

Experimental Studies on the Sulfide Capacities of CaO-SiO₂-CrO_x Slags

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To understand the desulfurization process during the refining of Cr-containing steel grades, this work was initiated to study the reactions between Cr-sulfur and chromium-containing slags. The sulfide capacities of CaO-SiO₂-CrO_x pseudo-ternary slags were measured using the traditional gas-slag equilibration technique between 1823 K and 1923 K. Sixteen different slag compositions were examined, and two different equilibrium oxygen partial pressures were used to understand the impact of the varying valence of Cr on the sulfide capacities. The results showed that log₁₀ Cs varied linearly with the reciprocal T, and the slope was higher than the corresponding value reported for the binary CaO-SiO₂ of corresponding composition. It was difficult to isolate the relative effects of the bi- and trivalent Cr in the slags because the Cr²⁺/Cr³⁺ ratio was influenced by the basicity of the slag. By using the equation developed by these authors earlier that related Cr²⁺/Cr³⁺ with basicity, oxygen partial pressure, and temperature, it was possible to obtain an approximate trend of the CrO effect on the sulfide capacities; *viz.* the sulfide shows a decreasing trend as Cr²⁺ replaces Ca²⁺ in the slag. With a continued increase of Cr²⁺ content, indications of the occurrence of a minimum point were observed; beyond which the sulfide capacities showed a slight increasing trend. The latter was attributed, based on slag-structure analysis by Gaskell *et al.*, to the increasing extent of the polymerization reaction releasing oxygen ions for sulfide reactions.

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I. INTRODUCTION

DESULFURIZATION during stainless-steel production generally is carried out during a reduction period in an argon oxygen decarburization converter after decarburization. Prior to this reduction period, an Ar-O₂ mixture is blown into the melt for decarburization, and a significant amount of chromium from the steel bath would enter the slag phase because of the inevitable oxidation caused by its high-oxygen affinity. It would be interesting to understand the impact of the chromium-oxide presence in the slag on the desulfurization process. Although earlier efforts have been focused on the measurements of the sulfide capacities of multicomponent slags between 1673 K and 1923 K,^[1-12] a survey of literature revealed only one earlier work on the sulfide capacities of chromium-oxide-containing slag.^[13] The experimental difficulties associated with these measurements because of the high liquidus temperatures of slags containing chromium oxide as well as the existence of chromium in two different valence states, *viz.* Cr²⁺ and Cr³⁺ under

different experimental conditions, present serious challenges to these measurements.

For the chromium-containing slag, measurements of the thermodynamic activities of chromium oxides have been carried out earlier by Pretorius and Muan,^[14] Xiao and Holappa,^[15] as well as Morita and Sano.^[16] The latter authors also have examined the solubility of chromium spinel MgO-Cr₂O₃ in CaO-MgO-Al₂O₃-SiO₂ melts.^[17] Phase diagram studies of chromium-oxide-containing slags under various conditions also have been found in literature.^[18-21] Several studies have been carried out earlier in regard to the distribution of chromium between Cr²⁺ and Cr³⁺ by several researchers.^[15,16,22-25] A critical survey of the earlier publications revealed that some of the results show a wide scatter. Furthermore, in some cases, the Cr²⁺/Cr³⁺ ratio reported showed an increase with an increasing basicity, which may be contrary to the trend shown for Fe²⁺/Fe³⁺ in FeO-containing slags.^[26] Efforts were made by Forsbacka and Holappa^[27,28] to understand the behavior of chromium-oxide-containing slags using viscosity measurements as a possible route. These authors determined the viscosities of CaO-SiO₂-CrO_x slags at 1873 K under two extreme oxygen potentials. This investigation is focused on the sulfur-removing capacity of melts in the CaO-SiO₂-CrO_x system, which is part of an extensive study of chromium-oxide-containing slags to optimize the alloy steelmaking processes, with a special reference to chromium loss in the slags.

Furthermore, sulfide-capacity measurements present an interesting path to understand slag structure. The

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reaction between the sulfur in the gas and the basic oxide in the slag—especially at silica contents higher than the orthosilicate compositions—involves the polymerization of silicates to supply the oxygen ions necessary for reactions with sulfur.^[29] Thus, the sulfide capacity measurements are likely suitable indicators of the extent of silicate polymerization with silica contents higher than orthosilicates and the impact of the various basic oxides on the same. Thus, this work is also part of a series of such efforts to correlate the structural measurements of silicate melts.

