Phosphorus Distribution between Soda- and Lime-based Fluxes and Carbon-saturated Iron Melts*

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Synopsis

The phosphorus distribution ratios between carbon-saturated iron melts and $\text{Na}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-SiO}_2\text{-MO}$ ($\text{M}=\text{Mg, Ca, Ba}$), $\text{CaF}_2\text{-CaO}$ or $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ slags have been obtained as a function of the slag compositions and the temperatures. The distribution ratios in the $\text{Na}_2\text{O-SiO}_2\text{-MO}$ ($\text{M}=\text{Mg, Ca, Ba}$) system were found to decrease when Na_2O was replaced by MgO , CaO , and BaO at a constant SiO_2 content. The temperature dependence of the phosphorus distribution ratios in the $\text{CaF}_2\text{-CaO}$ and $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ systems has been observed in the temperature range between 1 430 °C and 1 550 °C, while in the $\text{Na}_2\text{O-SiO}_2$ system, it has not been observed at 1 250 and 1 350 °C. The phosphorus distribution ratios in the $\text{MF}_2(\text{MF})\text{-MO}(\text{M}_2\text{O})$ ($\text{M}=\text{Mg, Ca, Ba, Na}$) system were found to decrease in the order of $\text{Na} > \text{Ba} > \text{Ca} > \text{Mg}$.

I. Introduction

In recent years many laboratory and plant data on the dephosphorization of hot metal by using soda- and lime-based fluxes have been reported in our country. Very little work, however, is currently available in the published literatures on the thermodynamic data for the activity of phosphorus oxide in these fluxes. The reason for this is mainly due to the experimental difficulties in the temperature range of a hot metal pretreatment. Iwasaki *et al.*¹⁾ have obtained the phosphorus distribution ratios between lime-based fluxes and solid iron at a controlling oxygen potential in the temperature range of a hot metal pretreatment. In their experimental method, however, the ratios between the solid iron and the fluxes containing the strong base such as a sodium oxide become too high with the decreasing temperature. The oxygen potentials therefore must be lowered to such an extent that the phosphorus content in metal can be determined within the accuracy of chemical analysis. The phosphorus partitions²⁻⁴⁾ between liquid iron and slags obtained in the temperature between 1 550 °C and 1 650 °C have been extrapolated to the temperatures in a hot metal pretreatment in order to discuss the dephosphorization of hot metal.⁵⁾

The present authors have previously obtained the sulfur distribution ratios between the $\text{Na}_2\text{O-SiO}_2$ slags and carbon-saturated iron melts at 1 250 and 1 350 °C.⁶⁾ These results indicate that the slag compositions can be chosen up to the $\text{Na}_2\text{O/SiO}_2=1.5$ (molar ratio) in the above temperature range without the significant change in the slag compositions due to the sodium evaporation, since the time for the attainment of the equilibrium can be considerably

shorten by stirring a melt. The sulfur distribution ratios⁷⁾ between the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ slags and carbon-saturated iron melts under the $P_{\text{CO}}=1$ atm were found to be in an excellent agreement with those calculated from the sulfide capacity, C_s ($=(\%S) \cdot a_{\text{O}}/a_s$) obtained by the gas-slag equilibration.⁸⁾ From these experimental findings, the distribution ratios between soda- and lime-based fluxes and carbon-saturated iron melts have been obtained under the CO atmosphere. These results are compared with those obtained by other investigators by using the concept of phosphate capacity, C_P ($=(\%P)/[a_{\text{P}} \cdot a_{\text{O}}^{5/2}]$).

