Dephosphorization of Liquid Iron by CaF_2 -base Fluxes*

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Synopsis

Dephosphorization of liquid iron by CaF_2 -base fluxes was studied at 1 600 °C. Iron oxide was added to metal or flux as the oxidizing agent. Dephosphorizing reaction proceeded rapidly and the rate increased with increasing CaF_2 content of flux. The rate of reaction was analyzed on the assumption that the reaction was controlled by the simultaneous transport of phosphorus, oxygen and sulfur.

The effect of CaF_2 on the distribution ratio of phosphorus between liquid iron and flux was examined.

I. Introduction

Needs for high quality steels of low phosphorus and sulfur content are now increasing in various industries using them. Therefore, processes for making clean steels have been actively investigated and one of them is the injection of fluxes into liquid iron.

CaF_2 -base fluxes are used in the ESR process for making clean steel, as they have a strong desulfurizing power. Also, it was shown that they have some dephosphorizing power in the presence of oxidizers.^{1,2)} Turkdogan and Pearson³⁾ showed that CaF_2 decreases the activity coefficient of phosphorus pentoxide in slags. Kor⁴⁾ and Suito and Inoue⁵⁾ examined the effect of CaF_2 on the distribution of phosphorus between liquid iron and slag.

This study was undertaken to obtain fundamental data for the rate of dephosphorization of liquid iron and to examine the dephosphorizing power of CaF_2 -base flux.

II. Experimental Procedure

The experimental apparatus is shown in Fig. 1. A vertical electric resistance furnace was used for heating and melting of iron and flux. An alumina tube of 60 mm I.D. and 1 000 mm in length was covered with water-cooled caps to prevent the penetration of air. A sampling hole and a gas outlet were provided to the upper cap and gas and thermocouple inlets to the lower cap. A fused magnesia crucible (30 mm I.D., 100 mm H) was used for melting the iron of about 200 g under argon gas atmosphere.

After holding it at 1 600 °C, a slag holder (an iron crucible) containing flux of 20 g was lowered through the sampling hole to a position just above the liquid iron surface. After the meltdown of the flux, the holder was further lowered slowly to touch the liquid iron. Then, the liquid flux flowed out from the bottom of the holder over the liquid iron and began to react. A magnesia crucible could hold the flux for

more than 30 min. Several metal samples were taken at appropriate intervals during a run by suctioning into silica tubes and a final flux sample was taken by inserting an iron wire.

The metal samples were analyzed for phosphorus, oxygen and sulfur and the flux samples for phosphorus, fluorine, sulfur, ferrous oxide, calcium oxide, magnesia and alumina contents.

Mother alloys were prepared by melting a mixture of electrolytic iron and ferro-phosphorus (about 26.5 % P) or iron sulfide in an alumina crucible in a vacuum induction furnace. These were added to electrolytic iron to make metals containing phosphorus and sulfur of about 0.1 and 0.05 %, respectively.

Fluxes were prepared by melting mixtures of reagent grade CaF_2 , CaCO_3 , Al_2O_3 , and MgO in a graphite crucible in a Tammann furnace. Liquid fluxes were rapidly cooled by pouring on an iron plate and crushed to small pieces. The composition of fluxes is shown in Table 1.

III. Experimental Results

Three methods were tried for adding iron oxide as the oxidizer, that is, (a) to liquid iron before the addition of flux, (b) to solid flux in the holder and (c) to liquid flux on a liquid iron. But the difference of the methods had little influence on the progress and the degree of dephosphorizing reaction.

Initial and final phosphorus and oxygen contents of liquid iron and composition of final fluxes are shown

Fig. 1. Furnace assembly.

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Table 1. Composition of fluxes used for dephosphorization experiments. (%)

Flux	CaF ₂	CaO	Al ₂ O ₃	MgO	MgF ₂
A	100	—	—	—	—
B	68.2	22.1	—	5.09	—
C	64.2	26.3	—	7.10	—
D	64.6	29.2	—	5.10	—
E	63.6	0.92	29.8	4.45	—
F*	55	30	—	—	15
G	40.6	31.9	19.7	5.39	—
H	40.9	20.6	33.5	4.49	—
I	17.8	38.2	29.9	11.3	—
J	—	50.2	47.6	—	—

* Mixing ratio of reagent.

