

Dephosphorization and Desulfurization of Hot Metal by CaO Based Fluxes Containing Fe-oxide and Mn-oxide as Oxidant*

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Synopsis

Experiments on hot metal dephosphorization by using the mixtures of Fe-oxide and Mn-oxide as oxidant were achieved by the use of Tammann furnace. The results were analyzed by the coupled reaction model which consisted of mass transfer equations of each component. Among many unknown parameters in the model, the effective equilibrium constants of P, Mn and S and the mass transfer coefficient in slag phase were changed by the experimental condition and determined by fitting to the experimental result. The observed distribution ratio of P, S and Mn was consistent with the calculated value for each experiment and the applicability of the coupled reaction model was proved.

(1) When a mixture of Fe-oxide and Mn-oxide was used as oxidant, as the ratio of FeO to the total content of Fe-oxide and Mn-oxide in flux decreased, the effective equilibrium constants of P and S and the mass transfer coefficient in slag decreased and the effective equilibrium constant of Mn increased. This result indicated that the degree of dephosphorization, desulfurization, Mn recovery and the reaction rate of these reactions increased as the increase of Fe-oxide ratio in flux.

(2) The addition of CaF_2 and CaCl_2 did not significantly change the effective equilibrium constants but modified the mass transfer coefficient in slag. Together with the result of temperature dependence, the necessary amount of CaF_2 to obtain the equivalent reaction rate for each temperature was clarified.

(3) The activity coefficients of FeO, P_2O_5 and MnO converted from the effective equilibrium constants were compared with those values calculated by the thermodynamic models. However satisfactory agreements were not obtained especially for γ_{MnO} .

Key words: hot metal treatment; dephosphorization; reduction of Mn-oxide; mass transfer; equilibrium constant.

I. Introduction

In steelmaking process, many reactions occur simultaneously. For example, during oxygen blowing in BOF, oxidation of P and Mn proceeds besides decarburization. In the recently developed hot metal dephosphorization, although simultaneous desulfurization is a prominent feature of this process, decarburization proceeds considerably. Thermodynamic consideration of one or two reactions had been discussed in the process analysis. Recently, some models were proposed to analyze the process in which many reactions simultaneously occur. These models consist of thermodynamics and mass transfer theory. Shinozaki *et al.*¹⁾ reported a method to solve the reaction between molten iron and $\text{MnO}-(\text{CaO}+\text{FeO}+\text{MgO})-\text{SiO}_2$ slag. Ohguchi *et al.*^{2,3)} proposed a similar model (coupled reaction model) and applied to the hot metal desulfurization and dephosphorization reaction in small scale experiments. Furthermore, Sawada *et al.*⁴⁾

tried to calculate the hot metal dephosphorization process in a flux injection method by a combination of coupled reaction model and fluid dynamics. Although these calculations showed fairly good agreements with the experimental results, more experiments under various conditions should be achieved to define many unknown parameters.

In the present study, the authors selected the hot metal dephosphorization reaction by using Fe-oxide, Mn-oxide and their mixtures as the oxidants because these systems are practically very important because an economic merit can be expected by the reduction of Mn-oxide. Nevertheless, there were few fundamental researches about the equilibrium of MnO rich slag in a low temperature range. In this experiment, the coupled reaction model was applied to analyze the results, and the influence of flux composition especially the basicity and the addition of CaF_2 and CaCl_2 were examined.

II. Experimental Method

The experiments were carried out by the use of Tammann furnace. A mother alloy of about 50 kg was melted in another furnace and poured into 15 pieces of sand molds which were designed to fit the crucibles used in a Tammann furnace to homogenize the initial composition of metal. In the Tammann furnace, a fired MgO crucible was used and about 1 kg hot metal was remelted. The composition of remelted hot metal is shown in Table 1. In the mother alloy, Si was not added and the basicity was controlled by addition of SiO_2 . After the temperature reached a predetermined level, a total of about 75 g flux was charged onto the metal surface in 10 times within 12 min. Some flux compositions used in the experiments are listed in Table 2. The composition of flux No. 4 corresponded to the actual dephosphorization flux containing iron-manganese ore, so the composition of this flux was determined as the standard. A mixture of reagents were used as the flux and, in some cases, premelted fluxes were used although a significant difference was not found in the chemical reactions. In the following section, No. 1

Table 1. Hot metal composition before experiment.

C	Si	Mn	P	S
3.95	<0.01	0.025	0.108	0.033

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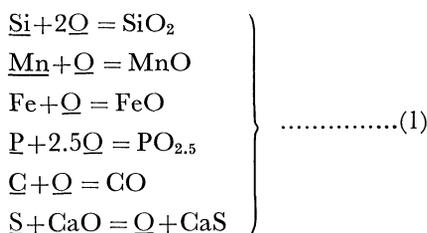
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flux in Table 2 is named as MnO free flux and No. 2 flux in Table 2 as FeO free flux. The experimental conditions are summarized in Table 3. Slag samples were taken by adhering to a steel rod and metal samples were sucked by a quartz tube of 5 mm in diameter. Temperature was automatically controlled in the range of ±10 K, but to ensure the constant temperature, a thermocouple was dipped in molten metal at about 30 min interval.