II. Experimental

The details of the experimental apparatus and method are described in the previous paper⁶⁾ on the sulfur distribution. Slag (8 g) and metal (30 g) were melted in a graphite crucible under a CO gas flow, being stirred by an alumina or graphite rod. In some of the experiments using the $\text{Na}_2\text{O-SiO}_2$ slags, copper was used instead of iron as a metal sample. The holding time was from 6 min to 4 h, depending on the slag compositions and the temperatures. The experimental temperatures for soda-based fluxes was 1 250 and 1 350 °C. Those for CaF_2 -based and $\text{BaF}_2(\text{MgF}_2, \text{NaF})$ -based fluxes were 1 500 and 1 350 °C, respectively. The temperature dependence of phosphorus distribution ratio, L_P was studied by use of the $\text{CaF}_2\text{-CaO}$ and $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ fluxes. Equilibrium was approached mostly from metal side, *i.e.*, by adding an Fe-4.5% C-1% P alloy in the metal phase, but in some of the experiments for $\text{Na}_2\text{O-SiO}_2$ and fluoride-based fluxes, it was approached from slag side also, *i.e.*, by adding $\text{NH}_4\text{H}_2\text{PO}_4$, $3\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$, $3\text{CaO} \cdot \text{P}_2\text{O}_5$, $2\text{BaO} \cdot \text{P}_2\text{O}_5$ and $3\text{MgO} \cdot \text{P}_2\text{O}_5$. In the experiment using copper, the phosphorus equilibrium was approached both from metal side (initial content of 0.1 % P) and from slag side (initial content of 2 % P_2O_5). Materials used in this work were the same as those described elsewhere⁶⁾ except for NaF (99.0 %), CaF_2 and BaF_2 (Merck Suprapur) and MgF_2 (99.9 %). The method for analysis of the slag and metal compositions were the same as those described in detail elsewhere^{2,6)} except for fluorine, barium, total iron and phosphorus in the slags.

The fluorine content in the slag was analyzed by the ionic electrode method and/or the La-alizarin complexone absorptiometry (JIS-K-0101) after the

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alkali fusion of samples with SiO₂.^{9,10)} The content of Ba was determined by the BaSO₄ gravimetric method.¹⁰⁾ Since the analytical results for phosphorus and total iron in the slags were significantly influenced by the residual metallic iron in the slags after magnetic separation, the following methods were used. As to the samples with NaF or soda-based slags, the bromine methanol was used to remove the metallic iron in the residue after filtration by hot water, and phosphorus and total iron were determined by molybdenum blue absorptiometry (JIS-M-8216) and 1, 10-Phenanthroline absorptiometry (JIS-K-1200), respectively. After the removal of the metallic iron in the slags containing MgF₂, CaF₂ and BaF₂ by bromine methanol, the alkali fusion of the residue with SiO₂ was made. Then, total iron was determined by 1, 10-Phenanthroline absorptiometry (JIS-M-8850, R-2522, R-3101) or 2, 2'-Dipyridyl absorptiometry (JIS-K-1417). As to phosphorus, pH was controlled after the addition of FeCl₃ to the solution so as to obtain the precipitate.¹¹⁾ After dissolution of this precipitate, phosphorus was determined by molybdenum blue absorptiometry.

III. Results

The Na₂O-SiO₂-P₂O₅ (≤19 %), Na₂O-SiO₂-MO (M=Mg, Ca, Ba)-P₂O₅ (≤4 %) and Na₂O-SiO₂-

CaF₂ (≤19 %)-P₂O₅ (<2 %) systems are used as the soda-based fluxes, whereas the CaF₂-CaO-P₂O₅ (<70 ppm), BaF₂-BaO-P₂O₅ (≤2 %), MgF₂-MgO-P₂O₅ (<5 ppm), NaF-Na₂O-P₂O₅ (<0.02 %), CaF₂-BaO-P₂O₅ (<20 ppm), BaF₂-CaO-P₂O₅ (<0.02 %), CaF₂-MgO-P₂O₅ (<20 ppm) and CaF₂-CaO-Al₂O₃-P₂O₅ (<70 ppm) systems are used as the fluoride-based fluxes. The chemical compositions of the slags and the metals (P, Si, S) before and after the experiments in the soda-based fluxes are listed in Tables 1 to 3 and those after the experiments in the fluoride-based fluxes are summarized in Tables 4 and 5.

