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Effect of slag basicity and oxygen potential on the distribution of boron and phosphorus between slag and silicon

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Abstract
The distribution of boron and phosphorus between $\text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{SiO}_2$ and $\text{Al}_2\text{O}_3-\text{BaO}-\text{SiO}_2$ slags and silicon metal was examined for the purposes of establishing the possibility of refining metallurgical grade silicon to solar grade silicon. Distribution coefficients of B and P were normalized with the estimated oxygen partial pressure of the system to isolate the influence of basicity as the composition of the slag was varied in terms of the basicity (as $\text{CaO}:\text{SiO}_2$ ratio) and oxygen potential (as $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio) of the former and of the basicity (as $\text{BaO}:\text{SiO}_2$ ratio) of the latter slag systems. For both of these impurity elements, the normalized distribution showed a different dependence on corrected optical basicity in each slag system studied. Values were highest in the $\text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{SiO}_2$ slag with varying $\text{SiO}_2:\text{Al}_2\text{O}_3$, where the impurities are thought to associate with Mg, and lowest in the $\text{Al}_2\text{O}_3-\text{BaO}-\text{SiO}_2$ slag, where the impurities are thought to associate with Ba. The different dependence on basicity in each system is attributed to the differing manner in which the activity coefficient of the actual impurity compound in the slag varies with basicity. From thermodynamic calculations it was concluded that the difference in normalized distributions between the slag systems is attributed to the magnitude of the ratio of equilibrium constant to activity coefficient of the impurity oxides. It was found that where basicity is equal and the form of the impurity oxide in the slag is equivalent, phosphorus is expected to have a much smaller activity coefficient in the slag than boron.

Keywords: boron; phosphorus; slag refining; impurity distribution; activity

1. Introduction

The extent of the extraction of impurity boron and phosphorus from molten metallurgical silicon to a slag is expected to be strongly dependent on the slag chemistry. Where the uptake is as an oxidised species, the slag basicity and oxygen potential are both considered to be of importance. However, the individual effect of these aspects is difficult to determine due to changing the chemistry of the slag often having an influence on both.

Boron and phosphorus can enter a basic slag phase as oxides with silica acting as the oxidizing agent via the ionic Reactions 1 and 2.

\[
[B] + 3/2O^{2-} + 3/4O_2 \rightleftharpoons (\text{BO}_3^{3-}) \quad (1)
\]

\[
[P] + 3/2O^{2-} + 5/4O_2 \rightleftharpoons (\text{PO}_4^{3-}) \quad (2)
\]

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The slag basicity is interpreted as the concentration of “free” oxygen ions, as provided by basic oxides (silicate network modifiers) such as lime (Eq. (3)). The oxygen potential \( (p_{O_2}) \) is the oxygen resulting from the equilibrium between Si and SiO\(_2\) (Eq. (4)).

\[
(CaO) \rightleftharpoons Ca^{2+} + O^{2-} \tag{3}
\]

\[
(SiO_2) \rightleftharpoons Si + O_2 \tag{4}
\]

However, since basic oxides such as CaO and MgO have a strong affinity for silica, an excess amount of these fluxes will give a highly basic slag at the expense of lowering the activity of SiO\(_2\) \( (a_{SiO_2}) \). Increasing the basicity too far may then have the effect of impeding the removal of these elements if the \( p_{O_2} \) is in turn lowered sufficiently.

In a previous study [1], the authors made use of a slag refining technique to examine the removal efficiency of a number of impurities from metallurgical-grade silicon (MG-Si). The experimental approach and major findings are summarised here. A slag-metal equilibrium technique was employed for the determination of distribution coefficients \((L_M, \text{ratio of impurity element M concentration in slag to metal})\) for boron and phosphorus between molten slag and Si. This data gave an indication of which phase (slag or metal) the impurity elements would preferentially partition into. Values greater than unity indicate a preference for the slag phase whereas a value less than unity indicate a preference for the metal phase.