III. Experimental Results and Discussion

1. Application of Coupled Reaction Model

The coupled reaction model (CRM) was proposed by Ohguchi *et al.*^{2,5)} They applied this model to the Fe-C-Si-P-S-Mn-O reactions in hot metal dephosphorization. In this model, the following reactions are taken into account.



For the reaction (2), the mass transfer can be represented by Eq. (3),

$$\underline{\text{M}} + n \cdot \underline{\text{O}} = \text{MO}_n, \dots\dots\dots(2)$$

Table 2. Flux compositions used.

Flux No.	Flux composition							Weight of flux (g/kg)
	FeO	MnO	MnO ₂	CaO	SiO ₂	CaF ₂	CaCl ₂	
1	58.4	0	0	24.8	6.0	7.4	3.4	74.5
2	0	58.4	0	24.8	6.0	7.4	3.4	74.5
3	29.2	29.2	0	24.8	6.0	7.4	3.4	74.5
4	20.0	17.2	16.9	27.4	6.7	8.1	3.7	67.5
5	17.7	15.2	15.0	32.2	5.9	9.6	4.3	76.1
6	15.8	13.6	13.3	36.3	5.3	10.8	4.9	85.4
7	18.5	15.9	15.7	33.7	6.2	10.0	0	72.8
8	16.6	14.3	14.0	30.0	5.5	19.5	0	81.4
9	15.0	12.9	12.7	27.2	5.0	27.2	0	90.0
10	17.6	15.2	14.9	32.0	5.9	14.4	0	76.5

Table 3. Experimental conditions.

Temperature	1 573~1 673 K
Atmosphere	Ar
Experiment time	90~180 min
Stirring	No
Flux	Mixture of reagents (mainly)
Method of flux addition	Added on metal surface divided in 10 times during 12.5 min

Table 4. Parameters used by the present calculation and by Ohguchi *et al.*

	E_C	E_{Si}	E_{Fe}	E_P	E_{Mn}	E_S	k_m	k_s	G_{CO}	G_{O_2}
Ohguchi <i>et al.</i> ²⁾	2 000	10 ¹¹	500	10 ⁹	1 000	0.015	0.04	0.02	3×10 ⁻⁷	5×10 ⁻⁵
Present work	1 800	5×10 ⁹	500	0.3×10 ⁸ ~1.8×10 ⁸	2 000~5 000	0.010~0.025	0.023	10 ⁻² ~10 ⁻⁴	7×10 ⁻⁸	5×10 ⁻⁷

$$\begin{aligned} J_M &= \{k_M \cdot \rho_M / (100 \cdot N_M)\} \cdot \{[\%M]^b - [\%M]^*\} \\ &= \{k_S \cdot \rho_S / (100 \cdot N_{MO_2})\} \cdot \{(\%MO_n)^* - (\%MO_n)^b\} \end{aligned} \dots\dots\dots(3)$$

and the effective equilibrium constant is defined by Eq. (4).

$$\begin{aligned} E_M &= (\%MO_n)^* / ([\%M]^* \cdot a_O^{*n}) \\ &= (100 \cdot C \cdot N_{MO_n} \cdot f_M \cdot K_M) / (\rho_S \cdot \gamma_{MO_n}) \dots\dots\dots(4) \end{aligned}$$

From Eqs. (3) and (4) and the requirement of electric neutrality, the concentration of each component in metal and slag phases can be calculated. Although this model is very useful, Ohguchi *et al.* did not apply to a wide variety of flux compositions and temperatures, and it was not used to analyze the refining ability of flux. One of the problem in application of this model is the inclusion of many unknown parameters (listed in Table 4) which must be defined by a fitting method and the interactions among the parameters. In the parameters listed in Table 4, the equilibrium constants should be determined from thermodynamic data, but reliable thermodynamic data are not available for CaF₂ or CaCl₂ containing fluxes around 1 623 K.

In this report, the following procedure was adopted to define the unknown parameters and the characteristics of each flux were represented by the difference of E_{Mn} , E_P , E_S and k_s since only these values were changed in each flux to fit the experimental results. At first E_C , E_{Fe} and E_{Si} were defined as 1 800, 500 and 5×10⁹, respectively, by the thermodynamic calculation based on the free energy data⁶⁾ and the activity coefficient measured by Suito and Inoue for FeO.⁷⁾ Secondly, G_{CO} and G_{O_2} were defined as 7×10⁻⁸ and 5×10⁻⁷ mol/(cm²·s) by fitting to the decarburization and dephosphorization curves. The value of k_m was defined as 0.023 cm/s by fitting to the dephosphorization curve. These values were determined from the experimental result of No. 3 flux shown in Table 2 and were fixed in the calculation for the other experimental results. However, when MnO₂ was used in the flux, it was regarded to decompose into MnO and O₂ and oxygen was added to G_{O₂}. The parameters which were used by Ohguchi *et al.*^{2,5)} and by the present authors are listed in Table 4. The difference of these values would be due to the different stirring condition and atmosphere of the experiment besides the flux composition and temperature.