Figure 1 shows the results for L_P (= (%P)/[%P]) which was obtained in the Na₂O-SiO₂ system equilibrated with carbon-saturated iron melts at 1 250 and 1 350 °C. The values for L_P in the Na₂O·SiO₂-MO·SiO₂, 3Na₂O·2SiO₂-3MO·2SiO₂ (M=Mg, Ca, Ba) and 3Na₂O·2SiO₂-CaO (CaF₂) pseudo-binary systems at 1 250 °C are shown in Fig. 2. Figure 3 indicates the values for L_P in the NaF-Na₂O (1 350 °C), CaF₂-CaO (1 500 °C), BaF₂-BaO (1 350 °C) and MgF₂-MgO (1 350 °C, 1 500 °C) systems. The results for the reciprocal salt mixture: BaF₂-CaO (1 350 °C), CaF₂-BaO (1 500 °C) and CaF₂-MgO (1 500 °C) systems are shown in Fig. 4. The values for L_P in the CaF₂-CaO-Al₂O₃ system (1 430 °C~1 550 °C) are shown in Fig. 5.

Table 1. Experimental data for soda-based flux. (wt%)

Temp. (°C)	No.	Initial				Final							Time (min)
		P	(P ₂ O ₅)	(Na ₂ O)	(SiO ₂)	P	Si	(P ₂ O ₅)	(Na ₂ O)	(SiO ₂)	(Fe _t O)	(Al ₂ O ₃)	
1 250	91	1.10	—	26.1	73.89	1.04	0.086	0.0100	25.2	73.64	0.843	0.3	122
	92	1.10	—	41.2	58.79	0.964	0.022	0.0113	36.1	62.34	0.462	1.1	119
	93	1.10	—	50.8	49.23	0.916	0.005	0.435	47.9	50.51	0.410	0.7	38
	94	1.10	—	60.5	39.53	0.635	0.004	3.11	55.4	40.51	0.133	0.8	14
	95	0.005	1.90	27.4	70.66	0.189	0.071	0.111	27.6	70.86	0.895	0.5	117
	96	0.005	1.90	51.0	47.07	0.110	tr.	0.857	47.0	50.55	0.580	1.0	46
	97	0.005	1.79	60.5	37.74	0.0070	0.004	1.92	56.3	39.98	0.409	1.3	17
	130	1.10	—	24.2	75.78	1.01	0.175	0.0086	24.0	74.77	0.765	0.4	232
	131	1.10	—	41.2	58.79	0.958	0.040	0.0079	36.2	61.73	0.437	1.6	131
	132	0.552	0.48	50.3	49.24	0.467	tr.	0.559	48.2	50.01	0.418	0.8	28
	133	0.054	1.45	59.7	38.84	0.0084	tr.	1.96	55.3	40.76	0.447	1.6	24
	140	0.005	10.3	52.1	37.52	0.121	0.002	9.47	51.5	37.70	0.452	0.9	15
	141	0.005	19.2	53.6	27.28	0.115	tr.	18.1	53.1	27.56	0.276	0.9	10
	142	0.005	12.3	58.9	28.81	0.0242	tr.	12.2	55.9	30.44	0.301	1.2	13
143	0.005	19.9	57.8	22.34	0.0363	tr.	19.3	56.1	23.32	0.241	1.1	11	
1 350	147	1.10	—	24.2	75.78	0.989	0.373	0.0138	25.4	73.21	0.662	0.7	119
	148	1.10	—	41.2	58.79	0.957	0.065	0.0143	37.5	61.00	0.458	1.0	58
	149	0.552	—	50.2	49.79	0.458	0.005	0.162	48.1	50.55	0.427	0.8	15
	150	0.552	—	59.8	40.18	0.211	0.003	2.56	55.4	41.10	0.220	0.7	6
1 250	83	0.098	1.90	27.4	70.66	0.171	—	1.00	27.6	70.17	0.495	0.7	60
	84	0.098	1.79	41.5	56.68	0.168	—	1.09	39.9	57.97	0.169	0.9	61
	85	0.098	1.91	51.2	46.84	0.0585	—	2.25	48.6	47.81	0.098	1.2	30
	86	0.098	1.91	46.2	51.88	0.123	—	1.65	44.4	52.45	0.138	1.4	60
	87	0.098	1.91	46.2	51.88	0.104	—	1.79	45.4	51.90	0.146	0.8	25
	88	0.098	2.08	60.3	37.63	0.00142	—	2.96	56.3	39.08	0.073	1.6	20

Table 2. Experimental data for soda-based flux at 1 250 °C. (wt%)