In this work, CaO-SiO₂-CrO_x was chosen as the base system, and it was proposed to build the understanding toward more complex systems using this base. The measurements were carried out between 1823 K and 1923 K by the classical gas-slag equilibration technique.

II. EXPERIMENT

CaO powder (99.9 pct, Alfa Aesar, Ward Hill, MA) was calcined at 1273 K for 12 hours to decompose any hydroxide and carbonate present. For SiO₂ (99.5 pct, Alfa Aesar) and Cr₂O₃, (99.9 pct, Sigma Aldrich, St. Louis, MO), these oxides were heated at 873 K for 6 hours to remove the residual moisture and stored in a desiccator before use. Appropriate amounts of the oxides were mixed to desired compositions, ground thoroughly in an agate mortar, and pressed into pellets. One gram of the sample was placed in a Pt cup (~Φ12 mm), which was hand-made from 0.14-mm-thick Pt foil (99.99 pct, Alfa Aesar) and then placed in an alumina holder (50 × 25 × 25 mm).

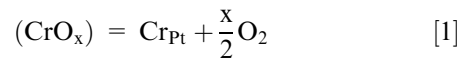
The sulfide capacities were measured by equilibrating the slag samples with a gas mixture containing CO, CO₂, SO₂, and Ar with well-defined sulfur and oxygen potentials at the experimental temperatures. Figure 1 shows the gas-purification system and experimental apparatus used. The furnace used in the current work was equipped with MoSi₂ heating elements and two sets of thermocouple; one connected to the proportional, integral, and derivative (aka PID) program controller and the other monitored the experimental temperature in the vicinity of the samples. The deviation of temperature was less

than ±3 K. The sample holder was placed in the even-temperature zone of the furnace, which was about 0.1 m at the center of the reaction tube.

With the help of high-tech flow-bus E600 mass-flow meters (Bronkhorst, Ruurlo, the Netherlands), the flow rates of the various gases were well controlled, and a gas mixture at a constant flow rate of 400 ml/min was introduced into the reaction tube (OD 0.06 m/ID 0.052 m/length 1.2 m). A narrow gas-inlet tube led the gas mixture directly into the reaction zone above the premelted slag samples. This precaution was taken to have a high linear gas velocity that avoided the thermal segregation of the gases during the equilibration with slags. The experimental conditions are presented in Table I. The partial pressures of oxygen and sulfur in the gas mixture at the experimental temperatures were calculated by ThermoCalc (Stockholm, Sweden) using the SSUB3 database in which 29 corresponding gaseous species were taken into consideration. The gas potentials of P_{O₂}/P_{S₂} obtained agreed with the values estimated from FactSage (Warrendale, PA) as well.

After equilibration, the sample holder was pulled out quickly to the cold end of the furnace under the flow of Ar gas. The samples then were taken out and subjected to chemical analysis. The sulfur contents of the slag samples were determined by LECO combustion method (St. Joseph, MI). CaO, SiO₂, and the total Cr in the slag were analyzed by X-ray fluorescence spectroscopy (XRF). The Pt foil with dissolved Cr was analyzed by XRF. The cross section of the foil was examined using scanning electron microscopy provided with an electron dispersive spectroscopy (EDS) attachment.

The equilibration time was set as 6 hours because this duration was adequate in earlier studies in this laboratory for sulfide capacity measurements. Furthermore, EDS analysis showed the Cr distribution across the thickness of the Pt-foil was uniform in this study, as shown in Figure 2. This finding confirmed that the entire crucible, which was in contact with the slag attained equilibrium, with respect to the following reaction:



The oxygen partial pressure corresponding to reaction [1] would be determined by the CO-CO₂-Ar gas mixture at the experimental temperature.

Reproducibility of the experiments could be confirmed by the consistency of the results for slag compositions close to each other at the same temperature.