These distribution coefficient data for boron and phosphorus are shown in Figs. 1a and 1b respectively against slag composition. It was shown that increasing the oxidizing potential of the ACMS slag while keeping the basicity constant leads to an increase in distribution coefficient for both boron and phosphorus. Where the basicity of this slag was increased, \( L_P \) only increased slightly, while \( L_B \) increased through a local maximum at a CaO:SiO\(_2\) ratio of 0.6, then decreased with a further increase in basicity. Where the basicity of the ABS slag was varied, both \( L_B \) and \( L_P \) increased with increasing basicity; however the dependence on basicity appeared less significant. This suggested that excess amounts of basic oxides lower the activity of silica and consequently the oxygen potential of the slag which could then lead to lower than expected distribution coefficients for these impurities. This emphasizes the complexity in determining the overall effect of slag chemistry on impurity behaviour. Further to this, because of the relatively weak preference of boron and phosphorus for the slag phase, slag refining, if used, would be one step in a more complex overall refining programme.

This paper presents a detailed thermodynamic analysis of the data gathered previously for boron and phosphorus equilibria between slag and MG-Si [1]. Whereas the original study focussed on the removal efficiency of impurities from MG-Si, the purpose of the present study was to examine the nature of the distribution coefficient parameter and to isolate its dependence on a single aspect of the changing slag chemistry. Because the “free” oxygen ion is a hypothetical species, its activity cannot be quantified; therefore, it was deemed appropriate to attempt to quantify and account for the contribution of O\(^{2-}\) through related alternative measures such as the slag basicity [2].
2. Experimental

Full details on experimental procedures have been published previously [1]. The high-temperature experiments involved equilibrating MG-Si doped with boron and phosphorus with various slags in an alumina or magnesia crucible inside a vertical tube furnace under an Ar atmosphere at 1500 °C. The effect of varying slag basicity on $L_B$ and $L_P$ was investigated in terms of the CaO:SiO$_2$ ratio ($0.27 < \text{CaO}:\text{SiO}_2 < 1.73$) of the Al$_2$O$_3$-CaO-MgO-SiO$_2$ (ACMS) slag and the BaO:SiO$_2$ ratio ($0.44 < \text{BaO}:\text{SiO}_2 < 1.26$) of the Al$_2$O$_3$-BaO-SiO$_2$ (ABS) slag. Further to this, the effect of varying oxidizing potential of the slag was investigated in terms of the $\text{SiO}_2$:Al$_2$O$_3$ ratio ($0.64 < \text{SiO}_2:\text{Al}_2\text{O}_3 < 3.80$) of the ACMS slag.

At the end of each experiment, the crucible assembly was removed from the top of the furnace and quenched in a water bath. The resulting slag and metal phases were physically separated and prepared for chemical analysis. Silicon alloys were analysed by ICP-OES while slags were analysed by ICP-OES for boron and iron and by XRF for all other elements reported. The total uncertainty in the distribution coefficient data arising from the chemical analysis used to calculate it is estimated to be ±5% relative.

3. Results

To account for the effect of any change in $a_{\text{SiO}_2}$ on $L_M$ and isolate the effect of basicity as the slag composition was varied, distribution coefficients were normalised by the $p_{O_2}$ at each slag composition. This new parameter, the normalised distribution, $(D_M)$ of impurity element M, was calculated as shown in Eq. (5).

$$D_M = \left( \frac{\text{[M]}}{\text{[M]}} \right) \left( \frac{a_{\text{Si}}}{a_{\text{SiO}_2} K_4} \right)^n$$  \hspace{1cm} (5)

Here, (M) and [M] represent the concentration (in wt%) of impurity M in the slag and metal phases respectively. The activity of silicon ($a_{\text{Si}}$) and $a_{\text{SiO}_2}$ were determined from thermodynamic calculations using the FactSage$^1$ package. The applications of FactSage are described in two recent review papers [3, 4]. The SiO gaseous phase was considered when performing these calculations, but the extent of its formation was found to make a negligible contribution to the $p_{O_2}$ of the system. The equilibrium constant for the reaction between Si and SiO$_2$ ($K_4$) was calculated using a $\Delta G$ value of $5.91 \times 10^5$ J [5] with solid SiO$_2$ and liquid Si as the standard states. The power $n$ corresponds to the appropriate number of moles of O$_2$ for the reactions (1) and (2) above; i.e. $n = 3/4$ for boron and 5/4 for phosphorus oxidation. Normalized distributions for boron and phosphorus in the ACMS slags with varying CaO:SiO$_2$ ratio are shown in Fig. 2.

This distribution is seen to increase with increasing basicity for both elements as expected. It is also apparent now, that the distribution of phosphorus is several orders of magnitude greater than that of boron, and that $D_P$ is more strongly dependent on basicity than is $D_B$. This is an expected behavior as phosphorus has the more acidic oxide based on

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$^1$ FactSage is a trademark of GTT Technologies, Herzogenrath, Germany.
recommended optical basicity (A) values for P₂O₅ (0.40) and B₂O₃ (0.42) [2], thus should have stronger attraction to a basic melt.