No.	Initial				Final							
	P	(Na ₂ O)	(SiO ₂)	(CaO)	P	Si	(P ₂ O ₅)	(Na ₂ O)	(SiO ₂)	(Fe ₂ O)	(CaO)	(Al ₂ O ₃)
134	0.552	25.5	50.43	24.1	0.464	0.012	0.0222	25.4	50.66	0.219	21.3	2.4
135	0.552	33.4	50.39	16.2	0.463	0.006	0.0477	33.8	50.85	0.309	14.0	1.0
136	0.552	41.8	50.15	8.03	0.458	tr.	0.164	42.6	50.25	0.392	5.80	0.7
137	0.552	53.0	40.38	6.58	0.281	0.005	1.50	50.7	40.81	0.296	6.14	0.6
138	0.552	47.5	40.49	12.0	0.350	tr.	1.34	46.2	40.74	0.257	10.9	0.5
139	0.552	41.9	40.27	17.8	0.416	tr.	0.678	40.3	40.38	0.219	17.4	1.0
621	0.552	56.2	37.77	6.0	0.128	—	4.30	51.6	37.47	0.168	6.46	—
622	0.552	52.8	35.36	12.0	0.103	—	4.39	47.7	34.93	0.135	12.8	—
623	0.552	53.8	36.16	10.0	0.341	—	1.86	50.9	35.89	0.144	0.19	10.8
624	0.552	47.8	32.14	20.0	0.463	—	0.932	45.9	33.52	0.114	0.33	19.2

Table 4. Experimental data for lime-based flux.

Temp. (°C)	No.	P (%)	S (ppm)	P ₂ O ₅ (ppm)	S (%)	CaF ₂ (%)	CaO (%)	Al ₂ O ₃ (%)	Fe ₂ O (ppm)
1 430	706	0.547	—	8.9	—	99.3	0.66	—	41
	707	0.556	—	24.4	—	90.1	9.86	—	47
	708	0.578	—	68.3	—	82.2	17.8	—	82
	721	0.594	—	9.2	—	80.6	9.50	9.87	63
	722	0.544	—	11.4	—	71.2	17.5	11.2	80
	723	0.573	—	63.1	—	59.3	29.6	11.1	97
	724	0.590	—	9.7	—	59.0	18.5	22.5	97
	725	0.547	—	11.1	—	50.8	27.4	21.8	107
1 500	332	0.554	—	12.4	—	90.1	9.92	—	48
	333	0.533	—	44.8	—	79.7	20.3	—	126
	334	0.534	—	40.8	—	72.8	27.2	—	164
	401	0.529	20	16.9	1.78	—	44.0	54.1	1 770
	403	0.517	20	9.7	2.00	10.2	41.8	46.0	614
	404	0.505	12	6.2	1.78	19.8	37.5	40.9	280
	405	0.520	11	5.9	1.72	38.4	28.5	31.4	159
	651	0.548	—	5.9	—	98.9	1.09	—	37
	652	0.551	—	4.4	—	99.4	0.62	—	31
	653	0.562	—	15.0	—	90.5	9.50	—	48
	654	0.581	—	53.5	—	80.9	19.0	—	132
	655	0.573	—	43.7	—	72.9	27.1	—	118
	681	0.545	—	11.3	—	45.2	32.4	22.4	123
	682	0.566	—	7.8	—	57.6	19.4	23.0	104
	683	0.592	—	6.6	—	63.6	14.9	21.5	97
	684	0.572	—	3.0	—	70.2	9.74	20.1	70
	686	0.584	—	6.6	—	79.1	10.5	10.4	61
	687	0.568	—	9.0	—	70.9	18.5	10.6	75
1 550	701	0.547	—	2.2	—	97.8	2.16	—	39
	702	0.554	—	7.7	—	89.6	10.4	—	48
	703	0.537	—	29.2	—	70.9	29.1	—	167
	711	0.555	—	4.8	—	80.3	9.35	10.3	70
	712	0.582	—	6.6	—	71.2	17.8	11.0	82
	713	0.553	—	20.0	—	61.4	27.9	10.6	92
	714	0.560	—	4.8	—	59.8	18.3	21.8	116
	715	0.570	—	7.1	—	51.0	26.2	22.8	149

Table 3. Experimental data for soda-based flux at 1 250 °C. (wt%)