Table I. Experimental Conditions in the Present Work (*Obtained from ThermoCalc, Stockholm, Sweden)

T/K	Inlet Gas Ratio				P _{O₂} /Pa*	P _{S₂} /Pa*
	Ar	CO	CO ₂	SO ₂		
1823	0.35	0.4	0.2	0.05	4.08 × 10 ⁻³	1.42 × 10 ³
1873	0.35	0.4	0.2	0.05	9.80 × 10 ⁻³	1.23 × 10 ³
1873	0.475	0.45	0.05	0.025	9.88 × 10 ⁻⁴	1.03 × 10 ³
1923	0.3625	0.5	0.1	0.0375	4.90 × 10 ⁻³	1.38 × 10 ³

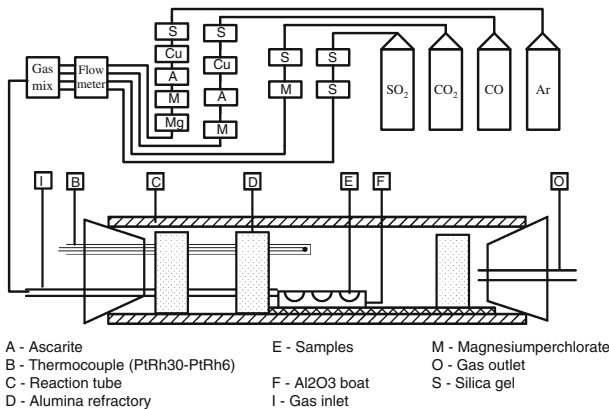


Fig. 1—A schematic diagram of gas-cleaning system and furnace assembly.

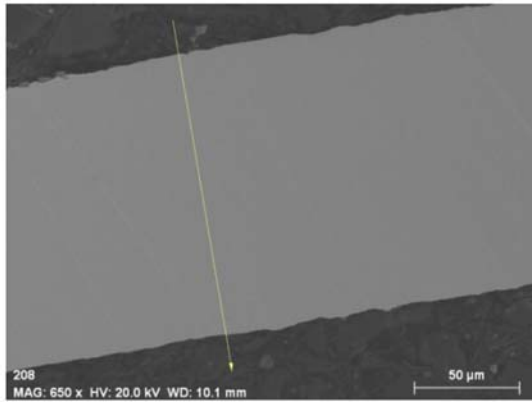
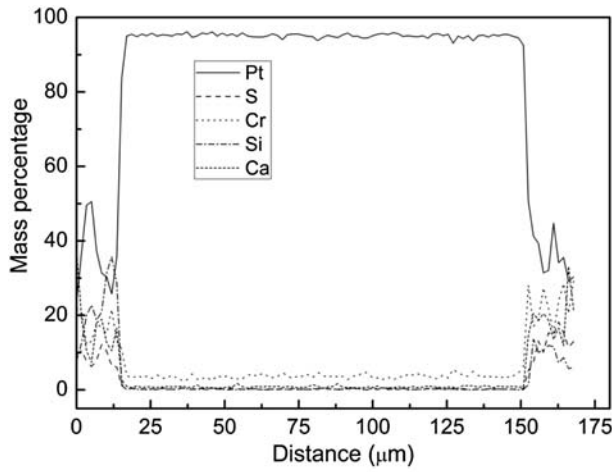


Fig. 2—A line analysis of Pt crucible cross section.

III. RESULTS

The slag compositions were chosen so that the slags were in the homogeneous liquid region, according to the phase diagram^[18,19] (Figure 3). As shown, the oxygen partial pressure prevailing would have a strong impact on the liquid region in the system. This behavior is analogous to the behavior of iron oxides^[30] in CaO-SiO₂ slags. When Cr³⁺ is the predominant valence state (for example in air), the solubility^[18] of chromium oxides in the slag at 1873 K is limited as a marked solid line, whereas, for the system in equilibrium with Cr metal at the same temperature, the solubility region is widened dramatically.^[19]

Because the oxygen pressures in these measurements as presented in Table I are low, the slags safely could be assumed to be completely molten. Microscopic examination of the slag samples after the experiments did not show any evidence of the presence of undissolved particles.

