Phosphorus Distribution between MgO-saturated CaO-Fe_tO-SiO₂-P₂O₅-MnO Slags and Liquid Iron*

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Synopsis

The phosphorus distribution ratios between CaO-MgO_{sat.}-Fe_tO-SiO₂-P₂O₅ (≤3wt%)–MnO (2~5wt%) or CaO-MgO_{sat.}-Fe_tO-SiO₂-P₂O₅ (4~5wt%) slags and liquid iron have been obtained in the temperature range from 1550 to 1650 °C. The dephosphorization quotients can be expressed by the following three different equations.

- (i) $\log (P_2O_5)/([P]^2(Fe_tO)^5) = 0.145[(\%CaO) + 0.3(\%MgO) - 0.5(\%P_2O_5) + 0.6(\%MnO)] + 22810/T - 20.506$
- (ii) $\log (P_2O_5)/([P]^2(Fe_tO)^5) = 7.87 \log [(\%CaO) + 0.3(\%MgO) - 0.05(\%Fe_tO) - 0.5(\%P_2O_5) + 0.6(\%MnO)] + 22240/T - 27.124$
- (iii) $\log (P)/([P](T.Fe)^{5/2}) = 0.0720[(\%CaO) + 0.3(\%MgO) + 0.6(\%P_2O_5) + 0.6(\%MnO)] + 11570/T - 10.520$

The activity coefficient of P₂O₅ by Turkdogan and Pearson's treatment can be expressed as follows:

$$\log \gamma_{P_2O_5} = -1.02(23N_{CaO} + 17N_{MgO} + 8N_{Fe_tO} - 26N_{P_2O_5} + 13N_{MnO}) - 22990/T + 9.490$$

In the plot of logarithms of activity coefficient of Fe_tO against mole fraction of SiO₂, the values for $\log \gamma_{Fe_tO}$ tend to increase with increase of the P₂O₅ content and with the addition of MnO in the range of $N_{SiO_2} < 0.1$.

I. Introduction

Dephosphorization is one of the most important reaction in the steelmaking process. However, few laboratory researches on phosphorus equilibrium between steelmaking slags and liquid iron have been reported so far. The present authors have previously obtained the phosphorus distribution ratio between liquid iron and MgO-saturated CaO-Fe_tO-SiO₂ slags in the temperature range from 1550 to 1650 °C.¹⁾ Applying these results to the phosphorus equilibrium relationships proposed by other investigators,²⁻⁵⁾ the present authors have discussed the applicability of those relationships and have proposed the revised dephosphorization equations.¹⁾ Furthermore experiments⁶⁾ have been made to study the effect of calcium fluoride (1~4 wt%) on phosphorus distribution between liquid iron and the above-mentioned slags. It was found from these results that with the addition of CaF₂, the activity coefficient of P₂O₅ decreases to the same extent as lime, while the activity coefficient of FeO increases.

In this work the phosphorus equilibrium between liquid iron and MgO-saturated CaO-Fe_tO-SiO₂-P₂O₅ slags containing 2~5 wt% MnO which is one of the most important component in the steelmaking slags have been studied by the same method described in the previous experiments.^{1,6)} The P₂O₅ content in the previous slags was less than 1 wt%, but in this work it was chosen as 4~5 wt% so as to study

the effect of the P₂O₅ content on the phosphorus equilibrium.

II. Experimental

The experimental apparatus and method are the same as those described in detail elsewhere.¹⁾ The equilibrium of phosphorus was approached mostly from the slag side, i.e., by adding a reagent grade 3CaO·P₂O₅ or NH₃HPO₄ in the slags; in some experiments, from the metal side by adding a piece of a Fe-26%P alloy. In the experiments in which a reagent grade MnO₂ was added, the P₂O₅ content in slags after experiments was adjusted to about 1 wt% or 2~3 wt%. The experimental temperature for slags containing MnO was in the range 1550 to 1650 °C and experiments for slags containing high P₂O₅ (4~5 wt%) were only carried out at 1600 °C. The holding time was 3 to 5 hr depending on slag compositions and temperatures. The yield of manganese was found to be about 80 to 100 % in the case of approaching the equilibrium of phosphorus from the metal side, while it was about 30 to 50 % in the case approaching from the slag side.

