SULFIDE CAPACITIES OF CaO-MgO-$AlO_{1.5}$, MgO-MnO- $AlO_{1.5}$ and CaO-MgO-MnO-$AlO_{1.5}$ SLAGS

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ABSTRACT

Modeling of sulfide capacities of CaO-MgO-$AlO_{1.5}$, MgO-MnO-$AlO_{1.5}$ and CaO-MgO-MnO-$AlO_{1.5}$ slag systems were investigated. Sulfide capacities of aluminates slags were experimentally determined using gas phase equilibration method. The Reddy-Blander model was applied to calculate the sulfide capacities "a priori" with the knowledge of chemical and solution properties of oxide and sulfides for the above slags systems. The sulfide capacities were determined as a function of temperature (1500-1650°C), composition ($0 < X_{AlO1.5} < 0.6$) and basic oxides (CaO, MnO and MgO). Sulfide capacities of aluminates increased with increase in temperatures, decreased with increase in alumina content in the slags. Very good agreement was observed between model and experimental data.

INTRODUCTION

The Reddy and Blander (RB) model for *a priori* prediction sulfide capacities of binary and multicomponent silicate melts using the Flory [7] model for polymeric silica chains was developed. They showed that sulfide capacities could be calculated *a priori* based on knowledge of the chemical and solution properties of oxides and sulfides [1, 2, 3, 4, 5, 6]. In another publication [7], the model was extended to binary aluminate melts. They applied the model to ternary silicate melts containing FeO [8]. In all systems, excellent agreement between the model and experimental data was observed. In this work, the RB model is extended to calculate the sulfide capacities of binary, ternary and multicomponent CaO-MgO-MnO-$AlO_{1.5}$.aluminate slags.

THEORETICAL ANALYSIS

Basic oxides like CaO, MgO and MnO completely dissociate and supply oxygen ions. Using CaO-SiO_2 as an example, the binary is divided into two regions; one basic and one acidic. The sulfide equilibrium reaction in the melt is written as:

$$MO\ (l) + ½\ S_2\ (g) = MS\ (l) + 1/2\ O_2\ (g) \tag{1}$$

The equilibrium constant, K_M for the reaction (1) is given by:

$$K_M = a_{MS}/a_{MO}\ (P_{O2}/P_{S2})^{1/2} \tag{2}$$

The Sulfide capacity, Cs of slags is expressed as [1]:

$$Cs = (wt\%S)\ (P_{O2}/P_{S2})^{1/2} \tag{3}$$

where (wt%S) is weight percent of sulfur in slag, P_{O2} and P_{S2} are the partial pressures of oxygen and sulfur respectively.

Combining Equations 2 and 3, and Cs can be obtained as:

$$Cs = K_M\ a_{MO}\ [(wt\%S)/a_{MS}] \tag{4}$$

where a_{MS} and a_{MO} are the activities of MS and MO respectively.

Reddy-Blander model for Basic Binary: $0 \leq X_{AlO_{1.5}} \leq 0.33$

The silicate melt is completely depolymerized with oxygen given by the dissociation of MO. Some oxygen anions will be left unattached in the solution since the molar ratio MO/SiO_2 is greater than 2. These anions (O^{2-}) are called free oxygen. For this system, the model assumes that the only species in solution are one cation M^{2+} and three anions O^{2-}, SiO_4^{4-}, and S^{2-}. The latter is present in very small amounts. The solution is thus a simple ternary MO-M_2SiO_4-MS. Substituting $AlO_{1.5}$ for SiO_2 in the melts and the equation for Cs can be written as [5]:

$$C_S = 100 \cdot M_S \cdot K_M \cdot a_{MO} \cdot \left(\frac{1 - 2X_{AlO_{1.5}}}{\overline{M}} \right) \tag{5}$$

Where M_S is the atomic weight of sulfur and K_M is the equilibrium constant for the sulfur reaction. Where a_{MO} is the activity of the basic metal oxide in the binary system, and $\overline{M}$ is the average molecular weight of solution given by:

$$\overline{M} = X_{MO} M_{MO} + X_{AlO_{1.5}} M_{AlO_{1.5}} \quad (6)$$

Given the slag's temperature and composition, K_M and a_{MO} were obtained from HSC 4.1 [9] and FactSage 5.1 [10], respectively.