Figure 1 compares the measured and calculated distribution ratio of P, S and Mn for each experiment. In these calculations, only FeO was considered as the iron oxide in slag and to compare with the observed (T.Fe) content in slag, the calculated (FeO) was numerically converted to (T.Fe). Since

these results show a good agreement, it is considered that the characteristics of each flux can be represented by the change in E_{Mn} , E_P , E_S and k_s .

2. Comparison of Dephosphorization and Desulfurization Behavior between Fe-oxide and Mn-oxide as Oxidant

The change of [P], [Mn], (MnO) and (T.Fe) contents in the typical experiment at 1 623 K are shown in Fig. 2. The curves in this figure are the calculation results by the coupled reaction model. From this figure, in terms of the minimum [P] level and the dephosphorization rate, MnO free flux (No. 1 in Table 2) had the best dephosphorization ability and FeO free flux (No. 2 in Table 2) had the poorest ability. Mixtures of FeO and MnO (Nos. 3 and 4 in Table 2) showed an intermediate ability.

Figure 3 shows the dependence of E_{Mn} , E_P , E_S and k_s on the ratio of FeO to the total content of FeO and MnO in flux. Figure 4 shows the change of calculated oxygen activity at the interface with time for some fluxes. In these calculation, for the MnO

free flux, k_s had to be modified from 1.15×10^{-2} to 5.75×10^{-5} (cm/s) when the content of FeO in slag decreased below 6.5 % to make the calculation consistent with the experimental result. In Fig. 3 the initial value of k_s was used, but this modification was not necessary for the other flux. This characteristics of the MnO free flux may arise from the change of slag melting point by the rapid change of (T.Fe) content in slag. Such a rapid change of slag composition was not observed in the other flux. From Fig. 3, the high refining ability of the MnO free flux is evident and with an increase of FeO content in the flux, dephosphorization, desulfurization and MnO reduction can be promoted. The FeO rich flux showed a higher E_S and lower E_{Mn} value in spite of the higher oxygen potential at interface shown in Fig. 4. This may suggest a more basic property of FeO than MnO. However, this argument is not consistent with the previous data⁸⁾ and more investigations should be necessary. On the other hand, a mixed flux of FeO and MnO showed a lower k_s value com-

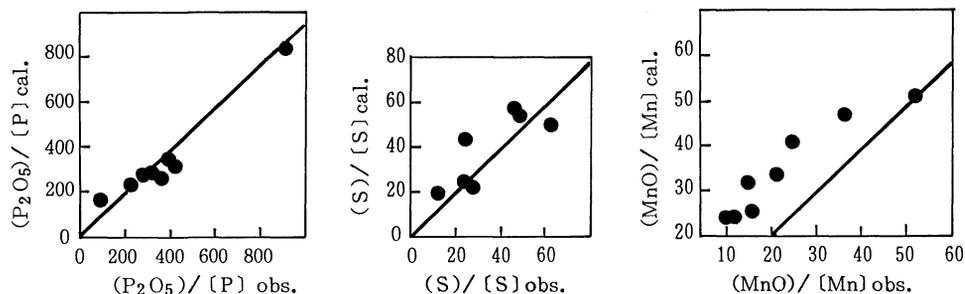


Fig. 1. Comparison between the observed and the calculated distribution ratio of P, S and Mn.