The normalized distributions of phosphorus and boron in the ABS slags are shown in Fig. 3. In this case, due to the limitations of the FactSage package in calculating $a_{\text{SiO}_2}$ in BaO-containing slags, it was calculated from the expression of Meraikib [6] while a constant $a_{\text{Si}}$ of 0.95 was used for each point under the assumption that silicon activity remains unchanged with variations in the concentration of trace boron and phosphorus.

In this system, normalized distributions increase with increasing basicity in a similar manner as in the ACMS slags, although the actual values are lower.

Normalized distributions were also calculated for boron and phosphorus for the ACMS slags with varying SiO₂:Al₂O₃ ratio and are shown in Fig. 4.

There is a slight increase in $D_B$ with increasing SiO₂:Al₂O₃ ratio, which indicates that there is still some other influence on phosphorus in these slags. This could be due to slight changes in basicity; however, the apparent increase in basicity (as indicated by the direction of the increase in $D_B$) is in the opposite direction to that in which the basicity would be expected to increase due to the smaller optical basicity of SiO₂ (0.48) compared to Al₂O₃ (0.61). The reason for this apparent discrepancy will be discussed in the following section.

4. Discussion

4.1. Structural Considerations

Mills and Sridar [7] have discussed the need to account for the structural effects of the Al₂O₃ content of a slag when quantifying the optical basicity and provide an expression for calculating the corrected value. This is due to changes in the slag structure brought about by the changing alumina content of the system. Alumina can behave as a network-forming oxide by joining the silicate chain structure within the slag as AlO₄⁻⁻ tetrahedra. The existence of the AlO₄⁻⁻ unit has been discussed by a number of authors, for example [8, 9]. However, due to the different charges of the Si and Al-based tetrahedra, the AlO₄⁻⁻ unit must be charge balanced by another cation. In this system where there are no alkali metals present, it is expected that Ca²⁺ acts as the charge-balancing cation. Thus, as the Al₂O₃ content of the slag increases, the proportion of CaO present as part of the Ca₀.₅AlO₄⁺⁺ unit also increases. This CaO is then not free to donate oxygen to the slag, thus only any excess contributes to the overall basicity of the slag [10]. This excess will become greater as the SiO₂:Al₂O₃ ratio of the ACMS slag was increased in the present work (Fig. 4), and it is in this direction where the increase in $D_B$ was observed. Thus, the increase in the distribution coefficient of phosphorus shown previously [1] for this system was not entirely due to the increasing $p_{O_{2}}$, but was in part due to the slag actually becoming more basic.

4.2. Dependence of Distribution on Basicity

The normalized distribution of boron where the SiO₂:Al₂O₃ ratio is varied in the ACMS slag shows no appreciable variation with slag chemistry as the influence of $p_{O_{2}}$ is removed, as would be expected if the slag basicity was constant. By expressing the slagging reactions in terms of activity coefficients, the normalized distribution is then seen to be a function of basicity
in two ways; namely, the activity of “free” oxygen \( (a_{O^{2-}}) \), and the inverse of the activity coefficient of the impurity oxide in the slag \( (\gamma_{MO_x^{-}}) \) as shown in Eq (6).

\[
D_M = K_{1,2} \left( a_{O^{2-}} \right)^{1.5} \frac{\gamma_M}{\gamma_{MO_x^{-}}} \tag{6}
\]

As the activity coefficients of B and P in Si \( (\gamma_M) \) do not change much across either slag system due to their small concentrations, the normalized distribution will be higher where \( \gamma_{MO_x^{-}} \) is lower. As phosphorus has a stronger acidic oxide than boron, it is expected that for equivalent compounds, \( \gamma_{PO_x^{-}} < \gamma_{BO_x^{-}} \) in these slags that are relatively basic. This would partly account for \( D_P \) being greater than \( D_B \) in Figs 1 and 2 above and more responsive to changing slag basicity as is the case where the CaO:SiO\(_2\) ratio is varied in the ACMS slag.