Reddy-Blander model for Acidic Binary: $0.33 \leq X_{AlO_{1.5}} < 1$

In this system, the anions are assumed to be randomly mixed. The CaO is completely consumed and allowing for the assumption that the concentration of O^{2-} ions is negligible. The model assumes a lattice consisting of sulfur (monomer) and a distribution of polymers (aluminate polymeric ions). The volume fraction of S^{2-} sites is given by:

$$\Phi_S = \frac{N_{S^{2-}}}{N_{Al} + N_{O^{2-}} + N_{S^{2-}}} \quad (7)$$

But since the solution is dilute, $N_{S^{2-}}$ is small compared to N_{Al}, and as a result it can be neglected in the denominator. As discussed earlier, $N_{O^{2-}}$ is also negligible. Equation 7 thus reduces to:

$$\Phi_S = \frac{N_{S^{2-}}}{N_{Al}} \quad (8)$$

Acidic binaries are divided into two regions. For intermediate acidic binaries ($0.33 \leq X_{AlO_{1.5}} \leq 0.5$), the solution is a mixture of polymeric species and monomer ions. The model equation for this region is:

$$C_S = 100 \cdot M_S \cdot K_M \cdot a_{MO} \cdot \exp\left(-1.25\left(1 - \frac{1}{m}\right)\right) \cdot \frac{X_{AlO_{1.5}}}{\overline{M}} \quad (9)$$

Where m is the polymer chain length given by:

$$\frac{1}{m} = \left(1 - a_{MO}\right) \cdot \left(\frac{1}{X_{AlO_{1.5}}} - 2\right) \quad (10)$$

For the remaining portion of the acidic binary ($0.5 \leq X_{AlO_{1.5}} < 1$), the solution is mostly polymeric. The model equation for this region is:

$$C_S = 100 \cdot M_S \cdot K_M \cdot a_{MO} \cdot \exp(-1.25) \cdot \frac{X_{AlO_{1.5}}}{\overline{M}} \quad (11)$$

The most complicated multicomponent system investigated in this work has four components. In this system, four oxides are basic; CaO, MgO and MnO, while one acidic oxide $AlO_{1.5}$. To calculate the sulfide capacity of this system, it is broken down into three ternaries;

$CaO\text{-}MgO\text{-}AlO_{1.5}$, $MgO\text{-}MnO\text{-}AlO_{1.5}$ and $CaO\text{-}MnO\text{-}AlO_{1.5}$. Equations 5, 9-1 can be used to calculate the sulfide capacities of each ternary system with few changes. The activity of the basic component is obtained from FactSage 5.1 [10] using the same mole fractions of the acidic components as in the multicomponent system. The average molecular weight of solution is obtained for the ternary system. Once the sulfide capacity of each ternary has been calculated, the following equation was used to calculate the sulfide capacity of the multicomponent system:

$$\log C_S = X'_{Ca} \log C_{S(Ca)} + X'_{Mg} \log C_{S(Mg)} + X'_{Mn} \log C_{S(Mn)} \quad (12)$$

Where X'_i is the equivalent cationic fraction of species i and can be calculated from the following equation:

$$X'_{Ca} = \frac{X_{CaO}}{X_{CaO} + X_{FeO} + X_{MgO} + X_{MnO}} \quad (13)$$

where the basic mole fractions are the same as in the multicomponent system. Equations similar to 13 were used for other basic components. The log C_s (i) is the sulfide capacity of the ternary system. The sulfide capacity of multi-component system using Equation 12 was calculated at a constant composition of acidic component (i.e., $AlO_{1.5}$) for binary melts.