The attainment of equilibrium between the slag and gas phases should ensure the attainment of uniform and constant concentration of sulfur and oxygen (corresponding to the oxygen and sulfur potentials in the gas phase) in the slag melt at the experimental temperature. Furthermore oxygen-ion diffusion in the slag was expected to be fast in the slag phase because of the

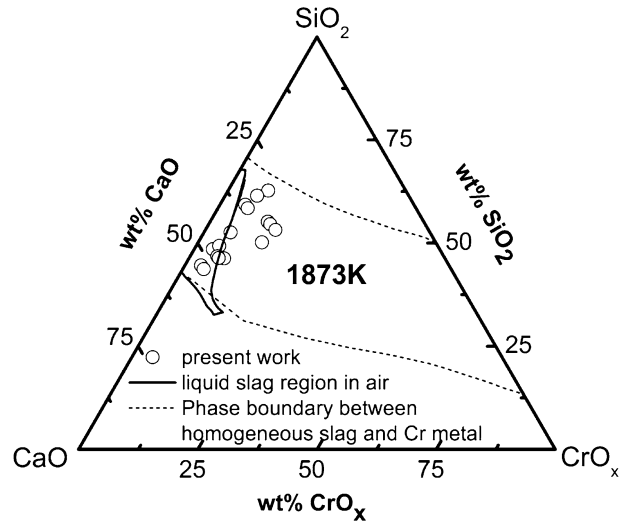


Fig. 3—A phase diagram of CaO-SiO₂-CrO_x at 1873 K with different oxygen potentials.^[17,18]

redox equilibrium that exists between the different valence states of Cr in the slag.

Sulfide capacities of 16 slag samples in the system CaO-SiO₂-CrO_x system were measured at 1823 K, 1873 K, and 1923 K. Table II summarizes the slag compositions as well as the experimental results. Note that the slag compositions in Table II are from the post-measurement analyses of the slags. The loss of chromium to the Pt container was generally low. The error in the sulfide capacity values presented in Table II was estimated to be ±0.02.

IV. DISCUSSION

Figure 4 shows the log₁₀ Cs from these results as a function of basicity (wt pct CaO/wt pct SiO₂). It shows that the sulfide capacity increases with increasing basicity, which was observed in all sulfide-capacity measurements.^[1-12]

Note that the slag system investigated in this work was in fact a quaternary system because of the existence of Cr²⁺ and Cr³⁺ in the slag. To investigate the roles of different chromium species, it is necessary to know the distribution of chromium oxide in the di- and trivalent states in the slag under these experimental conditions. A correlation between the Cr²⁺ and Cr³⁺ ratio and three factors, *viz.* temperature (T), oxygen partial pressure (P_{O₂}), and basicity (B)—the latter defined as (CaO + MgO)/(SiO₂ + Al₂O₃)—was established by these authors,^[31] based on works carried out in this laboratory combined with same with the data published earlier.^[14,22-25] The corresponding mathematical expression derived by these authors is represented as follows:

$$\log \left(\frac{x_{\text{Cr}^{2+}}}{x_{\text{Cr}^{3+}}} \right) = -\frac{11534}{T} - 0.25 \times \log (P_{\text{O}_2}) - 0.166 \times \log (B) + 5.84 \quad [2]$$

Table II. Experimental Results of CaO-SiO₂-CrO_x System

T/K	Composition (wt pct)			B	$\left(\frac{P_{O_2}}{P_{S_2}}\right)^{\frac{1}{2}}$	S/wt pct	Cs × 10 ⁴	log Cs
	CaO	SiO ₂	Cr					
1823	47.0	47.9	2.63	0.98	0.001695	0.111	1.882	-3.73
1823	35.3	59.0	3.63	0.60	0.001695	0.046	0.780	-4.11
1873	44.4	47.7	3.22	0.93	0.002828	0.104	2.930	-3.53
1873	35.1	58.2	4.25	0.60	0.002828	0.056	1.578	-3.80
1873	27.6	59.9	5.51	0.46	0.002828	0.041	1.155	-3.94
1873	32.7	55.2	8.21	0.59	0.002828	0.043	1.216	-3.92
1873	47.5	46.8	4.84	1.01	0.002828	0.104	2.941	-3.53
1873	40.1	55.2	2.61	0.73	0.002828	0.047	2.274	-3.64
1873	41.8	52.6	3.2	0.79	0.002828	0.06	2.488	-3.60
1873	47.4	46.4	3.52	1.02	0.002828	0.111	3.198	-3.50
1873	52.0	44.6	1.51	1.17	0.000978	0.355	3.472	-3.46
1873	31.8	61.5	4.43	0.52	0.000978	0.089	0.870	-4.06
1873	32.5	54.6	8.69	0.60	0.000978	0.147	1.438	-3.84
1873	46.3	46.3	4.38	1.00	0.000978	0.151	1.477	-3.83
1923	51.9	43.7	2.42	1.19	0.001884	0.320	6.029	-3.22
1923	32.1	53.2	10.2	0.60	0.001884	0.168	3.165	-3.50