The methods for the analysis of CaO, SiO₂, MgO, Fe²⁺, total Fe and metallic Fe in slag and $\underline{P}$ and $\underline{O}$ in metal were the same as those described elsewhere.^{6,7)} The manganese content in the metal and slag samples was determined by the sodium periodate oxidation absorptiometry (JIS-G-1213) and (JIS-M-8215), respectively.

III. Results

The equilibrium compositions of CaO-MgO_{sat.}-Fe_tO-SiO₂ slags containing 4~5 wt% P₂O₅ and metals are listed in Table 1. Those of CaO-MgO_{sat.}-Fe_tO-SiO₂-P₂O₅ slags containing 2~5 wt% MnO and metal are tabulated in the paper⁸⁾ on the manganese distribution equilibrium.

IV. Discussion

1. Representation of Dephosphorization Equilibrium

1. CaO-MgO_{sat.}-Fe_tO-SiO₂-P₂O₅ (≤1wt%) Slags

In the previous work,¹⁾ the dephosphorization equations were derived by the consideration of FeO and Fe₂O₃ as iron oxides. But in this study, t in Fe_tO was calculated from the total iron content, and Fe_tO was used for the treatment of the dephosphorization equations. Then, logarithms of the equilibrium quotient k_p , Eq. (2), for the dephosphorization

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Table 1. Equilibrium slag and metal compositions.
CaO-MgO_{sat.}-FeO_x-SiO₂-P₂O₅ (1 600 °C)

No.	P	O	FeO	Fe ₂ O ₃	CaO	MgO	SiO ₂	P ₂ O ₅
901	0.0690	0.1276	21.48	2.25	28.33	15.50	26.67	4.94
902	0.0575	0.1281	27.57	2.94	27.03	13.40	26.16	5.39
903	0.0346	0.1553	33.63	4.90	27.39	10.51	17.91	5.33
904	0.0879	0.1666	40.92	3.90	18.69	13.60	16.90	5.01
905	0.182	0.1718	48.76	3.77	10.99	15.97	15.71	4.22
906	0.0256	0.1636	37.53	5.99	27.53	8.56	14.09	5.41
907	0.0315	0.1610	46.88	7.21	24.29	6.72	9.39	5.35
908	0.0804	0.1645	54.78	5.85	15.85	9.35	9.11	4.97
909	0.243	0.1679	60.59	4.88	7.80	13.59	8.59	4.01
910	0.0594	0.1875	68.12	9.10	11.90	5.97	0.48	4.24

equation given by Eq. (1) can be represented by either Eq. (3) or Eq. (4) by use of the previous data.¹⁾ The details of the derivation of Eqs. (3) and (4) as a function of temperature are described elsewhere.^{1,6)}

2P+5(Fe₂O)=5Fe+(P₂O₅)(1)

$k_p = (\%P_2O_5)/[(\%P]^2(\%Fe_2O)^5]$(2)

$\log k_p = 0.141[(\%CaO)+0.3(\%MgO)]$
 $+21\,110/T-19.546$ (3)

$\log k_p = 7.93 \log [(\%CaO)+0.3(\%MgO)$
 $-0.05(\%Fe_2O)]+21\,660/T-26.929$
.....(4)

The values for the coefficients in Eqs. (3) and (4) are slightly different from those in the previous investigations,^{1,6)} since Fe₂O is used as an iron oxide in this report.

The following expression based on the ionic concept is proposed by Healy.⁴⁾

$\log (\%P)/[(\%P)(\%T.Fe)^{5/2}] = 0.08(\%CaO)$
 $+22\,350/T-16.0$ (5)

Logarithms of (%P)/[(%P) (%T.Fe)^{5/2}] calculated from the previous data¹⁾ for the slags with P₂O₅≤1 wt% are plotted against the [(%CaO)+0.3(%MgO)] term as open circles in Fig. 1, where three lines for the corresponding temperatures were obtained by the method of linear regression in the composition range of [(%CaO)+0.3(%MgO)]≥10 wt%. By employing the average values of the slopes, the intercepts of the three lines at respective temperatures were determined by passing through the center of the lines indicated in Fig. 1. Then the following linear relationship was obtained as a function of temperature:

$\log (\%P)/[(\%P)(\%T.Fe)^{5/2}] = 0.0720[(\%CaO)$
 $+0.3(\%MgO)]+11\,690/T-10.554$ (6)

The temperature dependence of Eq. (6) is about half of that given by Eq. (5) by Healy.