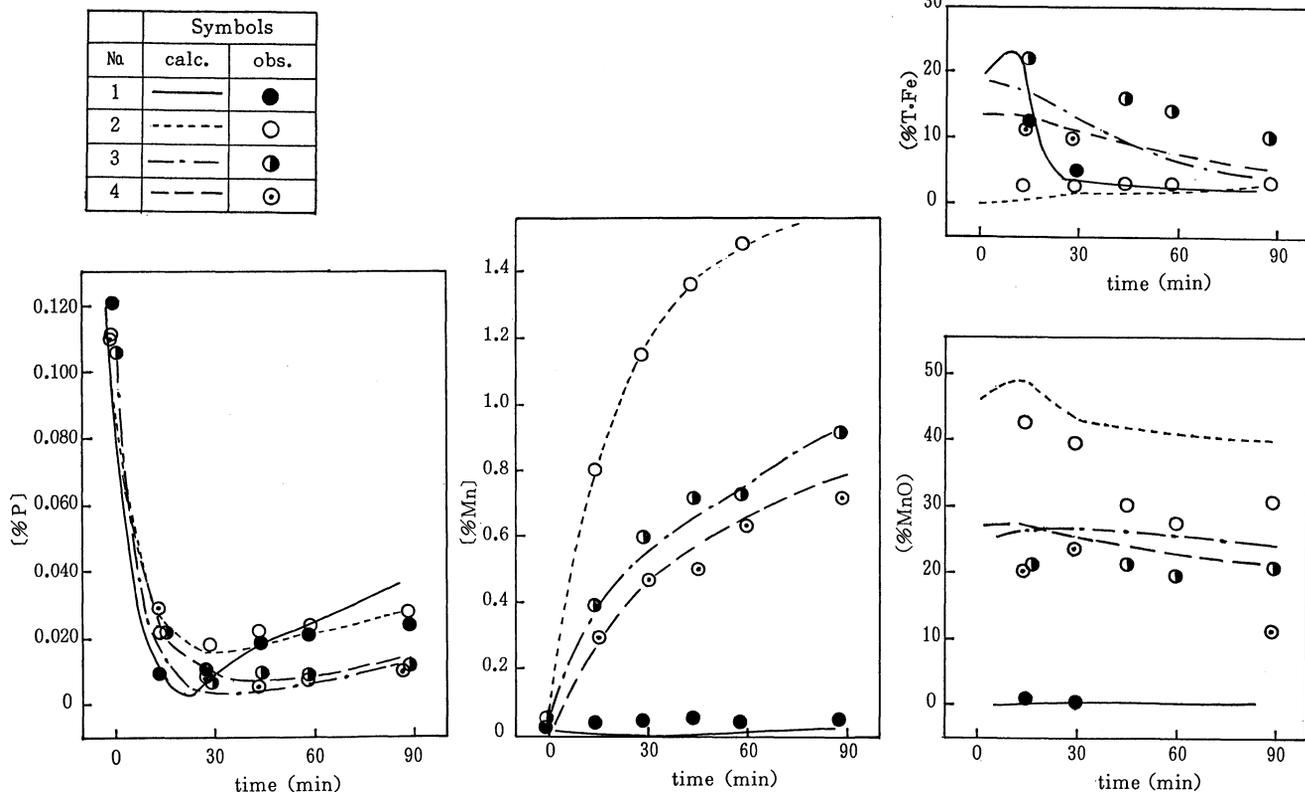


Fig. 2. Comparison of dephosphorization and desulfurization behavior between Fe-oxide and Mn-oxide.

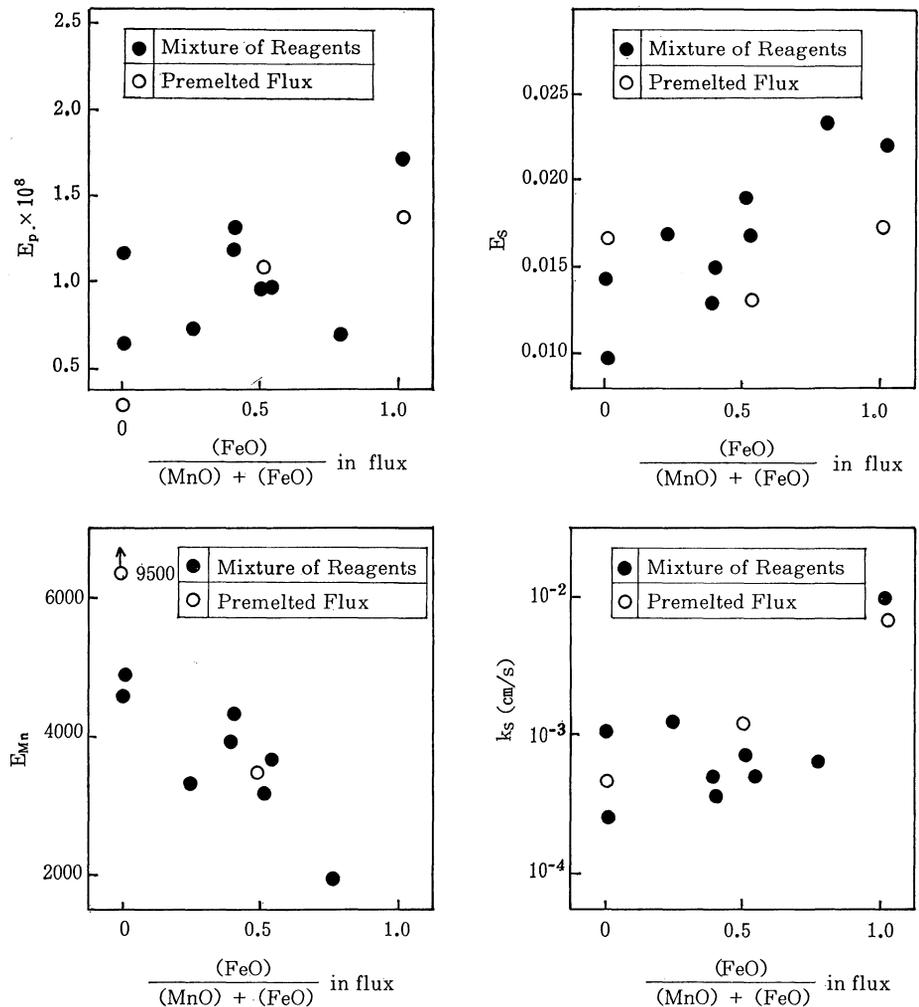


Fig. 3. Dependence of E_{Mn} , E_p , E_s and k_s on the ratio of FeO and MnO in flux.