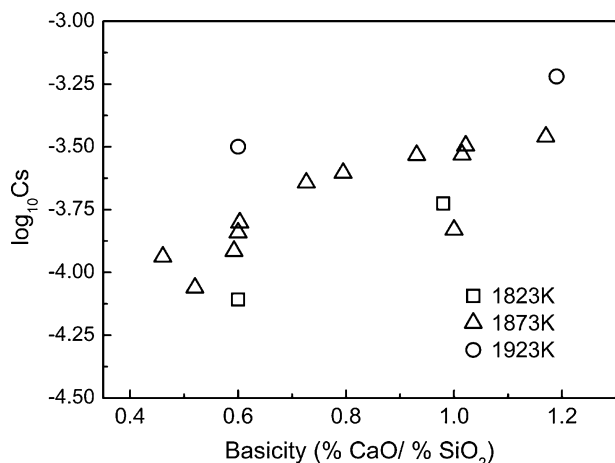


Fig. 4—Log₁₀ Cs obtained in this study and plotted as a function of slag basicity.

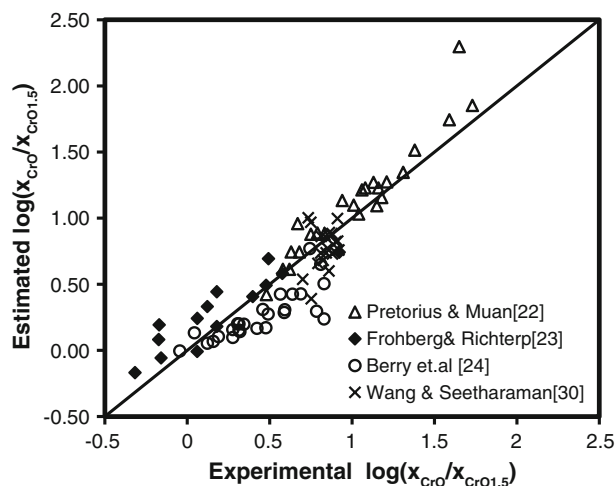


Fig. 5—A comparison of the experimental values of Cr²⁺/Cr³⁺ with those estimated from Eq. [1], which was obtained by the authors in a parallel work.

Note that in arriving at Eq. [2], some of the earlier work in which the authors reported a large spread in the (Cr²⁺/Cr³⁺) ratio or a trend in which the ratio increased with increasing basicity were omitted. The correlation between the estimated and experimental values of the ratio (Cr²⁺/Cr³⁺) was satisfactory as shown in Figure 5. Note that this evaluation includes the work carried out for all slag systems involving CrO_x, which include complex slag systems (e.g., CaO-MgO-Al₂O₃-SiO₂-CrO_x system reported by Berry *et al.*)^[24]

The experimental sulfide capacities (log₁₀ Cs) at 1873 K were examined as a function of the (CrO/CrO_{1.5}) ratio calculated from Eq. [2] in Figure 6. It is shown that the sulfide capacity decreased with increasing X_{CrO}/X_{CrO_{1.5}} at constant basicity. This trend was shown at three different basicity levels, which separated the impacts of basicity as well as the X_{CrO}/X_{CrO_{1.5}} on sulfide capacities.

