\phi_S + (1 - 1/m)\phi_P + \mu\phi_P^2] \qquad (3)$$

For finite values of m (average polymer chain length), we obtain the expression

$$\ln(a_{MS}/\phi_S) = (1 - 1/m)\phi_p + \mu\phi_P^2 \qquad (4)$$

The ratio of (a_{MS}/ϕ_s) was calculated with the knowledge of m, ϕ_P and μ and these derived expressions are presented below.

(a) Expression for μ:

For high polymer mixture, Flory [4] derived an useful relationship between μ and m, from the consideration of the solubility and phase relationship of a hypothetical homogenous polymer, on the assumptions that all of polymers are not only identical in chemical structure, but also in chain length.

For a critical value of μ_C, from equation (3), Flory deduced the following expression between μ_C and m

$$\mu_C = \tfrac{1}{2} \left(1+ \frac{1}{m^{0.5}}\right)^2 \qquad (5)$$

(b) Expression for m:

From Masson's model, the following expression between the known quantities a_{MO}, X_{SiO2} and m can be deduced [5].

$$1/m = (1-a_{MO})(1/X_{SiO2} - 2) \qquad (6)$$

For $X_{SiO2}>0.5$, m is considered to be very large value (i.e. $m \approx \infty$).

(c) Expression for ϕ_P:

Consider an anion species that do not break Si-O-Si bridges in a silicate and the lattice is consisting of sulfur and SiO_4^{4-} unit monomers and a distribution of polymers (silicate polymeric ions). The monomer ions and the SiO_2 units in the polymer do not differ greatly in size. The volume fraction of polymer can be expressed as

$$\phi_P = n_p/\Sigma n_i \qquad (7)$$

where n_p is the number of moles of polymer units in the solution and Σn_i is the total moles in the solution. For small concentrations of sulfur in the melt (i.e. dilute solutions), equation (7) can be written as

$$\phi_p \cong 1 - X_{SiO4}{}^{4-} \qquad (8)$$

From the Masson's expression for the molecular size distribution in polymers, the following expression for $X_{SiO4^{4-}}$ can be deduced

$$X_{SiO4^{4-}} = [\frac{(1-a_{MO})/(X_{SiO2} + 2a_{MO})}{3}]^3 (1 - a_{MO}) \qquad (9)$$

The sulfide capacities of MnO-SiO$_2$ slags were calculated using equations 1,2 and 4 to 9 for the entire composition range and for several temperatures. The results obtained are discussed below.

3. Results and Discussions:

The calculated results for C_s in the MnO-SiO$_2$ slags are presented here. The free energy of formation of compounds for $MnO_{(l)}$ and $MnS_{(l)}$ and $MnS_{(l)}$ were taken from the tables data [6,7]. The activities of MnO were calculated using the reported results of Lee [8] which were computed from an analysis of experimental data [9]. From known values of a_{MnO} and K_{Mn}, C_S values were calculated using equation (1) up to $X_{SiO2} = 0.33$ and equation (2) for the composition range of $X_{SiO2} = 0.33$ to 1.0. The calculated values at 1773 and 1923 K along with the experimental data of Abraham et al [10] are shown in Figure 1 and 2 respectively. As can be seen from the figures, the agreement between the theoretically calculated and experimentally determined sulfide capacities is excellent.

It is clear from the above, that sulfide capacities of slags are directly proportional to the equilibrium constant K_{Mn}, and to the values of a_{MnO}. From the analysis presented here, it can be concluded that the variation of these two independent properties can not be corrected by a single parameter such as basicity but need to be predicted in a more fundamental manner using known thermodynamic data on the properties of the pure oxides, sulfides, and solutions.

4. Conclusions:

The methods we propose for calculating C_S in slags "a priori" is shown to be in excellent agreement with the available experimental data. This lends support to our method of calculation in which the values of C_S for slags are proportional to two independent factors K_M and a_{MO}. Further work on calculations of C_S in other binary and multicomponent slag systems is in progress.