No.	Initial				Final							
	<u>P</u>	<u>S</u>	(Na ₂ O)	(SiO ₂)	<u>P</u>	<u>S</u>	(P ₂ O ₅)	(S)	(Na ₂ O)	(SiO ₂)	(Fe _t O)	(Al ₂ O ₃)
321	0.552	0.499	50.8	49.23	0.467	0.0097	0.491	1.76	47.4	48.40	1.27	0.7
322	0.545	0.985	60.5	39.53	0.270	0.0031	2.26	3.29	54.7	38.18	0.872	0.7
				(BaO)								(BaO)
301	0.552	0.499	42.7	46.58	0.486	0.0138	0.315	1.75	41.6	44.90	1.30	0.8 9.38
302	0.552	0.499	35.1	43.36	0.497	0.0179	0.191	1.76	34.2	42.51	1.19	0.7 19.41
303	0.552	0.499	27.6	40.14	0.538	0.0213	0.105	1.77	27.8	39.17	0.953	0.9 29.35
306	0.545	0.985	54.5	37.59	0.383	0.0040	1.93	4.53	47.2	35.08	1.24	0.6 9.43
307	0.545	0.985	48.5	35.65	0.403	0.0049	1.44	3.94	42.6	34.70	1.03	0.5 15.84
308	0.545	0.985	42.4	33.83	0.414	0.0056	1.39	3.41	39.5	33.29	0.822	0.6 21.00
				(MgO)								(MgO)
311	0.552	0.499	42.7	51.33	0.510	0.0166	0.110	1.69	42.1	48.93	0.818	0.4 5.93
312	0.552	0.499	35.1	52.86	0.569	0.0290	0.0435	1.62	34.9	50.70	0.546	0.6 11.62
313	0.552	0.499	27.6	54.27	0.572	0.0647	0.0321	1.40	28.8	51.75	0.466	0.3 17.25
316	0.545	0.985	54.5	40.46	0.365	0.0047	1.38	3.22	49.5	39.09	0.896	0.4 5.54
317	0.545	0.985	48.5	41.52	0.426	0.0078	0.748	3.49	46.0	40.34	1.10	0.6 7.71
318	0.545	0.985	42.4	42.58	0.480	0.0164	0.329	3.66	42.3	44.26	2.14	0.6 6.68

Table 5. Experimental data for fluoride-based flux.

No.	Temp. (°C)	<u>P</u> (%)	P ₂ O ₅ (ppm)	BaF ₂ (%)	BaO (%)	Fe _t O (ppm)
386	1 350	0.519	62.8	94.9	5.1	78
387	1 350	0.468	2.01×10 ³	86.8	13.0	118
388	1 350	0.295	1.96×10 ⁴	72.9	25.0	187
389	1 350	0.251	1.52×10 ⁴	76.2	22.3	153
660	1 350	0.503	8.2	100.0	—	58
661	1 350	0.548	8.8	99.5	0.5	65
662	1 350	0.538	7.2	100.0	—	60
663	1 350	0.709	500	90.9	9.0	90
664	1 350	0.368	1.98×10 ³	82.3	17.5	135
				(MgF ₂)	(MgO)	
372	1 500	0.527	2.3	92.9	7.1	74
666	1 350	0.617	1.5	98.6	1.4	61
667	1 350	0.523	1.2	99.3	0.68	56
668	1 350	0.531	4.5	93.8	6.2	85
				(NaF)	(Na ₂ O)	
671	1 350	0.547	112	98.0	2.0	568
672	1 350	0.535	22.4	99.4	0.6	430
				(CaF ₂)	(BaO)	(CaO)
351	1 500	0.494	8.2	89.8	9.9	32 0.3
352	1 500	0.565	13.3	79.8	19.6	37 0.7
353	1 500	0.541	14.7	71.6	28.4	41 —
				(CaF ₂)	(MgO)	(CaO)
361	1 500	0.533	8.2	89.3	10.5	56 0.2
362	1 500	0.550	12.9	78.6	21.0	170 0.4
363	1 500	0.545	15.3	69.2	30.5	273 0.3
				(BaF ₂)	(CaO)	(BaO)
396	1 350	0.512	73.6	92.0	8.0	140 —
397	1 350	0.493	159	83.4	16.6	166 —

Fig. 1. Logarithms of $L_P(C_P)$ in the Na₂O–SiO₂ system at 1 250 and 1 350 °C.