However, since there is actually an increase in slag basicity in terms of \( \Lambda \), the activity coefficient of the boron oxide in the slag \( (\gamma_{BO_x^{-}}) \) must therefore be changing. Optical basicity is an indirect measure of \( a_{O^{2-}} \), so from Eq (6) above, as \( \Lambda \) increases, \( \gamma_{BO_x^{-}} \) must increase accordingly for \( D_B \) to remain constant. It follows then that the activity coefficient of the phosphorus oxide in the slag \( (\gamma_{PO_x^{-}}) \) must not increase significantly over the same interval to account for the observed increase in \( D_P \).

Figs. 5 and 6 show all the normalized distribution data for phosphorus and boron respectively, plotted against the corrected optical basicity \( (\Lambda_{corr}) \). Values for the individual slag components used were those recommended by the Slag Atlas [2] with the expression of Sosinsky and Sommerville [11] for overall basicity. A sample calculation of \( \Lambda_{corr} \) is described in Appendix 1.

In both figures, the three series of data for the individual element do not all fit the same trend against \( \Lambda_{corr} \). Instead, the data for the individual slag systems appear to follow separate trends. For both phosphorus and boron, normalized distributions are highest in the ACMS slags with varying SiO\(_2\):Al\(_2\)O\(_3\) ratio and lowest in the ABS system over the basicity range studied. This is an expected result, as \( \Lambda_{corr} \) are highest in the former and lowest in the latter system. The implication of this is that if each system was extended to cover the same range of \( \Lambda_{corr} \), a different particular \( D_M \) should result from each system at a single \( \Lambda_{corr} \). This effect can be seen at about \( \Lambda_{corr} = 0.54 \) for \( D_B \) (Fig. 6) where the value in the CS system is greater than that in the BS system. Since \( a_{O^{2-}} \) may be related to \( \Lambda_{corr} \), from Eq. (6) above, the variations of \( D_M \) with slag system at constant \( \Lambda_{corr} \) would then be due to variations in \( \gamma_M, \gamma_{MO_x^{-}} \) or both. Since the Si metal is very dilute in P and B, \( \gamma_M \) is virtually constant. This implies that it is the activity coefficient of the actual form the impurity takes in the slag that influences its distribution.

4.3. Activity of Impurity Forms in the Slag

Where the SiO\(_2\):Al\(_2\)O\(_3\) ratio was varied in the ACMS slag, the MgO content of the equilibrated slags is in the range 20-33 wt%, compared to only 2-4 wt% for the slags with
varying CaO:SiO\(_2\) ratio. The FactSage calculations confirm that the mole fraction of Mg\(_3\)(PO\(_4\))\(_2\) is greater than that of Ca\(_3\)(PO\(_4\))\(_2\) in the ACMS slags with varying SiO\(_2\):Al\(_2\)O\(_3\) ratio, and vice versa in the ACMS slags with varying CaO:SiO\(_2\) ratio. Thus, phosphorus is expected to form associations with Mg and Ca in the former and latter slags respectively, whereas it forms compounds with Ba in the ABS slag. It was also revealed that in the ACMS system, the activity coefficient of Mg\(_3\)(PO\(_4\))\(_2\) in the slags with varying SiO\(_2\):Al\(_2\)O\(_3\) ratio was less than that of Ca\(_3\)(PO\(_4\))\(_2\) in the slags with varying CaO:SiO\(_2\) ratio, which would lead to \(D_P\) being higher in the former than the latter at the same basicity. From the plots in Fig. 5, this is expected to be the case at \(\Lambda_{\text{corr}} < 0.59\). However, both these activity coefficients increase with increasing \(\Lambda_{\text{corr}}\), meaning normalized distributions should decrease. The increase in \(a_{O^2-}\) associated with the increasing \(\Lambda_{\text{corr}}\) must therefore be great enough to counterbalance this in Eq (6). Values of \(D_P\) for the ABS system are lower than those in the varying CaO:SiO\(_2\) slags at \(\Lambda_{\text{corr}} > 0.54\), which suggests that the activity coefficient of Ba\(_3\)(PO\(_4\))\(_2\) is greater than that of Ca\(_3\)(PO\(_4\))\(_2\) for the majority of the basicity range covered in this work. This could not be confirmed however, due to the lack of thermodynamic data for Ba-containing slags.

As with phosphorus, \(\gamma_{B O_3^-}\) from the present results is expected to be lowest in the varying SiO\(_2\):Al\(_2\)O\(_3\) slags of the ACMS system (as an Mg compound) and highest in the ABS system (as a Ba compound). It is suggested that boron forms the same associations in the different slag systems as does phosphorus, although this could not be confirmed with the thermodynamic calculations carried out.