5. Acknowledgement:

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6. References:

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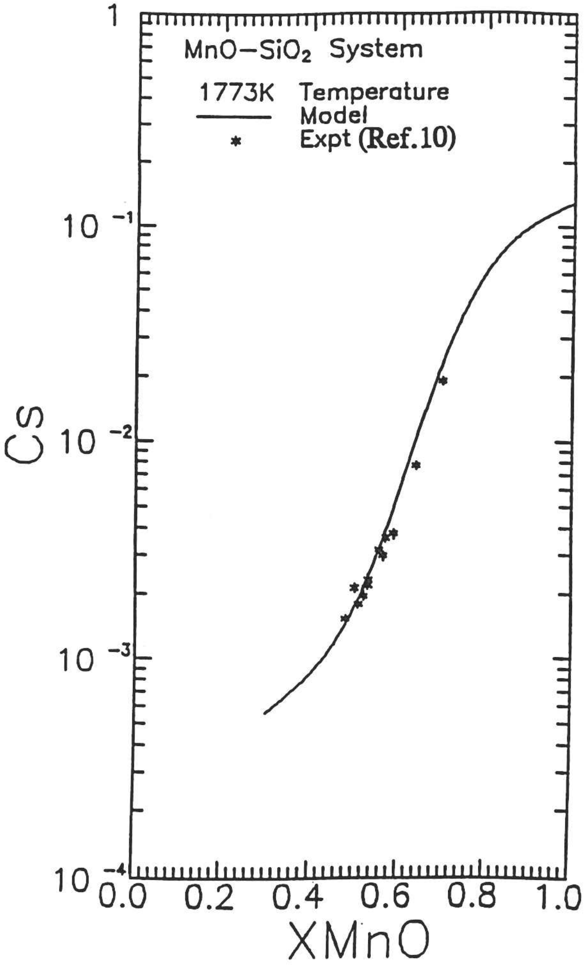

Fig.1. Plot of measured sulfide capacities in the MnO-SiO$_2$ system and calculated based on the model described here.

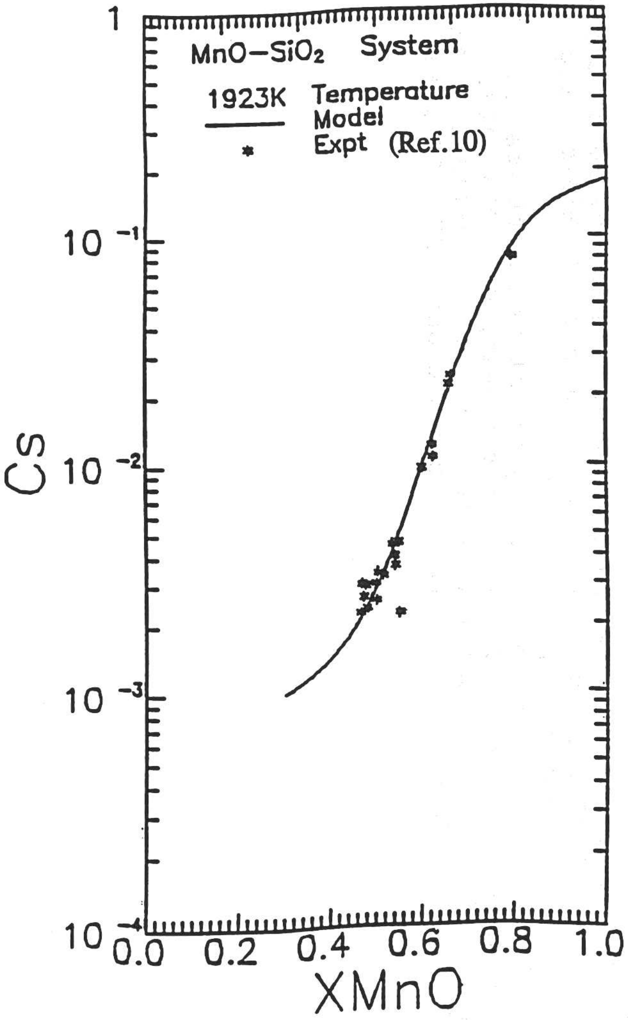

Fig.2. Plot of measured sulfide capacities in the MnO-SiO$_2$ system and calculated based on the model described here.