2. CaO-MgO_{sat.}-Fe₂O-SiO₂-P₂O₅(4~5wt%) Slags

Logarithms of *k_p* in CaO-MgO_{sat.}-Fe₂O-SiO₂-P₂O₅(4~5wt%) slags listed in Table 1 are plotted against the [(%CaO)+0.3(%MgO)] term in Fig. 2 as solid triangles. The values for log *k_p* obtained

Fig. 1. Revised Healy's relationship⁴⁾ at 1 650, 1 600 and 1 550 °C.

from the previous results¹⁾ for the slags with P₂O₅≤1 wt% are also plotted against the [(%CaO)+0.3(%MgO)] term as small solid circles for comparison.

The effect of P₂O₅ on log *k_p* on weight percent basis was obtained in the following. The values for log *k_p* calculated from the results in the high P₂O₅-containing slags and those in the previous¹⁾ slags with P₂O₅≤1 wt% are plotted against the [(%CaO)+0.3(%MgO)+α_{P₂O₅}(%P₂O₅)] term and then the CaO-equivalency of P₂O₅, α_{P₂O₅}, was obtained as -0.5 so that the best linearity was observed in the above plot. These values for log *k_p* are plotted against the [(%CaO)+0.3(%MgO)-0.5(%P₂O₅)] term in Fig. 2 as open triangles and small circles, respectively. By use of the average values of the slopes and the intercepts obtained from the data at 1 600 °C indicated by the symbols Δ, ○ in Fig. 2 and the previous data¹⁾ at 1 550 and 1 650 °C, we obtain

$\log k_p = 0.145[(\%CaO)+0.3(\%MgO)$
 $-0.5(\%P_2O_5)]+22\,810/T-20.506$
.....(7)

Fig. 2. Logarithms of the equilibrium quotient k_p as a function of $[(\% \text{CaO}) + 0.3 (\% \text{MgO}) - 0.5 (\% \text{P}_2\text{O}_5)]$ for slags containing high- and low-content of P_2O_5 .

The experimental values for the compositions of $[(\% \text{CaO}) + 0.3 (\% \text{MgO}) - 0.5 (\% \text{P}_2\text{O}_5)] < 10 \text{ wt}\%$ were excluded for the derivation of Eq. (7). The line in Fig. 2 corresponds to Eq. (7) at 1 600 °C.

The experimental points given by open circles and triangles lie well on the line given by Eq. (7). This indicates that the effect of P_2O_5 addition on $\log k_p$ is one half and is adverse with respect to the effect of lime. Accordingly, one must use Eq. (7) rather than Eq. (3), unless the content of P_2O_5 is negligible.

Logarithms of k_p for the present results for the slags with 4~5 wt% P_2O_5 listed in Table 1 and for the previous slags with $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$ are plotted against the $\log [(\% \text{CaO}) + 0.3 (\% \text{MgO}) - 0.05 (\% \text{Fe}_t\text{O}) - 0.5 (\% \text{P}_2\text{O}_5)]$ term in Fig. 3 as open triangles and circles, respectively. The values for $\log k_p$ obtained in the slags containing 4~5 wt% P_2O_5 are plotted against the $\log [(\% \text{CaO}) + 0.3 (\% \text{MgO}) - 0.05 (\% \text{Fe}_t\text{O})]$ term as solid triangles. From the experimental points represented by open circles and triangles at 1 600 °C and those for the previous data¹⁾ for the slags with $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$ at 1 550 and 1 650 °C in the composition range of $\log [(\% \text{CaO}) + 0.3 (\% \text{MgO}) - 0.05 (\% \text{Fe}_t\text{O}) - 0.5 (\% \text{P}_2\text{O}_5)] > 1.2$, the average values of the slopes and the intercepts were obtained. The following equation was derived by use of these values.

$$\begin{aligned} \log k_p = & 7.87 \log [(\% \text{CaO}) + 0.3 (\% \text{MgO}) \\ & - 0.05 (\% \text{Fe}_t\text{O}) - 0.5 (\% \text{P}_2\text{O}_5)] \\ & + 22\,240/T - 27.124 \dots\dots\dots(8) \end{aligned}$$

The line in Fig. 3 corresponds to Eq. (8) at 1 600 °C.