Table 2. Composition of metal and flux at the end of run.

Run No.	Time (min)	[%P]		[%O]		Composition of final flux (%)					
		Initial	Final	Initial	Final	CaF ₂	CaO	Al ₂ O ₃	MgO	FeO	P ₂ O ₅
A*-43	60	0.096	0.018	0.096	0.071	83.5	1.14	—	10.4	3.77	1.68
B- 5	15	0.170	0.009	0.032	0.037	68.5	14.6	—	7.06	6.48	2.63
B- 6	15.5	0.166	0.020	0.147	0.065	67.2	12.0	—	6.28	6.51	1.83
B-12	15	0.097	0.004	—	0.076	61.1	13.9	—	6.61	14.4	1.36
B-13	15	0.019	0.002	0.125	0.068	65.4	11.8	—	5.17	11.7	0.51
C-24	25	0.053	0.022	0.043	0.008	59.2	24.6	—	6.70	1.64	0.67
E-19	60	0.082	0.066	0.052	0.018	53.7	5.36	30.5	9.24	1.86	0.20
F-44	53.5	0.104	0.024	0.096	0.036	68.1**	4.69	—	15.1	2.92	1.96
G- 7	15	0.108	0.014	0.125	0.036	40.3	22.0	21.2	4.46	6.53	1.92
G-33	60	0.056	0.030	0.055	0.013	40.0	28.7	18.1	7.37	2.64	0.64
H-15	20	0.109	0.071	0.111	0.027	32.5	17.2	29.3	15.9	4.15	0.73
H-16	30	0.111	0.069	0.041	0.022	34.8	14.7	30.3	14.5	2.71	0.69
H-36	60	0.055	0.044	0.058	0.029	40.7	16.4	25.7	14.0	3.66	0.25
I-10	20	0.108	0.024	0.062	0.047	17.5	30.4	25.3	9.84	13.5	1.30
I-34	60	0.023	0.015	0.100	0.039	21.1	33.8	30.0	9.30	3.97	0.41
I-37	60	0.051	0.040	0.052	0.023	22.5	33.7	28.6	6.75	3.40	0.24
J-14	16.4	0.049	0.007	0.152	0.049	—	39.1	43.7	6.58	13.8	0.29
J-17	30	0.106	0.068	0.100	0.025	—	36.7	44.6	7.51	7.73	0.53
J-18	30	0.108	0.072	0.046	0.020	—	35.4	45.0	8.78	7.45	0.54
J-35	60	0.017	0.013	0.093	0.034	—	39.5	44.7	7.36	3.52	0.18
J-38	60	0.055	0.047	0.046	0.019	—	43.9	41.7	6.94	2.83	0.10

* A-J indicates the kind of flux.

** F in flux was assumed to be CaF₂.

in Table 2.

Examples of the effect of flux composition on the dephosphorizing reaction are shown in Figs. 2(a) and (b). As shown in these figures, the rate of dephosphorization increased with increase of CaF₂ content. From the comparison of the result by flux H (H-36) with that by flux G (G-33), it is seen that the dephosphorizing power of CaO in CaF₂-base flux is higher than that of Al₂O₃. And, from the results obtained by fluxes B and F in which the fluorine content was nearly the same, it was found that the dephosphorizing power of MgF₂ was weaker than that of CaF₂. These results correspond with the values of phosphate capacity which are shown later.

Some experiments were made to examine the pos-

Fig. 2. Effect of flux composition on the dephosphorization of liquid iron at 1 600 °C.

sibility of simultaneous dephosphorization and desulfurization by CaF₂ fluxes. In these cases iron oxide was added to liquid iron (method (a)). Composition of initial and final samples is shown in Table 3.

The dephosphorization and desulfurization reactions proceeded simultaneously as shown in Fig. 3. It was found that in some cases where relatively large amounts of sulfur were removed (for example, C-26 and G-28) the dephosphorization proceeded slightly more rapidly than that in the case of metals without sulfur, that is, dephosphorization was enhanced by desulfurizing reaction.