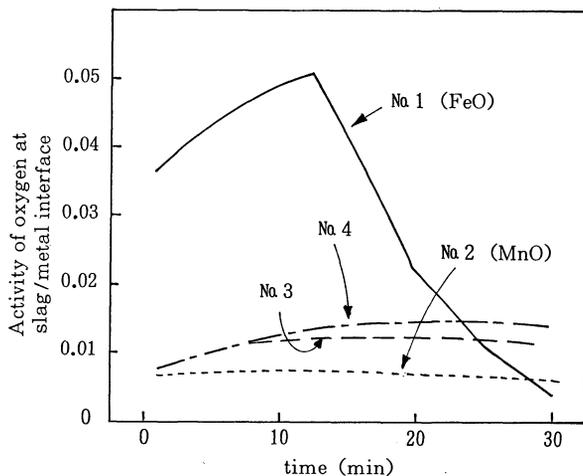


Fig. 4. Change of oxygen activity at interface with time by various fluxes.

pared with the MnO free flux. This result would correspond to the elevation of flux melting point by the addition of MnO.⁹⁾ Although Shinme *et al.*⁹⁾ reported that some mixing ratio of Fe_2O_3 and MnO_2 in a flux showed the best refining ability in a similar experiment, such a result was not obtained in the present experiment. In the case of industrial application, the ratio of Fe-oxide and Mn-oxide in flux should be determined by optimization between the

required [%P] and [%S] level and the Mn yield in terms of the production cost.

3. Influence of CaO/SiO₂ and Additional CaF₂ and CaCl₂ on Dephosphorization and Desulfurization Behavior

Figure 5 shows the results of experiments at 1 623 K showing the effect of basicity defined as the ratio of CaO and SiO₂ in the flux. From this figure, an increase of basicity was shown to promote dephosphorization, desulfurization and Mn recovery. In these experiments, the fluidity of slag was good enough and the effect of melting rate of flux could be ignored.

As the auxiliary flux, CaF₂ and CaCl₂ are well known in the hot metal dephosphorization process. Figure 6 shows the effect of the fraction of CaF₂ in comparison with the simultaneous addition of CaCl₂ at 1 623 K. When the addition of CaF₂ was not enough, the rate of each reaction was low because of the high melting point of the flux. When a small amount of CaCl₂ was added to this slag, a drastic decrease of melting point was observed for the slag in the furnace and the reaction rate also became high. The nearly identical effect was achieved when CaF₂ was added up to 19.5 % in flux.

Figure 7 shows the dependence of E_{Mn} , E_p , E_s and k_s on the ratio of CaF₂ to CaO in flux with various

No.	Symbols	
	Calc.	Obs.
4	---	○
5	---	●
6	—	●

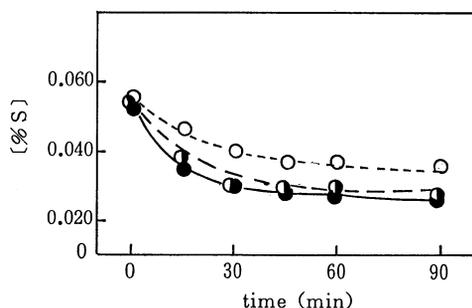
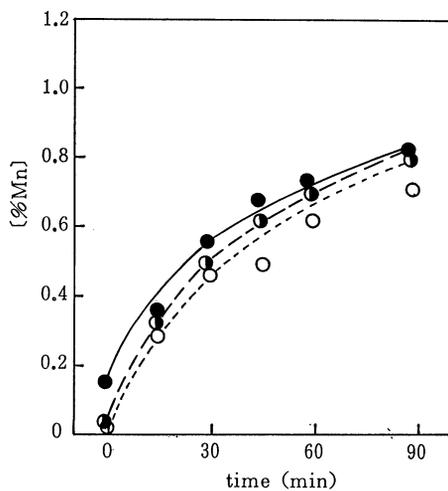
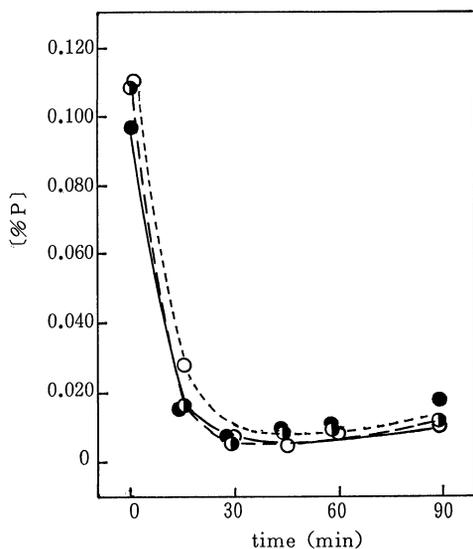


Fig. 5. Influence of basicity on the concentration change of [P], [S] and [Mn].