RESULTS AND DISCUSSION

The model equations were used to calculate sulfide capacities for binary, ternary and higher order systems given a slag's temperature and composition. The model was used to calculate sulfide capacity of many systems, but only aluminate systems with available experimental data are reported in this work. Experimental results for sulfide capacities of binary $CaO\text{-}AlO_{1.5}$ were obtained from [11, 12, 13, 14, 15, 16, 17, 18, 19].

Sulfide Capacities of Ternary Slag Systems

The sulfide capacities of ternary slag systems experimental and model calculated data are presented in the Table 1. The sulfide capacities of the ternary system $CaO\text{-}MgO\text{-}AlO_{1.5}$ at 1550, 1600 and 1650ºC as reported by [13] are compared to model results in Figure 1. The ternary system $MgO\text{-}MnO\text{-}AlO_{1.5}$ was studied by [20] at 1600 and 1650˚C. Figure 2 compares reported experimental values to model results for the ternary $MgO\text{-}MnO\text{-}AlO_{1.5}$. The liquids data for basic sulfides (i.e., MgS) and also experimental sulfide capacities of $CaO\text{-}MnO\text{-}AlO_{1.5}$ are not available. The available solid data for solid sulfides and activity of basic activity in aluminates was used in calculating the sulfide capacities as a function of temperature. The predicted sulfide capacities for $CaO\text{-}MgO\text{-}AlO_{1.5}$ are lower than the experimental data. However, it is expected that the use of the liquids data will increase the sulfide capacities of this ternary slags. The sulfide capacities of $CaO\text{-}MgO\text{-}AlO_{1.5}$ decreases with the increase in composition of $AlO_{1.5}$. But the decrease is much smaller for the $MgO\text{-}MnO\text{-}AlO_{1.5}$ system. Effect of temperature on sulfide capacities of these ternary systems is not significant.

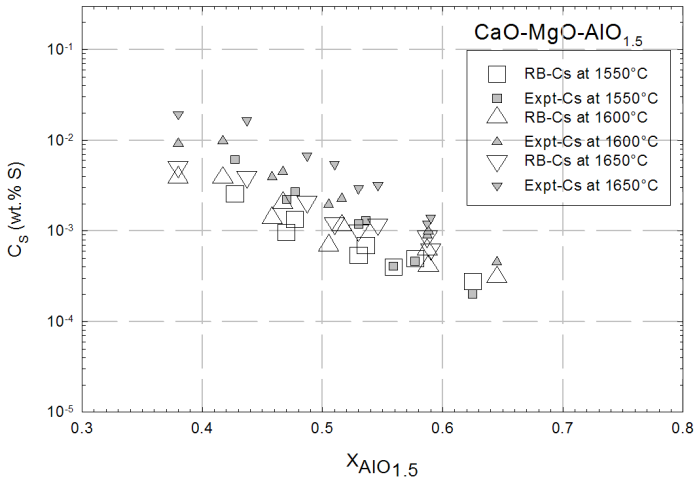

Figure 1: Comparison of available experimental data to model results of CaO-MgO-$AlO_{1.5}$ at 1550, 1600 and 1650°C. Experimental data are from [13]

Table 1: Sulfide capacities model and experimental data for ternary slag systems at various temperatures*