Logarithms of $(\% \text{P})/[(\% \text{P})(\% \text{T.Fe})^{5/2}]$ calculated from the data listed in Table 1 and the previous data¹⁾ for the slags containing $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$ are plotted against the $[(\% \text{CaO}) + 0.3 (\% \text{MgO}) + 0.6 (\% \text{P}_2\text{O}_5)]$ term in Fig. 4 as open triangles and small circles, respectively. The constant 0.6 before (wt% P_2O_5) which should be added in the first term of the right

Fig. 3. Revised Balajiva *et al.*'s relationship²⁾ for slags containing high- and low-content of P_2O_5 .

Fig. 4. Revised Healy's relationship⁴⁾ for slags containing high- and low-contents of P_2O_5 .

hand side of Eq. (6) was obtained by the similar method described previously. The values for $\log (\% \text{P})/[(\% \text{P})(\% \text{T.Fe})^{5/2}]$ in the slags containing 4~5 wt% P_2O_5 and the previous data¹⁾ are plotted against the $[(\% \text{CaO}) + 0.3 (\% \text{MgO})]$ term as solid triangles and small solid circles. The values for $\log (\% \text{P})/[(\% \text{P})(\% \text{T.Fe})^{5/2}]$ calculated from the previous data¹⁾ at 1 550, 1 600 and 1 650 °C are also plotted against the $[(\% \text{CaO}) + 0.3 (\% \text{MgO}) + 0.6 (\% \text{P}_2\text{O}_5)]$ term in Fig. 1 by small solid circles.

By use of the present data listed in Table 1 and the previous data¹⁾ whose compositions of the $[(\% \text{CaO}) + 0.3 (\% \text{MgO}) + 0.6 (\% \text{P}_2\text{O}_5)]$ term is more than 10 wt%, the following expression was derived by the similar method described previously.

$$\begin{aligned} \log (\% \text{P}) / ([\% \text{P}](\% \text{T.Fe})^{5/2}) &= 0.0720[(\% \text{CaO}) \\ &+ 0.3(\% \text{MgO}) + 0.6(\% \text{P}_2\text{O}_5)] \\ &+ 11\,570/T - 10.520 \dots\dots\dots(9) \end{aligned}$$

The relationship between Eq. (7) and Eq. (9) will be considered in the following. From Eq. (7), one obtains

$$\begin{aligned} \log (\% \text{P}_2\text{O}_5)^2 / ([\% \text{P}]^2(\% \text{Fe}_t\text{O})^5) &= 0.145[(\% \text{CaO}) \\ &+ 0.3(\% \text{MgO}) - 0.5(\% \text{P}_2\text{O}_5)] + \log (\% \text{P}_2\text{O}_5) \\ &+ 22\,810/T - 20.506 \dots\dots\dots(10) \end{aligned}$$

The term in the left hand side in Eq. (10) can be rearranged as

$$\begin{aligned} \log (\% \text{P}_2\text{O}_5)^2 / ([\% \text{P}]^2(\% \text{Fe}_t\text{O})^5) \\ = \log (\% \text{P})^2 / ([\% \text{P}]^2(\% \text{T.Fe})^5) + 0.173 \dots\dots(11) \end{aligned}$$

From Eqs. (10) and (11), one obtains

$$\begin{aligned} \log (\% \text{P}) / ([\% \text{P}](\% \text{T.Fe})^{5/2}) &= 0.0727[(\% \text{CaO}) \\ &+ 0.3(\% \text{MgO}) - 0.5(\% \text{P}_2\text{O}_5)] \\ &+ 1/2 \log (\% \text{P}_2\text{O}_5) + 11\,405/T - 10.340 \dots\dots\dots(12) \end{aligned}$$

The $(\% \text{P}_2\text{O}_5)$ term in Eq. (12) is $(0.5/0.0727) \log (\% \text{P}_2\text{O}_5) - 0.5(\% \text{P}_2\text{O}_5)$, while that in Eq. (9) is $0.6(\% \text{P}_2\text{O}_5)$. The calculated phosphorus contents by Eqs. (9) and (12), however, are both in agreement with the observed values to the same degree.