No.	Symbols	
	Calc.	Obs.
5	---	×
7	---	○
8	---	●
9	—	○

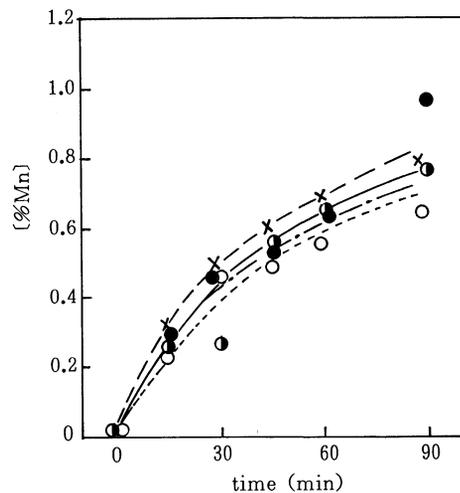
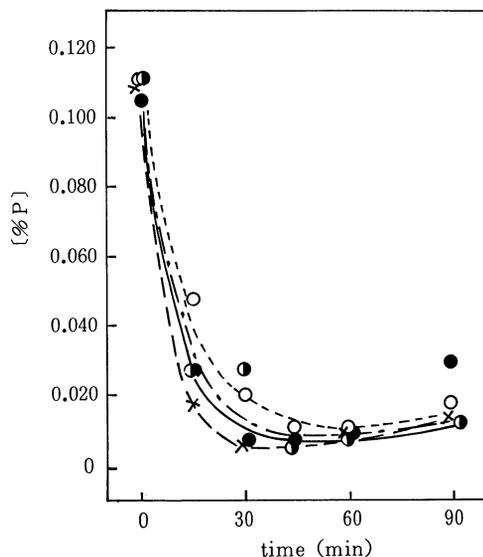


Fig. 6. Influence of CaF_2 and CaCl_2 on the concentration change of [P] and [Mn].

basicity. This figure shows that E_P and E_S increased and E_{Mn} decreased as increasing basicity. However, no significant influence was found by changing the ratio of CaF_2 to CaO and also by adding CaCl_2 . On the other hand, k_s increased with increasing the ratio of CaF_2 to CaO and adding CaCl_2 but the basicity did not significantly affect on k_s .

To compare with the thermodynamic data, E_{Mn} , E_P and E_S were converted to the activity coefficients in accordance with the definition of an effective equilibrium constant cited in Eq. (1). In this calculation the equilibrium constant (K_M in Eq. (1)) was determined from a thermodynamic table.⁶⁾ In Fig. 8, the

activity coefficients of MnO , FeO and P_2O_5 obtained by this experiment are compared with those calculated from the regular solution model¹⁰⁾ and the equations obtained by Suito *et al.*^{7,11,12)} was shown. In the regular solution model, as the effect of F^- and Cl^- could not be taken into consideration, the content of CaF_2 and CaCl_2 were ignored and the composition was assigned to be the slag at 20 min after starting each experiment. Agreement was not good enough especially for γ_{MnO} . Activity coefficients calculated by the thermodynamic models varied widely with the slag composition, but effective equilibrium constants should not be changed so widely to fit the