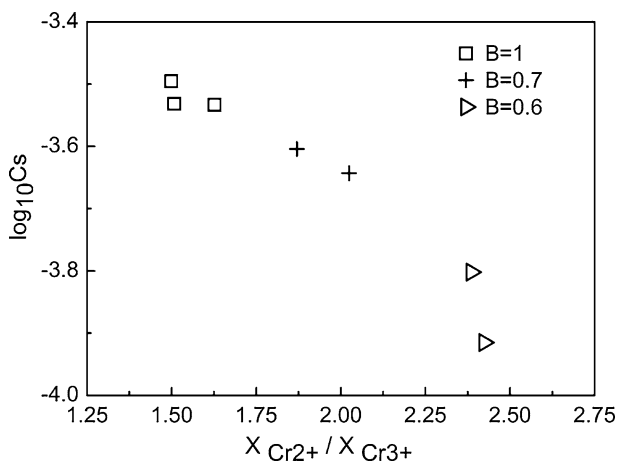


Fig. 6—Log₁₀ Cs plotted as a function of the CrO/CrO_{1.5} ratio at 1873 K.

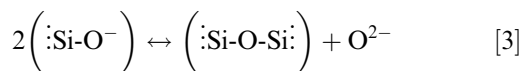
Thus, in this system, the variation of the sulfide capacity may be attributed to the following two factors, *viz.*

- (i) the increasing affinity of the basic oxide (CaO in this case) to the sulfide ion that would cause an increase of sulfide capacity;
- (ii) a decrease in the sulfide capacity with an increase in the $X_{\text{CrO}}/X_{\text{CrO}_{1.5}}$ at a given temperature.

Both of these effects are seen in Figures 4 and 6. In addition, the slag basicity had a strong influence on the ratio $X_{\text{CrO}}/X_{\text{CrO}_{1.5}}$ as shown by Eq. [2].^[31] The $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio decreased with an increasing basicity. This behavior was analogous to that of the variation of ($\text{Fe}^{2+}/\text{Fe}^{3+}$) ratio in silicate slags.^[26] With the addition of CrO to the CaO-SiO₂ system, the Ca^{2+} was gradually replaced by less basic Cr^{2+} and, consequently, one would expect a decrease in the sulfide capacities. This result is confirmed by Figure 6; the increase in the divalent chromium content led to a decrease in the sulfide capacity.

To understand better the specific effect of CrO on the sulfide capacities, these results ($\log_{10} C_s$) were plotted in Figure 7 as a function of the CrO content in the slag, as estimated by Eq. [2].

Despite the scatter in the results, the figure presents an approximate trend of the impact of CrO on the C_s values. It is shown that the sulfide capacity exhibited a decreasing trend as the Cr^{2+} in the slag increased and reached a minimum value. As described earlier, this decrease can be attributed to the dilution of Ca^{2+} by Cr^{2+} in the slag. With a continued increase of the CrO content, the oxygen potential in the system may have shown a slight increase because of the presence of CrO. At silica concentrations above the orthosilicate composition, Richardson^[29] suggested that polymerization of the silicate network would provide the necessary oxygen ions for the exchange reaction with sulfur. The polymerization reaction may be represented as follows:



Reaction [3] would release oxygen ions for a sulfide reaction.

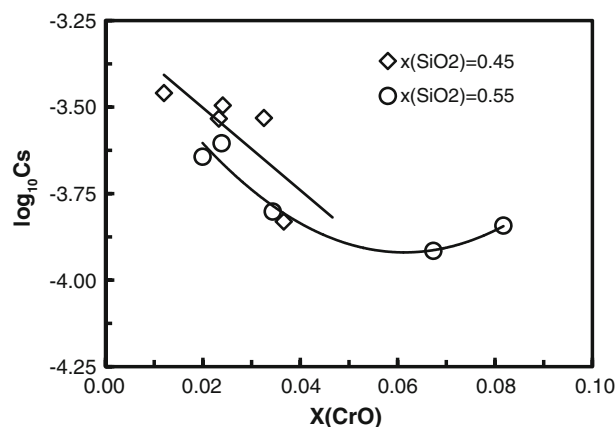


Fig. 7—The variation of $\log_{10} C_s$ with CrO content in the slag estimated from Eq. [1] at 1873 K.