From the present results it is seen that the following reactions proceed simultaneously:

IV. Discussion

1. Reaction Rate

At high temperatures as in this study it is generally considered that chemical reactions at the interface may proceed rapidly and cannot be the rate controlling step. Then, the present results were analyzed assuming a reaction controlled by the simultaneous mass transport of reaction components.

The rate of transport of phosphorus from liquid iron to flux is given by Eq. (3), according to the two film theory.

$$\begin{aligned} -\frac{d[\%P]}{dt} &= \frac{F}{W_m} k_m^p \rho_m ([\%P] - [\%P]^*) \\ &= \frac{F}{W_m} k_s^p \rho_s ((\%P)^* - (\%P)) \dots\dots\dots(3) \end{aligned}$$

where, F : the interfacial area
 W_m : weight of metal
 k_m^p, k_s^p : mass transport coefficients in metal and flux
 ρ_m, ρ_s : densities
 $*$: the concentration at the interface.

When the concentrations of basic components of flux are nearly constant, the distribution ratio of phosphorus between metal and flux, $L_P = (\%P)^* / [\%P]^*$, will be given by the following equation from the equilibrium constant of Eq. (1):

$$L_P = A[\%O]^{5/2} \dots\dots\dots(4)$$

where, A : a constant.
Equation (3) will be rewritten by using L_P as follows:

$$-\frac{d[\%P]}{dt} = \frac{F}{W_m} K_P \{A[\%O]^{5/2}[\%P] - (\%P)\} \dots\dots\dots(5)$$

Table 3. Composition of metal and flux at the end of run (Simultaneous dephosphorization and desulfurization experiments).

Run No.	[%P]		[%S]		[%O]		Composition of final flux (%)						
	Initial	Final	Initial	Final	Initial	Final	CaF ₂	CaO	Al ₂ O ₃	MgO	FeO	P ₂ O ₅	T. S
C-25	—	—	0.049	0.019	0.052	0.015	63.3	21.4	—	5.79	1.95	—	0.40
C-26	0.057	0.010	0.048	0.011	0.050	0.007	64.6	21.4	—	7.35	1.14	0.73	0.47
C-39	0.077	0.020	0.045	0.043	0.039	0.042	61.4	19.9	—	10.6	4.09	0.93	0.02
D-41	0.097	0.023	0.053	0.042	0.062	0.051	59.2	24.6	—	7.82	5.60	1.72	0.04
G-28	0.060	0.019	0.045	0.030	0.082	0.029	34.4	31.1	17.9	10.0	5.64	0.64	0.38
H-29	0.046	0.022	0.043	0.037	0.098	0.060	38.5	14.0	28.3	10.9	5.74	0.54	0.05
I-27	0.074	0.060	0.037	0.026	0.048	0.012	22.8	38.7	24.2	10.7	2.46	0.42	0.31
I-32	0.064	0.048	0.058	0.039	0.057	0.023	19.6	35.4	26.9	10.2	7.70	0.57	0.30
J-31	0.058	0.055	0.048	0.038	0.064	0.023	—	41.7	42.1	7.37	3.77	0.18	0.28

Fig. 3. Simultaneous reaction of dephosphorization and desulfurization at 1 600 °C.

where, $1/K_P = L_P/k_m^P \rho_m + 1/k_s^P \rho_s$

Rate equations of transport of oxygen and sulfur will be given similarly as follows:

$$-\frac{d[\%O]}{dt} = \frac{F}{W_m} k_m^O \rho_m ([\%O] - [\%O]^*) \dots\dots\dots(6)$$

$$\frac{d(\%FeO)}{dt} = \frac{F}{W_s} k_s^{FeO} \rho_s \{L_O[\%O]^* - (\%FeO)\} \dots\dots\dots(7)$$

$$-\frac{d[\%S]}{dt} = \frac{F}{W_m} K_S \left\{ \frac{B}{[\%O]^*} [\%S] - (\%S) \right\} \dots\dots\dots(8)$$

In the equations,

$$L_O = (\%FeO)^* / [\%O]^* \dots\dots\dots(9)$$

$$\frac{1}{K_S} = \frac{L_S}{k_m^S \rho_m} + \frac{1}{k_s^S \rho_s} \dots\dots\dots(10)$$

$$L_S = (\%S)^* / [\%S]^* = B / [\%O]^* \dots\dots\dots(11)$$

where, B : a constant.