Expressing Eq (6) in the form

\[
\log D_M = 1.5 \log a_{O^2-} + \log \frac{K}{\gamma_{MO_3^-}}
\]

shows that the difference in \(D_M\) between the different slag systems where basicity is equal will be due to the magnitude of \(K/\gamma_{MO_3^-}\) for the different impurity compounds. It follows that where the increase in basicity is the same, the increase in \(D_M\) for the individual impurities over a single system is related to changes in the particular \(\gamma_{MO_3^-}\). The equation of the trend line through each series of data in Figs 5 and 6 above were determined by least-squares linear regression and are given in Tables 1 and 2. These give a quantitative indication of the responsiveness of each impurity to changes in slag basicity in relation to one another.

<table>
<thead>
<tr>
<th>System</th>
<th>Compound</th>
<th>Equation</th>
<th>(R^2)</th>
<th>(\Delta G) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>Mg(_3)(PO(_4))(_2)</td>
<td>(\log D_P = 17.5\Lambda_{\text{corr}} + 13.2)</td>
<td>0.665</td>
<td>-1140</td>
</tr>
<tr>
<td>CS</td>
<td>Ca(_3)(PO(_4))(_2)</td>
<td>(\log D_P = 54.4\Lambda_{\text{corr}} - 8.19)</td>
<td>0.996</td>
<td>-1400</td>
</tr>
<tr>
<td>BS</td>
<td>Ba(_3)(PO(_4))(_2)</td>
<td>(\log D_P = 23.9\Lambda_{\text{corr}} + 8.39)</td>
<td>0.752</td>
<td>No data</td>
</tr>
</tbody>
</table>
Table 2. Relationship between $D_B$ and $\Lambda_{\text{corr}}$ at 1500 °C.

<table>
<thead>
<tr>
<th>System</th>
<th>Compound</th>
<th>Equation</th>
<th>$R^2$</th>
<th>$\Delta G$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>$\text{Mg}_3(\text{BO}_3)_2$</td>
<td>$\log D_B = 1.04\Lambda_{\text{corr}} + 13.9$</td>
<td>0.265</td>
<td>-1050</td>
</tr>
<tr>
<td>CS</td>
<td>$\text{Ca}_3(\text{BO}_3)_2$</td>
<td>$\log D_B = 18.8\Lambda_{\text{corr}} + 3.39$</td>
<td>0.955</td>
<td>-1090</td>
</tr>
<tr>
<td>BS</td>
<td>$\text{Ba}_3(\text{BO}_3)_2$</td>
<td>$\log D_B = 36.0\Lambda_{\text{corr}} - 6.68$</td>
<td>0.583</td>
<td>No data</td>
</tr>
</tbody>
</table>

Also included in Table 1 above are the reaction Gibbs energies for the formation of the borate and phosphate of Ca and Mg as determined by FactSage. These show that the Ca compounds are more stable and will therefore have a higher $K$ than those of Mg. By Eq (7) above, where $K$ is higher, $D_M$ will also be higher. It follows that, in this range of $\Lambda_{\text{corr}}$, the magnitude of the activity coefficients for the Mg compound and the Ca compound for a single impurity must be such that $K/\gamma_{\text{MO}_x^{+}}$ is actually greater where associations are with Mg. However, for both impurities, the slope in the system with varying CaO:SiO$_2$ is greater than that with varying SiO$_2$:Al$_2$O$_3$ for the ACMS slags. Thus, if each slag system was extended to higher basicity, the $D_M$ where Ca compounds are formed will eventually be higher than for the corresponding Mg compounds, as their relative stabilities would suggest.

A similar effect was also observed for phosphorus in MgO-FeO-SiO$_2$ based slags [12]. In this case, values of the activity coefficient of phosphorus in the slag (as $\gamma_{\text{P}_2\text{O}_5}$) were lower for Na$_2$O-containing slags compared to those containing CaO in the range $0.6 < \Lambda < 0.7$. This implies that $\gamma_{\text{P}_2\text{O}_5^{3-}}$ is lower when associated with sodium in the slag than when associated with barium or calcium in this region. It is also apparent that $\gamma_{\text{P}_2\text{O}_5}$ in the Na$_2$O-containing slags will be greater than in the CaO-containing slags at a basicity in the range $0.55 < \Lambda < 0.6$. This would correspond with a decrease in $K/\gamma_{\text{P}_2\text{O}_5^{3-}}$ and, in turn, $D_P$. The corresponding $\Delta G$ value for Na$_3$PO$_4$ is -895 kJ, so should in fact be less stable than Ca$_3$(PO$_4$)$_2$.