Equations (7) to (9) represent the phosphorus distribution ratio between slag and metal as a function of slag compositions and temperatures. The dephosphorization reaction may be expressed properly by either the ionic equation:

or the molecular equation:

It should be noted that Eqs. (3), (4), (7) and (8) seem different from Eqs. (6) and (9), if one may consider the apparent dependence of oxygen potential on the phosphorus distribution ratios at a fixed slag composition: $(\% \text{P}_2\text{O}_5)^{1/2} / [\% \text{P}] \propto P_{\text{O}_2}^{3/4}$ for Eqs. (3), (4), (7) and (8); $(\% \text{P}_2\text{O}_5) / [\% \text{P}] \propto P_{\text{O}_2}^{3/4}$ for Eqs. (6) and (9), where all the activity coefficients are assumed to be constant.

The observed phosphorus contents in metal ($< 0.024\% \text{P}$) in the previous experiment¹⁾ for $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$ and those in the present experiment with $4 \sim 5 \text{ wt}\% \text{P}_2\text{O}_5$ ($< 0.24\% \text{P}$) are compared with those calculated from Eq. (9) as shown in Fig. 5. The agreement between the observed and calculated phosphorus contents by Eq. (9) is found to be good.

3. **CaO-MgO_{sat}-Fe_tO-P₂O₅-MnO(2~5wt%) Slags**

Logarithms of k_p calculated from the present data for $\text{CaO-MgO}_{\text{sat}}\text{-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5$ slags containing 2~5 wt% MnO are plotted against the $[(\% \text{CaO}) + 0.3(\% \text{MgO}) - 0.5(\% \text{P}_2\text{O}_5)]$ term as open squares (1650 °C) and circles (1550 °C) in Fig. 6. The P_2O_5 contents in these experimental points are less than 1 wt%. The data points at 1600 °C are represented by different symbols of the triangles de-

Fig. 5. Comparison of the phosphorus content in metal between observation and calculation from Eq. (9).

Fig. 6. Logarithms of the equilibrium quotient as a function of $[(\% \text{CaO}) + 0.3(\% \text{MgO}) - 0.5(\% \text{P}_2\text{O}_5) + 0.6(\% \text{MnO})]$ for MnO-containing slags.

pending on the MnO and P_2O_5 contents: Δ ($\text{MnO} = 4 \sim 5 \text{ wt}\%$, $\text{P}_2\text{O}_5 \leq 3 \text{ wt}\%$), $\triangle$ ($\text{MnO} = 3 \sim 4 \text{ wt}\%$, $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$) and $\blacktriangle$ ($\text{MnO} = 2 \sim 3 \text{ wt}\%$, $\text{P}_2\text{O}_5 \leq 1 \text{ wt}\%$). The three lines for respective temperatures correspond to Eq. (7) which is obtained from the data for the slags without containing MnO. The differences $\Delta \log k_p$ between these lines and the experimental points obtained in the present slags containing MnO are plotted against the (wt% MnO) term. The CaO-equivalency of MnO indicating the effect of MnO on $\log k_p$ on weight percent basis was found to be 0.6 ± 0.5 . The values for $\log k_p$ calculated from the data on the slags containing 2~5 wt% MnO are also plotted against the $[(\% \text{CaO}) + 0.3(\% \text{MnO}) - 0.5(\% \text{P}_2\text{O}_5) + 0.6(\% \text{MnO})]$ term as small solid circles in Fig. 6. It is apparent that all the data points by solid circles are well on the lines.