At steady state the following mass balance equation holds:

$$-\frac{5}{2} \frac{W_m}{M_P} \frac{d[\%P]}{dt} + \frac{W_s}{M_{FeO}} \frac{d(\%FeO)}{dt} + \frac{W_m}{M_O} \frac{d[\%O]}{dt} + \frac{W_m}{M_S} \frac{d[\%S]}{dt} = 0 \dots\dots\dots(12)$$

Substituting Eqs. (5) to (8) into Eq. (12),

$$\begin{aligned} & \frac{5}{2} \frac{K_P}{M_P} A [\%P] [\%O]^{5/2} \\ & + \left(\frac{k_m^O \rho_m}{M_O} + \frac{k_s^O \rho_s}{M_{FeO}} L_O \right) [\%O]^* - \frac{K_S \cdot B [\%S]}{M_S [\%O]^*} \\ & - \frac{5}{2} \frac{K_P}{M_P} (\%P) - \frac{k_m^O \rho_m}{M_O} [\%O] + \frac{K_S}{M_S} (\%S) \\ & - \frac{k_s^O \rho_s}{M_{FeO}} (\%FeO) = 0 \dots\dots\dots(13) \end{aligned}$$

From this equation the values of $[\%O]^*$ can be determined by giving proper values for parameters, $k_m^O \rho_m$, $k_s^O \rho_s$, A , B , and L_O . By use of the values of $[\%O]^*$ thus obtained, changes of phosphorus, oxygen and sulfur contents of liquid iron during a run can be determined by the Runge-Kutta method. Repeating calculation by computer by selecting the values of parameters will give the best values expressing the experimental results. But, it is difficult to do this calculation procedure because of too many parameters. Then, in the present study, to make the calculation simpler it was assumed that mass transport coefficients of reaction components in liquid iron and flux were equal, that is,

$$k_m^P = k_m^O = k_m^S = k_m \text{ and } k_s^P = k_s^{FeO} = k_s^S = k_s.$$

Also, it was assumed that parameters A , B and L_O were constant during a run.

The parameter $k_m^O \rho_m$ was determined from the experimental results obtained with fluxes B and C in which the dephosphorizing reaction at the beginning period seemed to be controlled by the transport of phosphorus in liquid iron because of the high distribution ratio of phosphorus.

The rate equation is

$$-\frac{d[\%P]}{dt} = \frac{F}{W_m} k_m^O \rho_m ([\%P] - [\%P]_{eq}) \dots\dots\dots(14)$$

The value of $k_m^O \rho_m = 0.17 \text{ g/cm}^2 \text{ sec}$ obtained by Eq. (14) was nearly the same as the value of $0.13 \text{ g/cm}^2 \text{ sec}$ which was determined for the mass transport coefficient of oxygen in liquid iron at 1600°C in another experiment⁶⁾ under the same experimental conditions.

A , B and L_O were determined so as to fit well to the experimental results, referring to the composition of final metal and flux samples.

The calculated values of parameters are given in Table 4.

The curves in Figs. 2 and 3 are those drawn by calculating the changes of phosphorus and oxygen contents by using parameters now obtained. It is seen that these curves express fairly well the experimental results.

The values of $k_s^O \rho_s$ were in the range between 0.003 and $0.14 \text{ g/cm}^2 \text{ sec}$ and were slightly higher than those obtained for dephosphorization by slags without CaF_2 .⁷⁾ The values of $k_s^O \rho_s$ increased slightly with decrease of viscosity of fluxes.

Table 4. Calculated values of parameters and FeO content in final fluxes.