4.4. Other Considerations

The slag chemistry needs further consideration, as contamination of the silicon by the slag components can cause impurities to be retained in the metal phase. Lynch [13] states that calcium in silicon can draw phosphorus back into the silicon through ternary interactions. Calcium may enter the metal phase by the reduction of lime by silicon as in Eq. (8).

$$2\text{CaO} + \text{Si} \rightleftharpoons \text{SiO}_2 + 2\text{Ca}$$  \hspace{1cm} (8)

By expressing the equilibrium constant ($K_8$) in terms of the activity coefficient of Ca ($\gamma_{\text{Ca}}$), a relationship between the concentration of Ca in the metal phase [$\text{Ca}$] and the activities of lime ($a_{\text{CaO}}$) and silica can be derived, as shown in Eq. (9).

$$[\text{Ca}] = \left( \frac{a_{\text{CaO}}}{(a_{\text{SiO}_2})^{1/2}} \right) \left( \frac{K_8 a_{\text{Si}}}{\gamma_{\text{Ca}}} \right)^{1/2}$$  \hspace{1cm} (9)
Thus, the distribution of these impurities may be additionally influenced by the ratio of $a_{CaO} \cdot a_{SiO_2}$ indirectly through the effect on the uptake of Ca and subsequent retention of impurities by the metal phase. The calculated values for $a_{SiO_2}$ were shown to decrease in the direction of decreasing SiO$_2$ in each case, and the removal data presented previously [14] showed the highest degree of contamination of the silicon by Ca was at the low SiO$_2$ end for both Al$_2$O$_3$-CaO-MgO-SiO$_2$ slags as expected. Any artificial lowering of $D_M$ through the increase in [Ca] as the CaO:SiO$_2$ ratio was increased does not show in Fig. 2, as values for both elements increase over the entire range studied. This suggests that the degree of drawback of these impurities is minimal in this case. Furthermore, where the SiO$_2$:Al$_2$O$_3$ ratio was increased in Fig. 4, $D_P$ values are already increasing, while $D_B$ values are constant. Any effect on $D_P$ therefore will not be obvious, while any drawback of boron to the metal phase is insufficient to artificially increase $D_B$. In the BS system, Ca was actually removed from the silicon, so there will be no drawback effect in this case. The other factors in Eq. (9) above, $a_{Si}$ and $\gamma_{Ca}$, showed minimal variation in all of the FactSage simulations, so are not expected to influence trends in Ca contamination or $D_M$ in this case. This adds further to the argument that an appropriate slag for removing phosphorus from silicon would be one with relatively high basicity and $p_{O_2}$, rather than just a more basic slag as may be first thought.

5. Summary and Conclusions

Distribution coefficients previously measured for boron and phosphorus between Al$_2$O$_3$-CaO-MgO-SiO$_2$ and Al$_2$O$_3$-BaO-SiO$_2$ slags and silicon metal and their associated trends with changing slag chemistry were re-examined. Values were normalized with the oxygen partial pressure resulting from the equilibrium between Si and SiO$_2$ in each case and were presented against the optical basicity of the slag. A correction of basicity was carried out due to structural effects arising from the alumina content of the slag that resulted in an unexpected apparent increase in normalized distribution with decreasing basicity in one case.

Phosphorus showed a much stronger preference for these slags than did boron in all the systems studied. However, different trends against basicity were identified for the individual compositional variation systems in each case. The ACMS slags with varying SiO$_2$:Al$_2$O$_3$ ratio had the highest optical basicity, and as expected, normalized distributions were highest here. Similarly, basicity and normalised distributions were lowest in the ABS slags system. An exception to this was for phosphorus at lower optical basicities ($A_{corr} < 0.54$) where values for the ACMS slags with varying CaO:SiO$_2$ ratio were lowest. It is suggested that phosphorus associates with Mg in the system with varying SiO$_2$:Al$_2$O$_3$ and with Ca in the system with varying CaO:SiO$_2$ ratios, as indicated by the concentrations of Mg$_3$(PO$_4$) and Ca$_3$(PO$_4$) in these slags determined by thermodynamic calculations. As Mg and Ca were not present in the ABS system, it is suggested that phosphorus associates with Ba in these slags. The difference in normalized distributions between the slag systems is attributed to the magnitude of the ratio $K/\gamma_{PO_4^-}$ for the respective forms in the slag. Such detailed activity data were not available for boron but it is expected that it makes the equivalent associations in the respective slag systems. The implication of this is that where basicity is equal and the form in the slag is equivalent, phosphorus is expected to have a much smaller activity coefficient in the slag than boron. However, while $\gamma_{BO_3^-}$ is expected to be smallest when associated with Mg, the observed
independence of $D_B$ against $\Lambda_{corr}$ in the varying SiO$_2$:Al$_2$O$_3$ slags suggests that in this system it actually increases with increasing slag basicity.