Lee and Gaskell^[32] reported that, for the system 1.273 (FeO, CaO) SiO₂, the experimental thermal expansivity showed a minimum at about 0.4 mole fraction of CaO at 1773 K. Lee and Gaskell attributed this behavior to the inherent expansivities of the cation-anion bond types as well as to the degree of polymerization—apart from the temperature dependence on the degree of polymerization. Lee and Gaskell demonstrated that calcium silicate melts were less polymerized than the corresponding iron silicates. It is reasonable to assume that the behavior of Cr^{2+} would be somewhat similar to that of Fe^{2+} , even though the chemistry of CrO-containing melts are not well known. Thus, it is reasonable that, beyond the minimum point, the polymerization reaction may favor an increase in the sulfide capacities.

It is admitted that, because of a lack of reliable data on CrO-containing slags, any such hypothesis would be highly speculative. Furthermore, more experimental points are needed to confirm the existence of the minimum point.

Richardson *et al.*^[33,34] examined the variation of sulfide capacities of ternary silicates along the constant mole fraction of silica by extending the Flood equation^[35] to silicates. Considering silicate mixtures containing two cations at a fixed-silica mole fraction, the logarithm of the molar-sulfide capacity (Richardson expressed as \log_{10}) can be expressed by the following:

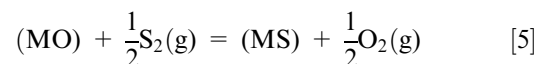
$$\log C'_s(\text{M}^{2+}, \text{N}^{2+}) = y_{\text{M}^{2+}} \log C'_s(\text{M}^{2+}) + y_{\text{N}^{2+}} \log C'_s(\text{N}^{2+}) \quad [4]$$

As shown in Figure 8, this relationship fit the experimental data for the cation pairs ($\text{Ca}^{2+} - \text{Mn}^{2+}$), ($\text{Ca}^{2+} - \text{Mg}^{2+}$), as well as ($\text{Mg}^{2+} - \text{Mn}^{2+}$) in the metasilicate region (even though a small deviation for the CaO-SiO₂-MnO-SiO₂ system exists). Thus, it could be reasonable to assume a linear variation of $\log C_s'$ between the two terminal binary silicates along a constant SiO₂ mole fraction in the metasilicate region.

In analogy with these systems, it can be reasonable to assume that $\log_{10} C_s'$ for the system CaO - SiO₂ and CrO - SiO₂ is linear with respect to the mole fraction of CrO. Extrapolation of the $\log_{10} C_s'$ values obtained for the ternary system obtained in this study to the CrO-SiO₂ end at 1873 K gives a $\log_{10} C_s'$ value of approximately -5, which is comparable to similar values for MnO-SiO₂ (-4.18 at 1973 K^[3]) and FeO-SiO₂ systems (-4.39 at 1773 K^[1]) at the metasilicate composition.

It is well known that sulfide capacities of a system of given composition increases with temperature. A survey of the earlier results^[1-12] showed that plots of $\log C_s$ vs the reciprocal temperature were linear for a wide range of compositions in binary and for more complex melts. This tendency was observed in this work for CaO-SiO₂-CrO_x, as shown in Figure 9.

Considering the sulfur removal reaction for the basic oxide component in the silicate is as follows:



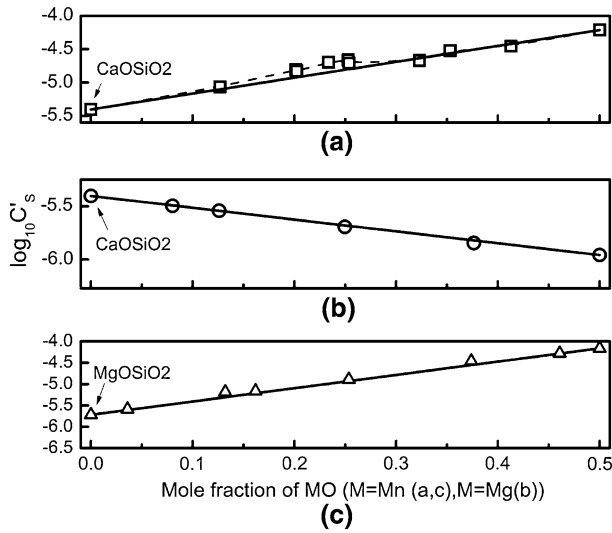


Fig. 8—Relationship between $\log C_s'$ and mole fraction of MO (where M = Mn or Mg) for metasilicates at 1923 K (C_s' corresponds to molar sulfide capacity).^[32,33]