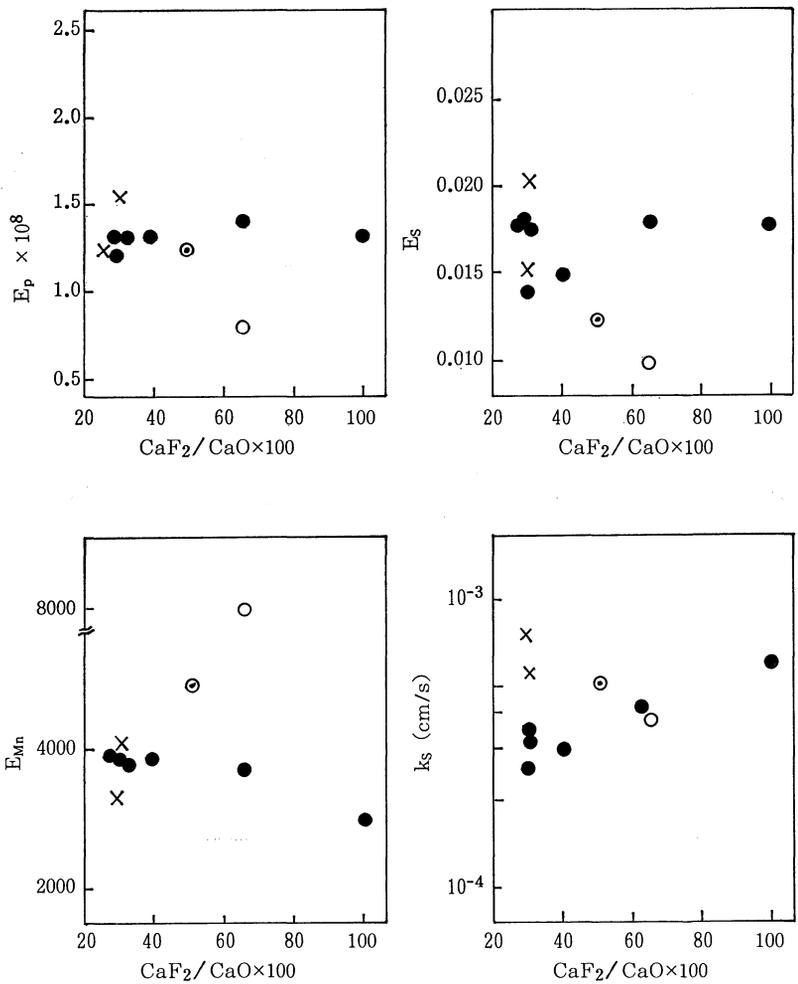


Fig. 7. Dependence of E_{Mn} , E_P , E_S and k_s on the ratio of CaF_2 to CaO content in flux and the $CaCl_2$ addition.

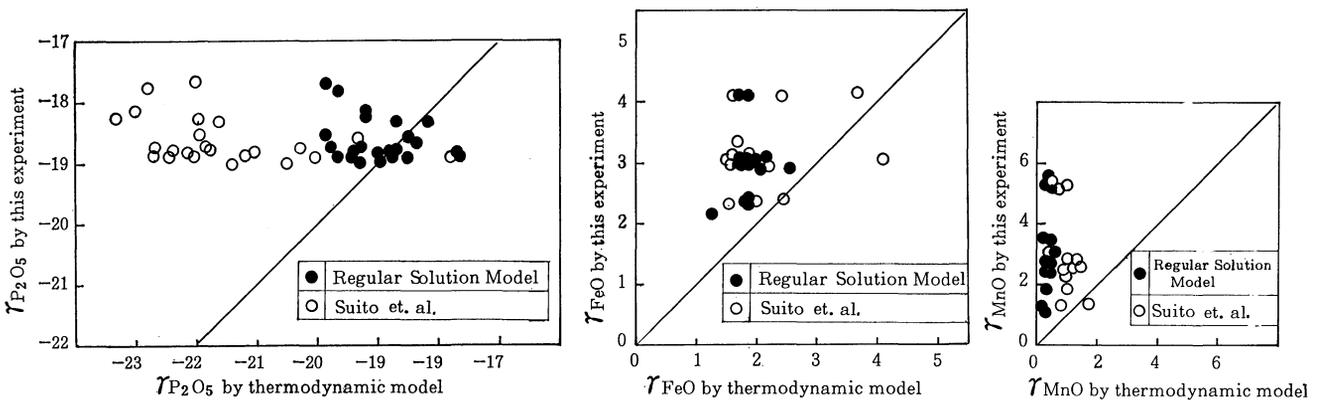


Fig. 8. Comparison of the activity coefficient of MnO , FeO and P_2O_5 obtained by the present experiment with the calculation by the thermodynamic models.

experimental results. The discrepancy may be ascribed to the difference of the experimental conditions, like temperature and flux composition between the present experiment and equilibrium measurements. Moreover it must be mentioned that the value of effective equilibrium constant has no important meaning in this calculation as it is influenced by the other parameters.

4. Influence of Temperature on Dephosphorization and Desulfurization Behavior

Figure 9 shows the results of experiments studying the temperature dependence by the fluxes of the same

composition. Elevated temperatures increased the degree of Mn recovery and decreased the degree of dephosphorization.

Figure 10 shows the influences of temperature and the addition of CaF_2 and $CaCl_2$ on k_s , which represents the reaction rate. The values of k_s was nearly equal for the fluxes of the CaF_2 to CaO ratio of 30 % with addition of $CaCl_2$ at 1 573 and 1 623 K, and the CaF_2 to CaO ratio of 40 % without addition of $CaCl_2$ at 1 623 and 1 673 K. From this result it can be considered that the addition of $CaCl_2$ would not be necessary if the ratio of CaF_2 addition and the temperature were adjusted because the addition of $CaCl_2$