Logarithms of $(\% \text{P}) / ([\% \text{P}](\% \text{T.Fe})^{5/2})$ term cal-

culated from the MnO-containing slags are plotted against the $[(\% \text{CaO}) + 0.3(\% \text{MgO}) + 0.6(\% \text{P}_2\text{O}_5)]$ term by the symbols ($\square$) at 1650 °C, (Δ , $\blacktriangle$, $\blacktriangle$) at 1600 °C and ($\circ$) at 1550 °C in Fig. 7. The symbols are equal to those explained in Fig. 6. The three lines are plotted in accordance with Eq. (9) at respective temperatures. The value of the coefficient of $(\% \text{MnO})$ in Eq. (9) was obtained as 0.6 ± 0.5 by the same method as described previously. The values of $\log (\% \text{P})/([\% \text{P}](\% \text{T.Fe})^{5/2})$ are also plotted against the $[(\% \text{CaO}) + 0.3(\% \text{MgO}) + 0.6(\% \text{P}_2\text{O}_5) + 0.6(\% \text{MnO})]$ term as the small solid circles in Fig. 7.

The phosphorus content in metal was calculated from the equation in which the $0.6(\% \text{MnO})$ term was added to the first term of the right hand side of Eq. (9). These calculated values are compared with the observed values in Fig. 8. Similarly, by use of the equation in which the $0.6(\% \text{MnO})$ term was added to Eq. (7), the calculated phosphorus content in metal was compared with the observed value; the agreement between the two was found to be almost the same ($\sigma = 0.0028$) as that found in Fig. 8 except the experimental points given by open triangles at 1600 °C. The calculated phosphorus content from the equation in which the $0.6(\% \text{MnO})$ term was added to Eq. (8) was not in agreement with the observed value ($\sigma = 0.0029$) as observed in the results in Fig. 8.

It is not significant to determine which equations among Eqs. (7) to (9) can most accurately represent the observed phosphorus content in steel in practical operations, because the establishment of the slag/metal equilibrium is questionable with varying temperature and ratio of ferrous to ferric iron content. It can be said, however, that the calculated phosphorus contents from Eqs. (7) and (9) agree well

Fig. 7. Revised Healy's relationship⁴⁾ for MnO-containing slags.

with the observed phosphorus content as far as the slag compositions lie in the present slag compositions; but the agreement between the observed and calculated values from Eq. (8) is not as good as that found in Eq. (7) or Eq. (9).

Therefore, one may use Eqs. (7) and (9) when the apparent dependence of oxygen potential on the phosphorus partitions is considered at a fixed slag composition.

2. Effect of P_2O_5 and MnO on Activity Coefficient of P_2O_5

1. $\text{CaO-MgO}_{\text{sat.}}\text{-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5(\leq 1\text{wt}\%)$ Slags

Turkdogan and Pearson³⁾ found that logarithms of activity coefficients of P_2O_5 can be expressed by a linear function of mole fractions of slag components. The present authors previously applied the data¹⁾ for $\text{CaO-MgO}_{\text{sat.}}\text{-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5(\leq 1\text{ wt}\%)$ slags to the Turkdogan and Pearson's treatment where FeO and Fe_2O_3 were considered as iron oxide components. In this study, however, Fe_tO is considered. Then the following relationship was obtained by the same method described previously.¹⁾

$$\log \gamma_{\text{P}_2\text{O}_5} = -0.985(23N_{\text{CaO}} + 17N_{\text{MgO}} + 8N_{\text{Fe}_t\text{O}}) - 22\,270/T + 8.818 \quad \text{.....(13)}$$

The data points in the range of $(23N_{\text{CaO}} + 17N_{\text{MgO}} + 8N_{\text{Fe}_t\text{O}}) < 10$ were excluded in Eq. (13).

One may see that the temperature dependence of Eq. (13) found in this study is lower than that found in the previous work. (Eq. (20) in Ref. 1))

2. $\text{CaO-MgO}_{\text{sat.}}\text{-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5(4\sim 5\text{wt}\%)$ Slags

By use of the data listed in Table 1 and the standard free-energy change for the reaction: $2\text{P} + 5\text{O} = \text{P}_2\text{O}_5$ (l) $\Delta G^\circ = -168\,600 + 133.0T$ (cal),³⁾ the activity coefficients of P_2O_5 , $\gamma_{\text{P}_2\text{O}_5}$ in $\text{CaO-MgO}_{\text{sat.}}\text{-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5(4\sim 5\text{wt}\%)$ slags are calculated assuming $a_{\text{O}} = [\% \text{O}]$ and $a_{\text{P}} = [\% \text{P}]$. Logarithms of $\gamma_{\text{P}_2\text{O}_5}$ calculated from the values for a_{O} and a_{P} by use of respective interaction parameters⁹⁾ were found to be different