Run No.	$k_s^O \rho_s$	L_O	A	B	$(\%FeO)_{cal}$
A-43	0.013	53.2	3.11×10^4	—	3.80
B- 5	0.023	173	4.97×10^5	—	6.57
B- 6	0.150	79.7	2.62 „	—	3.90
B-12	0.130	141	1.26 „	—	10.6
B-13	0.140	122	1.31 „	—	7.88
C-24	0.030	214	2.18×10^6	—	1.78
E-19	0.006	101	4.42×10^4	—	1.83
F-44	0.005	80.3	1.72×10^5	—	2.74
G- 7	0.012	183	2.43 „	—	6.04
G-33	0.003	197	2.22 „	—	2.84
H-15	0.012	133	2.23×10^4	—	4.25
H-16	0.020	192	7.05 „	—	4.29
H-36	0.008	125	1.34 „	—	3.56
I-10	0.005	239	5.05 „	—	12.2
I-34	0.003	102	1.60 „	—	3.91
I-37	0.012	126	3.17 „	—	2.86
J-14	0.012	184	5.36 „	—	9.84
J-17	0.010	266	4.32 „	—	6.73
J-18	0.003	317	5.55 „	—	6.86
J-35	0.005	94.1	1.70 „	—	3.22
J-38	0.012	127	2.73 „	—	2.38
C-25	0.030	155	—	0.199	2.38
C-26	0.100	125	7.05×10^6	0.254	1.05
C-39	0.030	113	2.07×10^5	0.029	3.85
D-41	0.030	126	8.29×10^4	0.066	5.53
G-28	0.018	134	1.27×10^5	0.131	3.77
H-29	0.013	85.5	1.35×10^4	0.081	5.08
I-27	0.015	200	1.31×10^5	0.050	2.46
I-32	0.006	262	3.14×10^4	0.086	5.92
J-31	0.005	138	6.26×10^3	0.060	3.29

With respect to Eq. (5), it was found that in the fluxes having high distribution ratio of phosphorus (fluxes A and B) the rate controlling step was the transport in liquid iron and in other cases the transport in liquid flux.

2. Distribution of Phosphorus

As shown in Figs. 2 and 3, after about 10 min phosphorus and oxygen contents of liquid iron reached constant values, indicating an arrival at the equilibrium.

Several approaches have been proposed for the expression of phosphorus equilibrium based on the concept of molecular or ionic constituents in slags and fluxes. The present results with samples taken at the end of runs were used to examine the effect of CaF₂ on the activity coefficient of phosphorus oxide and on the distribution ratio, referring to equations proposed by previous investigators.

Turkdogan and Pearson³⁾ gave the following equation:

$$2P + 5O = P_2O_5(l),$$
$$\log K_P \left(= \frac{a_{P_2O_5}}{[\% P]^2 [\% O]^5} \right) = \frac{36850}{T} - 29.07 \dots\dots (15)$$
$$\log \gamma_{P_2O_5} = -1.12(22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} + 31N_F - 2N_{SiO_2}) - 42000/T + 23.58 \dots\dots (16)$$

where, [%P], [%O]: weight percent concentrations
N: the mole fraction of slag components
Ca_TO means that total calcium was assumed to be lime.

Recently Suito and Inoue⁸⁾ measured the distribution of phosphorus between liquid iron and slags saturated with magnesia and gave the following equation:

$$\log \gamma_{P_2O_5} = -1.01(23N_{CaO} + 17N_{MgO} + 8N_{FeO}) - 26300/T + 11.2 \dots\dots (17)$$

The values of $\gamma_{P_2O_5}$ determined by Eq. (15) from phosphorus and oxygen contents of the final metal samples and phosphorus pentoxide content of the flux samples, $\gamma_{P_2O_5}^{obs}$, were compared with those calculated by Eq. (16) from the composition of final fluxes, $\gamma_{P_2O_5}^{cal}$. The former was larger than the latter in the high CaF₂ concentration range as shown in Fig. 4 where logarithms of $\gamma_{P_2O_5}^{cal}/\gamma_{P_2O_5}^{obs}$ were plotted against N_F . Assuming that the difference may be ascribed to the effect of CaF₂ on $\gamma_{P_2O_5}$ and a linear relationship holds, the following equation will be obtained:

$$\log \gamma_{P_2O_5}^{cal}/\gamma_{P_2O_5}^{obs} = -24.7N_F + 3.5 \dots\dots (18)$$