The possibility of contamination of the Si metal phase by calcium having an effect on $D_M$ was considered but the observed trends do not provide evidence for this having any additional influence on the distributions of boron and phosphorus.

Acknowledgements

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References


Appendix

1. Sample calculation of corrected optical basicity

The value of $\Lambda_{corr}$ is calculated thusly for a slag of composition (in wt%) 30.3% CaO-19.8% MgO-17.4% SiO$_2$-27.3% Al$_2$O$_3$.

Step 1: convert composition to mole fractions ($\chi$)

$\chi$(CaO) = 0.340, $\chi$(MgO) = 0.310, $\chi$(SiO$_2$) = 0.182, $\chi$(Al$_2$O$_3$) = 0.168.

Step 2: account for charge balance

Subtract $\chi$(Al$_2$O$_3$) from $\chi$(CaO)

$\chi$(CaO) = 0.340 - 0.168 = 0.172.

Step 3: calculate equivalent cation fraction ($X$) of each oxide, using

$$X_i = \frac{X_i n_i}{\sum X_i n_i}$$

where $n_i$ is the number of oxygen atoms in a single molecule of each component $i$. i.e. for CaO and MgO, $n = 1$; for SiO$_2$, $n = 2$; for Al$_2$O$_3$, $n = 3$, giving

$X$(CaO) = 0.127, $X$(MgO) = 0.204, $X$(SiO$_2$) = 0.240, $X$(Al$_2$O$_3$) = 0.332

Step 4: calculate basicity

$\Lambda_{corr} = \sum X_i \Lambda_i$

where $\Lambda_i$ is the optical basicity of the individual slag component $i$, using $\Lambda$(CaO) = 1, $\Lambda$(MgO) = 0.78, $\Lambda$(SiO$_2$) = 0.48, $\Lambda$(Al$_2$O$_3$) = 0.61.

$\Lambda_{corr} = (0.127)(1) + (0.204)(0.78) + (0.240)(0.48) + (0.332)(0.61) = 0.604$

Where the mole fraction of Al$_2$O$_3$ is greater than that of CaO, the remainder is subtracted from the mol fraction of MgO, ignoring negative values. For barium-containing slags, charge balance is taken into account using $\chi$(BaO); for basicity, $\Lambda$(BaO) = 1.15.
Fig. 1. a). Effect of varying slag composition on the distribution coefficient of boron in ACMS and ABS slags at 1500 °C [1]. Trendlines are shown as a guide only. b). Effect of varying slag composition on the distribution coefficient of phosphorus in ACMS and ABS slags at 1500 °C [1]. Trendlines are shown as a guide only.

Fig. 2. Normalized distribution coefficients for boron and phosphorus in varying CaO:SiO₂ (35%Al₂O₃–CaO–3%MgO–SiO₂) slags at 1500 °C. Trendlines are shown as a guide only.
Fig. 3. Normalized distribution coefficients for boron and phosphorus in varying BaO:SiO$_2$ (20%Al$_2$O$_3$–BaO–SiO$_2$) slags at 1500 °C. Trendlines are shown as a guide only.

Fig. 4. Normalized distribution coefficients for boron and phosphorus in varying SiO$_2$:Al$_2$O$_3$ (Al$_2$O$_3$–42%CaO–10%MgO–SiO$_2$) slags at 1500 °C. Trendlines are shown as a guide only.

Fig. 5. Normalized distribution coefficient of phosphorus in ACMS and ABS slags for all compositional variations as a function of the optical basicity of the slag.
Fig. 6. Normalized distribution coefficient of boron in ACMS and ABS slags for all compositional variations as a function of the optical basicity of the slag.