Fig. 8. Comparison of the phosphorus contents in metal between observation and calculation for MnO-containing slags.

only by 0.09 ± 0.02 in the range of $\log \gamma_{P_2O_5} < -13$ and only by 0.08 ± 0.01 in the range of $\log \gamma_{P_2O_5} > -13$ in Fig. 9. To analyze the effect of P_2O_5 content on $\log \gamma_{P_2O_5}$, the coefficient of $N_{P_2O_5}$ in the first term of the right hand side of Eq. (13) was calculated by the same method described in Section IV. 1. 2. As a result, it was found to be -26 . Logarithms of $\gamma_{P_2O_5}$ calculated from the previous data¹⁾ for the slags with $P_2O_5 \leq 1$ wt% and from the present data for the 4~5 wt% P_2O_5 containing slags are plotted against the $(23N_{CaO}+17N_{MgO}+8N_{FeO}-26N_{P_2O_5})$ term in Fig. 9 as open circles and triangles, respectively. These calculated values are plotted against the $(23N_{CaO}+17N_{MgO}+8N_{FeO})$ term as solid circles and triangles. The line indicated in Fig. 9 corresponds to Eq. (13). By use of the present and the previous data,¹⁾ logarithms of $\gamma_{P_2O_5}$ was calculated in a way analogous to that described previously as follows:

$$\log \gamma_{P_2O_5} = -1.02(23N_{CaO}+17N_{MgO}+8N_{FeO}$$

$$-26N_{P_2O_5})-22\,990/T+9.490 \dots\dots\dots(14)$$

3. **CaO-MgO_{sat}-Fe_tO-SiO₂-P₂O₅-MnO(2~5wt%) Slags**

The values for $\log \gamma_{P_2O_5}$ obtained from the data for the MnO-containing slags are plotted against the $(23N_{CaO}+17N_{MgO}+8N_{FeO}-26N_{P_2O_5})$ term in Fig. 10 by the symbols ($\square$) at 1 650 °C, (Δ , $\blacktriangle$, $\blacktriangle$) at 1 600 °C and ($\circ$) at 1 550 °C. The symbols are the same as those given in Fig. 6. The lines indicated in Fig. 10 are plotted by Eq. (14) at respective temperatures. By the same method described in Section IV. 1. 3, the coefficient of N_{MnO} in the first term of the right hand side of Eq. (14) was obtained as 13 ± 9 . The values for $\log \gamma_{P_2O_5}$ are also plotted against the $(23N_{CaO}+17N_{MgO}+8N_{FeO}-26N_{P_2O_5}+13N_{MnO})$ term in Fig. 10 as solid circles.

Fig. 9. Turkdogan and Pearson's relationship³⁾ for slags containing high- and low-contents of P_2O_5 .

3. **Effect of P_2O_5 and MnO on Activity Coefficients of Fe_tO**

Activities of Fe_tO obtained in the previous^{1,6)} and present works will be reported in detail in a subsequent paper.

Logarithms of activity coefficient of Fe_tO , γ_{Fe_tO} were calculated by use of the previous data¹⁾ at 1 600 °C, the standard free-energy change $\Delta G^\circ = -27\,740 + 11.66T$ (cal)⁸⁾ for the reaction: $Fe(l) + \underline{O} = FeO(l)$, and interaction parameters⁹⁾:

$$e_0^{(O)} = -1\,750/T + 0.734, \quad e_0^{(P)} = 0.07$$

and
$$e_0^{(Mn)} = -0.021.$$

These values for $\log \gamma_{Fe_tO}$ are analyzed as a function of mole fractions of slag compositions by the method of a multiple regression. Consequently, $\log \gamma_{Fe_tO}$ was found to be only related to mole fraction of SiO_2 . In Fig. 11 the values for $\log \gamma_{Fe_tO}$ calculated from the previous data¹⁾ are plotted against N_{SiO_2} as small solid circles. The values for $\log \gamma_{Fe_tO}$ obtained in the slags with 4~5 wt% P_2O_5 are plotted against N_{SiO_2} as solid triangles. The line is calculated from the experimental points indicated by solid circles by the method of quadratic form regression. It is seen from Fig. 11 that activity coefficients of Fe_tO increase with increasing the P_2O_5 content. The values for $\log \gamma_{Fe_tO}$ calculated from the data for the 4~5 wt% P_2O_5 -containing slags are plotted against the $(N_{SiO_2}+N_{P_2O_5})$ term as open triangles.