Fig. 2. Logarithms of $L_P(C_P)$ in the 3Na₂O·2SiO₂–3MO·2SiO₂ and Na₂O·SiO₂–MO·SiO₂ (M=Mg, Ca, Ba) pseudo-binary systems at 1 250 °C.

Fig. 3. Logarithms of $L_P(C_P)$ in the $MF_2(MF)-MO(M_2O)$ ($M=Na, Ba, Ca, Mg$) system.

Fig. 4. Logarithms of $L_P(C_P)$ in the BaF_2-CaO , CaF_2-BaO and CaF_2-MgO systems.

IV. Discussion

1. Phosphorus Equilibrium between Slag and Metal

Slag-metal equilibria concerning phosphorus can be expressed in terms of molecular and ionic forms as follows;

where the equilibrium constants for Eqs. (1) and (2) are now represented by K_P and K_{ion} , respectively.

$$K_P = N_{PO_{2.5}} \cdot \gamma_{PO_{2.5}} / [a_P \cdot a_O^{5/2}] \dots\dots\dots(3)$$

$$K_{ion} = a_{PO_4^{3-}} / [a_P \cdot a_O^{5/2} \cdot a_{O^{2-}}^3] \dots\dots\dots(4)$$

From Eqs. (3) and (4), we obtain

$$(\%P) / [a_P \cdot a_O^{5/2}] = K_P / \gamma_{PO_{2.5}} \times (\%P) / N_{PO_{2.5}} \dots\dots\dots(5)$$

$$(\%P) / [a_P \cdot a_O^{5/2}] = K_{ion} / \gamma_{PO_4^{3-}} \times (\%P) / N_{PO_4^{3-}} \dots\dots\dots(6)$$

where $N_{PO_4^{3-}}$ denotes the anionic fraction of PO_4^{3-} ion and a_i , γ_i and N_i represent their usual meanings.

It should be noted that the activities, and the activity coefficients of ionic species as well as the equilibrium constant, K_{ion} cannot be experimentally determined and cannot be calculated without nonthermodynamic assumptions. The left hand side of Eq. (5) or Eq. (6) is now defined by phosphate capacity, C_P . Provided that the terms $(\%P) / N_{PO_{2.5}}$ and $(\%P) / N_{PO_4^{3-}}$ in Eqs. (5) and (6) are independent of slag compositions at a constant temperature, the phosphate capacity is inversely proportional to the activity coefficients of $PO_{2.5}(PO_4^{3-})$. The following relation-ship concerning C_P , L_P and a_O can be obtained as

$$L_P = C_P \cdot a_O^{5/2} \cdot f_P \dots\dots\dots(7)$$

where f_P denotes the activity coefficient of phosphorus in metal which can be obtained in the present work from the values for $e_P^{(P)}=0.062$,¹²⁾ $e_P^{(O)}=0.13$,¹³⁾ $e_P^{(S)}=0.028$ ¹²⁾ and $e_P^{(Si)}=0.12$ ¹²⁾ as well as the value¹⁴⁾ for $[\%C]_{sat.}=1.30+2.57 \times 10^{-3} \cdot T(^{\circ}C)-0.33$ [%P]-0.36 [%S]-0.317 [%Si]. In this work, the second order interaction coefficient ($r_P^{(O)}$)¹³⁾ has not been used for

Fig. 5. Logarithms of L_P in the $CaF_2-CaO-Al_2O_3$ system at 1430, 1500 and 1550 °C.

the calculation of f_P , although its effect on $\log C_P$ is about 0.3 at maximum. The value of a_O under the present experimental conditions, *i.e.*, $a_C=1, P_{CO}=1$ atm can be obtained from the standard free-energy change ΔG° for the reaction:

The values of C_P obtain by substituting the value of a_O at corresponding temperatures into Eq. (7) are also shown in Figs. 1 to 4. The value for C_P which is the experimentally obtainable quantity is not only a function of slag compositions and temperatures, but also is the value only limited to a liquid iron-slag system. The value of $C_{PO_4^{3-}}$ ($=\%(\text{PO}_4^{3-})/[P_2^{1/2} \cdot P_{O_2}^{5/4}]$) defined by Wagner¹⁶⁾ is only a function of slag compositions at a given temperature. The present authors, however, recommend to use C_P rather than $C_{PO_4^{3-}}$, since it is more convenient to use C_P rather than $C_{PO_4^{3-}}$, when compared with the plant data.⁵⁾ By use of the free-energy change for the following reactions, the relation between C_P and $C_{PO_4^{3-}}$ is calculated and given by Eq. (11).