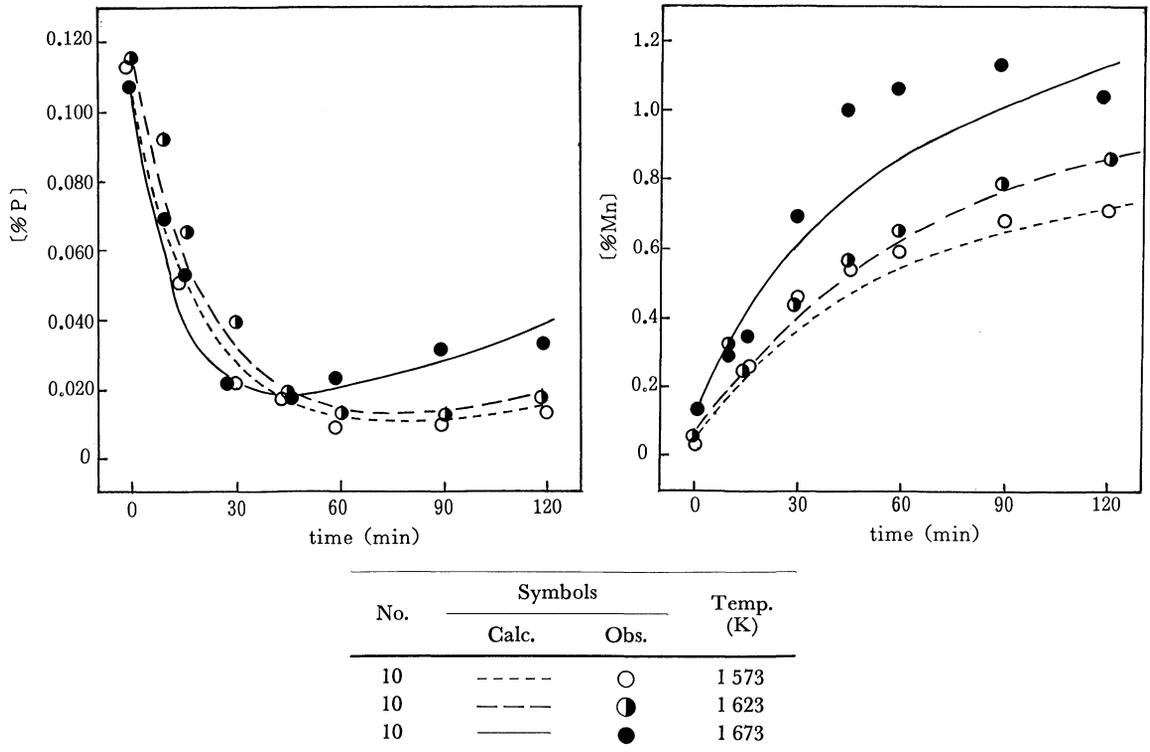


Fig. 9. Concentration change of [P] and [Mn] with temperature.

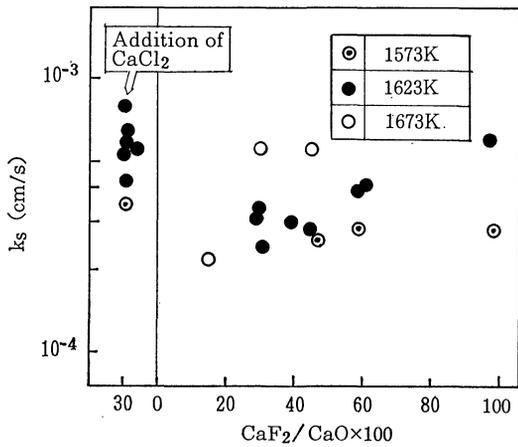


Fig. 10. Dependence of k_s on the temperature and the addition of CaF_2 , CaCl_2 .

and the ratio of CaF_2 to CaO did not significantly affect the effective equilibrium constants of P, Mn and S shown in Fig. 7.

VI. Conclusion

The experimental results of hot metal dephosphorization by using the mixtures of Fe-oxide and Mn-oxide as oxidant were analyzed by the coupled reaction model and the following points were clarified.

(1) The observed distribution ratio of P, S and Mn and the calculated values for each experiment showed good agreements and the applicability of the coupled reaction model was proved.

(2) When a mixture of Fe-oxide and Mn-oxide was used as oxidant, the effective equilibrium constants of P and S decreased and that of Mn increased, and the mass transfer coefficient in slag decreased

comparing with the case when Fe-oxide was used as oxidant.

(3) Addition of CaF_2 and CaCl_2 did not significantly change the effective equilibrium constants but modified the mass transfer coefficient in slag.

Nomenclature

- a_0^* : Henrian activity of oxygen at slag/metal interface on the weight percent basis
- C : total molar concentration in slag ($\text{mol}\cdot\text{cm}^{-3}$)
- E : effective equilibrium constants defined by Eq. (2)
- f : Henrian activity coefficient
- G_{CO} : phenomenological rate parameter for CO evolution ($\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$)
- G_{O_2} : mass transfer coefficient of oxygen to the reaction interface ($\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$)
- J : molar flux density ($\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$)
- k : mass transfer coefficient ($\text{cm}\cdot\text{s}^{-1}$)
- K : equilibrium constant
- N : molecular weight ($\text{g}\cdot\text{mol}^{-1}$)
- γ : activity coefficient with respect to the pure substance as standard state
- ρ : density ($\text{g}\cdot\text{cm}^{-3}$)
- (): component in slag phase
- []: component in metal phase

Subscript

- m : metal
- s : slag
- M : component M

Superscript

- *: interface

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