Figure 12 shows the effect of MnO on $\log \gamma_{Fe_tO}$. The values for $\log \gamma_{Fe_tO}$ in the previous MnO-free

Fig. 10. Turkdogan and Pearson's relationship³⁾ for MnO-containing slags.

Fig. 11. Logarithms of the activity coefficients of Fe_tO plotted against N_{SiO_2} and $N_{\text{SiO}_2} + N_{\text{P}_2\text{O}_5}$ for slags containing high- and low-content of P_2O_5 .

Fig. 12. Logarithms of the activity coefficients of Fe_tO plotted against N_{SiO_2} for MnO-containing and -free slags.

$\text{CaO-MgO}_{\text{sat.}}-\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5$ ($\leq 1 \text{ wt}\%$) slags are plotted against N_{SiO_2} in Fig. 12 as small solid circles. These data points are regressed by the quadratic forms which are shown in Fig. 12 for respective temperatures. The values for $\log \gamma_{\text{Fe}_t\text{O}}$ calculated from the present data for the 2~5 wt% MnO-containing slags are plotted against N_{SiO_2} by the symbols ($\square$) at 1650 °C, (Δ , $\triangle$, $\blacktriangle$) at 1600 °C and ($\circ$) at 1550 °C. The experimental points given by open triangles and circles correspond to the slags containing less than 1 wt%

P_2O_5 and 2~3 wt% MnO. As can be seen from these points of $N_{\text{SiO}_2} \leq 0.1$, the addition of MnO increases activity coefficients of Fe_tO . Most of the points $\log \gamma_{\text{Fe}_t\text{O}}$ indicated by the symbol (Δ) are higher than the line in the whole composition range for high MnO (3~4 %) and low P_2O_5 ($\leq 1 \text{ wt}\%$). Furthermore those indicated by the symbol (Δ) at 1600 °C are also higher than the line in the whole range of N_{SiO_2} since the contents of MnO (4~5 wt%) and P_2O_5 (2~3 wt%) are both high.

V. Summary

The results obtained in this work are summarized in the following.

(1) The following three different dephosphorization equations are proposed on the basis of the phosphorus distribution ratios between $\text{CaO-MgO}_{\text{sat.}}-\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{MnO}$ slags and liquid iron in the temperature range from 1550 to 1650 °C.

$$\text{(i)} \quad \log k_p = 0.145[(\% \text{CaO}) + 0.3(\% \text{MgO}) + 0.6(\% \text{MnO}) - 0.5(\% \text{P}_2\text{O}_5)] + 22810/T - 20.506$$

$$\text{(ii)} \quad \log k_p = 7.87 \log [(\% \text{CaO}) + 0.3(\% \text{MgO}) - 0.05(\% \text{Fe}_t\text{O}) + 0.6(\% \text{MnO}) - 0.5(\% \text{P}_2\text{O}_5)] + 22240/T - 27.124$$

$$\text{(iii)} \quad \log (\% \text{P}) / [(\% \text{P})(\% \text{T. Fe})^{5/2}] = 0.0720[(\% \text{CaO}) + 0.3(\% \text{MgO}) + 0.6(\% \text{MnO}) + 0.6(\% \text{P}_2\text{O}_5)] + 11570/T - 10.520$$

(2) The following expression of the activity coefficient of P_2O_5 in $\text{CaO-MgO}_{\text{sat.}}-\text{Fe}_t\text{O}-\text{SiO}_2-\text{P}_2\text{O}_5-\text{MnO}$ slags is derived by Turkdogan and Pearson's treatment.

$$\log \gamma_{\text{P}_2\text{O}_5} = -1.02(23N_{\text{CaO}} + 17N_{\text{MgO}} + 8N_{\text{Fe}_t\text{O}} + 13N_{\text{MnO}} - 26N_{\text{P}_2\text{O}_5}) - 22990/T + 9.490$$

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