$\log C_P = \log C_{PO_4^{3-}} - 21\,680/T - 1.87$ .....

(11)

2. Phosphate Capacity C_P in Soda- and Lime-based Fluxes
1. Soda-based Fluxes

As shown in Fig. 1, the values for L_P in the $\text{Na}_2\text{O-SiO}_2$ slags obtained by approaching the phosphorus equilibrium from the slag side are greater than those from the metal side. This trend is not observed in the $\text{CaF}_2\text{-CaO}$ system shown in Fig. 3, but observed only in the $\text{Na}_2\text{O-SiO}_2$ system. It was found in the $\text{Na}_2\text{O-SiO}_2$ slags that the sulfur⁶⁾ and manganese¹⁷⁾ distribution ratios approached from the metal side agreed well with those from the slag side. The results⁷⁾ for C_S obtained from the sulfur distribution ratios between the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3$ slags and carbon-saturated iron melts at 1 500 °C are in good agreement with those from the gas-slag equilibrium experiments.⁸⁾ Smith and Davies¹⁸⁾ obtained the activity coefficient of MnO from the manganese distribution equilibrium between the $\text{CaF}_2\text{-CaO}$ slags and a solid Pt. The manganous capacity, C_{Mn} ($=\%(\text{Mn})/[a_{Mn} \cdot a_O]$) calculated from their results was found to be in agreement with that obtained from the manganese distribution equilibrium between the $\text{CaF}_2\text{-CaO}$ slags and carbon-saturated iron melts.¹⁷⁾ These experimental findings thus suggest that the oxygen potentials in the experiments of sulfur and manganese partitions are undoubtedly controlled by the $\text{C}(a_C=1)\text{-CO}(P_{CO}=1\text{ atm})$ equilibrium. It can be seen from Fig. 1 that no apparent difference between L_P obtained at 1 250 °C and that at 1 350 °C was observed.

As listed in Table 1, the phosphorus content in the

carbon-saturated copper melts equilibrated with the $\text{Na}_2\text{O-SiO}_2$ fluxes is less than 0.2 wt% and the carbon content is also extremely low (<10 ppm). The activity of phosphorus in the carbon-saturated copper melt, $a_{P\text{ in Cu}}$ therefore is considered to be equal to the phosphorus content [%P]. The activities of Cu in the Cu-P alloy were calculated at 1 200 °C by Kramss¹⁹⁾ from the phase diagram of the Cu-P system by assuming the regular solution. By use of the Gibbs-Duhem relationship, the activity coefficient of phosphorus with respect to the Raoultian standard state, γ_P° was obtained as 0.025. From this value and the regular solution approximation, the free-energy change for the following reaction was derived as

It can be seen from Eqs. (9) and (12) that the activity of phosphorus in iron is 91 times as high as that in copper at 1 250 °C. The values for C_P obtained in the copper melts were converted to those for C_P in the carbon-saturated iron melts by use of the above relation. These results are given in Fig. 6, indicating the comparatively good agreement with those obtained in the carbon-saturated iron melts.