T (°C)	X_{CaO}	X_{MgO}	X_{MnO}	$X_{AlO1.5}$	RB-C_s	Expt-C_s
1550	0.521	0.053		0.427	2.5827E-03	6.1518E-03
1550	0.427	0.103		0.470	9.6587E-04	2.2233E-03
1550	0.471	0.052		0.477	1.3332E-03	2.7102E-03
1550	0.412	0.052		0.536	6.9279E-04	1.3032E-03
1550	0.384	0.039		0.577	4.9629E-04	4.6238E-04
1550	0.336	0.039		0.625	2.7639E-04	2.0277E-04
1550	0.380	0.090		0.530	5.3700E-04	1.1995E-03
1550	0.351	0.090		0.559	3.9897E-04	4.0884E-04
1600	0.530	0.053		0.417	3.8896E-03	9.8401E-03
1600	0.504	0.117		0.380	3.9067E-03	9.1622E-03
1600	0.426	0.116		0.458	1.3917E-03	3.9355E-03
1600	0.481	0.052		0.467	2.0452E-03	4.5290E-03
1600	0.432	0.052		0.516	1.1518E-03	2.2803E-03
1600	0.374	0.039		0.587	6.2475E-04	9.0365E-04
1600	0.316	0.039		0.645	3.1022E-04	4.5709E-04
1600	0.367	0.128		0.505	6.9496E-04	1.9679E-03
1600	0.322	0.090		0.588	4.1348E-04	9.9083E-04
1650	0.504	0.117		0.380	5.1045E-03	1.9364E-02
1650	0.511	0.053		0.437	3.9352E-03	1.6596E-02
1650	0.461	0.052		0.487	2.0964E-03	6.7764E-03
1650	0.402	0.052		0.546	1.1834E-03	3.1842E-03
1650	0.374	0.039		0.587	8.6713E-04	1.2078E-03
1650	0.399	0.090		0.510	1.2145E-03	5.4450E-03
1650	0.380	0.090		0.530	1.0205E-03	2.9309E-03
1650	0.333	0.077		0.590	6.2580E-04	1.3900E-03
1600		0.091	0.528	0.381	6.1422E-03	8.1670E-03
1600		0.091	0.528	0.381	6.1422E-03	7.9400E-03
1600		0.218	0.505	0.277	1.1842E-02	1.5490E-02

1600	0.218	0.505	0.277	1.1842E-02	1.5750E-02
1650	0.091	0.528	0.381	7.7209E-03	1.2160E-02
1650	0.091	0.528	0.381	7.7209E-03	1.1940E-02
1650	0.123	0.534	0.343	8.9671E-03	1.2790E-02
1650	0.123	0.534	0.343	8.9671E-03	1.3100E-02
1650	0.133	0.543	0.324	1.5074E-02	1.4400E-02
1650	0.133	0.543	0.324	1.5074E-02	1.6500E-02
1650	0.218	0.505	0.277	1.5140E-02	1.9290E-02
1650	0.218	0.505	0.277	1.5140E-02	1.8360E-02

* CaO-MgO-$AlO_{1.5}$ at 1550, 1600 and 1650°C experimental data are from [13] MgO-MnO-$AlO_{1.5}$ at 1600 and 1650°C experimental data are from [20]

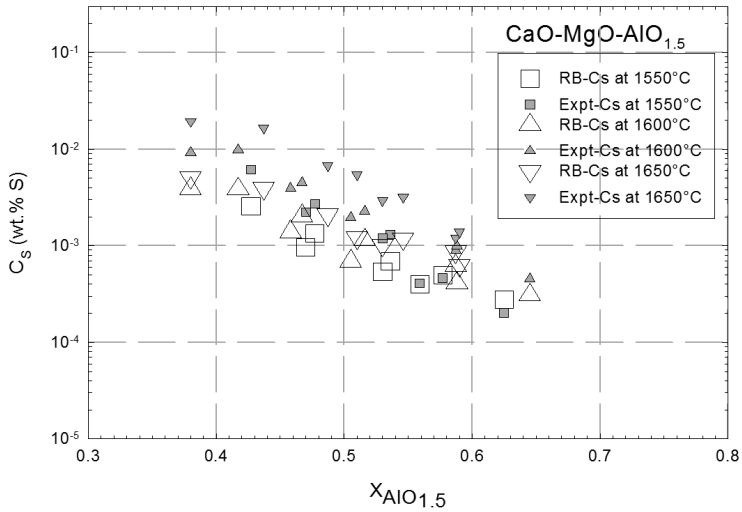

Figure 2: Comparison of available experimental data to model results of MgO-MnO-$AlO_{1.5}$ at 1600 and 1650°C. Experimental data are from [20]