Consequently, the value of coefficient for N_F in Eq. (16) will be corrected from 31 to 9. Kor⁴⁾ pointed out from his experimental result with slags containing a small amount of CaF₂ that the coefficient of 31 for N_F seemed to be too large and gave the value of 20. Suito and Inoue⁵⁾ found that CaF₂ had the same effect as CaO on the molar basis on the activity coefficient of P₂O₅, when fluorine in the slag was treated as CaF₂ in the calculation. These discrepancies with

the effect of CaF₂ must be further investigated. Healy⁹⁾ gave the following equation for the distribution of phosphorus between liquid iron and slag, $L_P = (\%P)/[\%P]$:

$$\log L_P = 22350/T - 16.0 + 0.08(\%CaO) + 2.5 \log (\%T.FeO) \dots\dots (19)$$

where, (%CaO), (%T.FeO): weight percent concentrations.

The distribution ratio, L_P^{obs} , determined from phosphorus contents of the final metal and flux samples was compared with that, L_P^{cal} , calculated by Eq. (19) in Fig. 5 where logarithms of the ratio of L_P^{obs} to L_P^{cal} are plotted against CaF₂ concentration. Though points are scattered somewhat widely comparing with those in Fig. 4, the following equation will be obtained assuming a linear relationship:

$$\log (L_P^{obs}/L_P^{cal}) = 0.049(\%CaF_2) - 0.21 \dots\dots (20)$$

This result indicates that the effect of CaF₂ must be taken into consideration in the equation for the distribution ratio.

As known from the measurement with CaF₂-FeO flux,^{10,11)} CaF₂ increases the activity coefficient of FeO and as seen from Eqs. (16) to (18), it decreases the activity coefficient of P₂O₅. These favor the dephos-

Fig. 4. Relation between mole fraction of F and $\log (\gamma_{P_2O_5}^{cal}/\gamma_{P_2O_5}^{obs})$.

Fig. 5. Relation between CaF₂ content and $\log (L_P^{obs}/L_P^{cal})$.

phorization by CaF_2 -base fluxes in addition to the decrease of viscosity.

The dephosphorizing power of slag and flux may be expressed by the phosphate capacity, C_{PG} , defined by Wagner.¹²⁾

$$C_{PG} = (\% \text{PO}_4^{3-}) \text{P}_{\text{P}_2}^{-1/2} \text{P}_{\text{O}_2}^{-5/4} \dots\dots\dots(22)$$

Logarithms of phosphate capacities calculated from the present results and the equilibrium constants of reactions (23) and (24) are plotted against $(N_{\text{CaO}} + 0.85 N_{\text{CaF}_2})$ in Fig. 6.

The value of 0.85 for N_{CaF_2} was determined from the relative influences of CaO and CaF_2 on the distribution ratio given in Eqs. (19) and (20). The phosphate capacity of CaF_2 fluxes increases with increasing $(\text{CaO} + \text{CaF}_2)$ content of fluxes from 10^{17} to 10^{20} . These values are larger than those of steelmaking slags which are from 10^{15} to 10^{18} .

V. Summary

Dephosphorization of liquid iron by CaF_2 -base fluxes was investigated at 1 600 °C. The results are summarized as follows:

- (1) Dephosphorization increased with increasing content of CaF_2 in flux.
- (2) Desulfurization occurred simultaneously with dephosphorization.
- (3) The rate of dephosphorization was interpreted as the reaction controlled by the mass transport in liquid iron and flux. Value of the mass transport coefficient in liquid iron was 0.17 g/cm² sec and those in liquid fluxes were from 0.003 to 0.14 g/cm² sec.
- (4) Equation derived by Turkdogan and Pearson for the activity coefficient of P_2O_5 and equation derived by Healy for the phosphorus distribution were modified to become applicable to fluxes containing large amounts of CaF_2 .

Fig. 6. Phosphate capacity of CaF_2 -base fluxes.

(5) Phosphate capacities of CaF_2 -base fluxes at 1 600 °C were 10^{17} to 10^{20} .

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