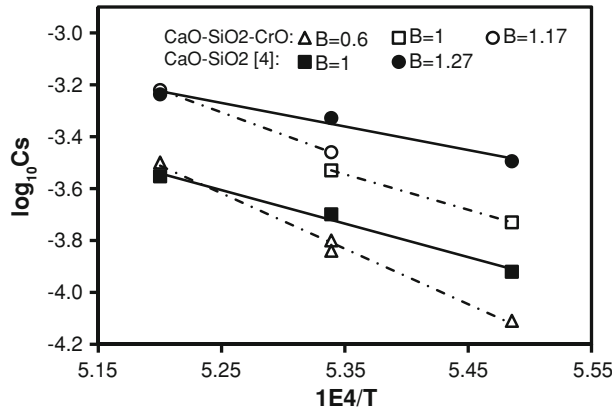


Fig. 9—Plots of $\log_{10} C_s$ vs $1/T$ for the CaO-SiO₂-CrO_x system from the results obtained in this work.

the sulfide capacity can be represented as follows:

$$\log C_s = -0.522 \times 10^{-5} \times \Delta H \times \left(\frac{10^4}{T}\right) + 0.0522 \times \Delta S + \log \left(\frac{a_{MO}}{f_{MS}}\right) \quad [6]$$

The enthalpy changes evaluated from the slopes of the lines in Figure 9 are summarized in Table III. For the CaO-CrO_x-SiO₂ system, the slopes of the lines were estimated to be 1.78 with $X_{SiO_2} = 0.45$ and 2.13 at $X_{SiO_2} = 0.58$. Comparing these values with the corresponding slopes for similar compositions for the CaO-SiO₂ system (−1.292 at unit basicity), the activation energy seemed to increase because of the chromium addition. The effect of the CrO_x addition may be complicated because of the existence of Cr cation in two different valence states. Although the trivalent chromium may have an impact on the thermodynamic

Table III. Slopes of the lines of $\log_{10} C_s'$ vs $(1/T)$

System	B	Slope	$\Delta H/J/mol$
CaO-SiO ₂ -CrO _x	1	−1.37	26245.21
	1.17	−1.73	33141.76
CaO-SiO ₂	1	−1.292	24750.96
	1.27	−0.9076	17386.97

activity of Ca²⁺ (in the high basicity region) probably because of the formation of chromate entities in the slag melt, the effect of the same material on the silicate network at the metasilicate compositions is uncertain. However, in analogy with Fe²⁺, Cr²⁺ is likely to promote polymerization according to reaction [3].

According to the ideal mixing theory proposed by Richardson,^[29] binary silicates of equal silica mole fraction mixed ideally with one another because the anionic structure was the same in both the pure silicates. Gaskell *et al.*^[36] as well as Lee and Gaskell accounted for the deviations from such an ideal behavior based on the cation dilation effect as well as silicate anion polymerization. As mentioned earlier, the latter factor may be influenced by the sulfide formation reaction.

Assuming an oxygen partial pressure corresponding to 10^{−3} Pa prevailing during the desulfurization step in the refining process, these studies indicated that, at about unit basicity, the sulfur removal capacity of the slag would reach a minimum value and would increase with a continued increase of Cr in the slag. On similar grounds, as chromium oxides are rereduced from the slag to the metal phase, a slight sulfur reversal is likely, depending upon the slag composition. This assumption, however, needs to be verified in industrial trials.

V. SUMMARY AND CONCLUSION

In this study, sulfide capacity of CaO-SiO₂ slags containing chromium oxide at selected temperatures and compositions, were measured by a slag-gas equilibration technique. A linear relationship between $\log_{10} C_s$ and the reciprocal temperature was observed in this study. The plots of $\log_{10} C_s'$ (C_s' is the molar sulfide capacity) vs $(1/T)$ obtained from these results exhibited a higher negative slope than the corresponding compositions for the CaO-SiO₂ system, which indicates a sharper increase of C_s with an increasing temperature. In the metasilicate region, mole sulfide capacity of CrO-SiO₂ ($\log_{10} C_s'$) was estimated to be approximately −5.0 at 1873 K.

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