Sulfide Capacities of Quaternary Slag Systems

The sulfide capacities of the system CaO-MgO-MnO-$AlO_{1.5}$ as measured by [20] at 1600 and 1650°C are compared to model results in Figure 3. The sulfide capacities of quaternary slag systems experimental and model calculated data are presented in the Table 2. A very good agreement between the *a priori* predicted and the experimental sulfide capacities of quaternary slags were observed.

Table 2: Sulfide Capacities Model and Experimental Data for Quaternary Slag Systems at Various Temperatures**

T (°C)	X_{CaO}	X_{MgO}	X_{MnO}	$X_{AlO1.5}$	RB-C_s	Expt-C_s
1600	0.431	0.067	0.054	0.448	2.4685E-03	2.9500E-03
1600	0.431	0.067	0.054	0.448	2.4685E-03	2.7560E-03
1600	0.427	0.067	0.039	0.467	1.9150E-03	2.4990E-03
1600	0.427	0.067	0.039	0.467	1.9150E-03	2.4830E-03
1600	0.414	0.093	0.032	0.460	1.6845E-03	2.3060E-03
1600	0.414	0.093	0.032	0.460	1.6845E-03	2.1570E-03
1600	0.423	0.067	0.048	0.463	2.0378E-03	1.9480E-03

1600	0.423	0.067	0.048	0.463	2.0378E-03	1.8750E-03
1650	0.431	0.067	0.054	0.448	3.2366E-03	3.5700E-03
1650	0.431	0.067	0.054	0.448	3.2366E-03	4.1640E-03
1650	0.427	0.067	0.039	0.467	2.5291E-03	2.7390E-03
1650	0.427	0.067	0.039	0.467	2.5291E-03	2.0250E-03
1650	0.414	0.093	0.032	0.460	2.2363E-03	2.9520E-03
1650	0.414	0.093	0.032	0.460	2.2363E-03	3.0130E-03
1650	0.423	0.067	0.048	0.463	2.6857E-03	2.2800E-03
1650	0.423	0.067	0.048	0.463	2.6857E-03	2.1110E-03

** CaO-MgO-MnO-$AlO_{1.5}$ at 1600 and 1650°C experimental data are from [20]

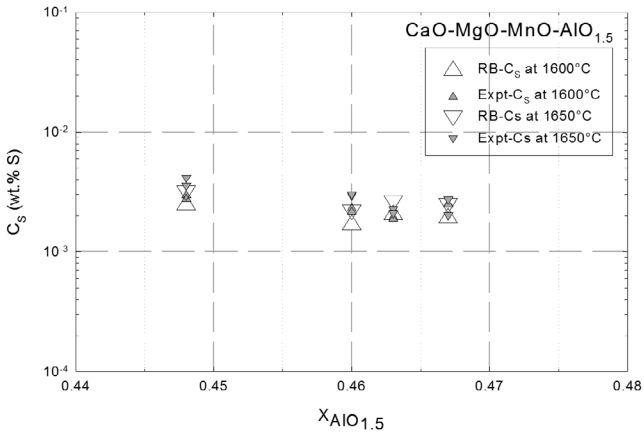

Figure 3: Comparison of available experimental data to model results of CaO-MgO-MnO-$AlO_{1.5}$ at 1600 and 1650°C. Experimental data are from [20]

CONCLUSIONS

The Reddy-Blander model can be used to calculate sulfide capacities of any system *a priori* given the slag's temperature and composition. The model agrees very well with experimentally measured values. For molten metal desulfurization, slag temperature and composition can be adjusted to obtain high sulfide capacity. Slag's with high sulfide capacities can be used effectively and economically to absorb and retain sulfur from molten metal. The low-sulfur steels can be used in more demanding applications.

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