From the results on the phosphorus equilibrium between the $\text{Na}_2\text{O-SiO}_2\text{-PO}_{2.5}\text{-Fe}_t\text{O}$ slags and an iron foil at 1 300 °C, Ito and Sano²⁰⁾ obtained the phosphorus partitions with respect to a carbon-saturated iron melt by calculation and the dependence of the $C_{PO_4^{3-}}$ value on slag compositions is given by use of the activities of Fe_tO ²¹⁾ in $\text{Na}_2\text{O-SiO}_2\text{-PO}_{2.5}\text{-Fe}_t\text{O-Na}_2\text{CO}_3$ system. The contents of $\text{PO}_{2.5}$ and Fe_tO in their slags were in the range of 3~44 wt% and 2~33 wt%, respectively. Although these values are higher than those in the present work ($\text{Fe}_t\text{O wt}\% \leq 1.3$), the values for C_P in their slags containing $\text{Fe}_t\text{O wt}\% = 2 \sim 6$ ($N_{\text{Fe}_t\text{O}} = 0.01 \sim 0.04$) and $\text{Fe}_t\text{O wt}\% = 10 \sim 14$ ($N_{\text{Fe}_t\text{O}} = 0.09 \sim 0.12$) were calculated by use

Fig. 6. Comparison of the present value for $\log C_P$ with the previous results.²⁰⁾

of Eq. (11). The results are shown in Fig. 6 by a dotted line for comparison. One may see that their results tend to approach the present results with a decrease of the Fe_2O content.

It is seen from Fig. 2 that when Na_2O is replaced by MgO (CaO , BaO) at a constant SiO_2 content in the Na_2O – SiO_2 – MgO (CaO , BaO) ternary system, $\log C_P$ gradually decreases in the order of $\text{Ba} > \text{Ca} > \text{Mg}$. The fact that the replacement of Na_2O by BaO lowers the value of C_P indicates that $\log C_P$ in the pure liquid Na_2O is greater than that in the pure BaO .

The activity coefficients of P_2O_5 in the Na_2O – P_2O_5 system were calculated by using the Gibbs–Duhem equation from the activity coefficients of Na_2O which were determined in the previous report.⁶⁾ The values for $\log C_P$ were obtained from the activity coefficients of P_2O_5 and are shown in Fig. 7. The details of this derivation of $\log C_P$ from $\gamma_{\text{P}_2\text{O}_5}$ are described elsewhere.⁴⁾ The phosphorus distribution ratios between the carbon-saturated iron melts and the Na_2O – SiO_2 slags containing 9–19 wt% P_2O_5 was studied by approaching the phosphorus equilibrium from the slag side. These results given in Table 1 (Nos. 140–143) and Fig. 1 are also shown in Figs. 6 and 7. As pointed out previously it appears that these values for C_P are considerably higher than those obtained by approaching the phosphorus equilibrium from the metal side.

Recently, Tsukihashi *et al.*²²⁾ obtained the phosphorus distribution ratios between the Na_2O (40–65 %)- SiO_2 – P_2O_5 (5–25 %) slags and carbon-saturated iron melts at 1 200 °C. Their results are also shown in Fig. 7, indicating an agreement with those obtained in the present work. Judging from the values for $\log C_P$ in the Na_2O – P_2O_5 system indicated in Fig. 7, the values for $\log C_P$ in the Na_2O – SiO_2 – P_2O_5 system appear to be unreasonably too high, since these values are obtained by approaching the phosphorus equilibrium from the slag side.

Fig. 7. Logarithms of C_P in the Na_2O – SiO_2 – P_2O_5 system at 1 250 °C.

2. Lime-based Fluxes

It can be seen from Fig. 3 that the values for $\log C_P$ in the fluoride-oxide system with common cations decrease in the order of $\text{Na} > \text{Ba} > \text{Ca} > \text{Mg}$. The chemical analysis for the pure fluorides indicated that the significant amount of oxide ($N_{\text{Na}_2\text{O}}=0.014$, $N_{\text{BaO}}=0.006$, $N_{\text{CaO}}=0.03$, $N_{\text{MgO}}=0.022$) was observed, although the CO as well as Ar gas used for purging was dried by P_2O_5 before the introduction into the furnace. The compositions in the saturation limit for the system CaF_2 – CaO ($N_{\text{CaO}}=0.26$, $\text{CaO wt}\%=20$ at 1 500 °C)⁸⁾ and MgF_2 – MgO system ($N_{\text{MgO}}=0.10$, $\text{MgO wt}\%=7$ at 1 350 °C)²³⁾ are indicated in Fig. 3 by the arrows. The maximum values for the logarithms of C_P in the liquid region of the CaF_2 – CaO system at 1 500 °C are roughly equal to those in the composition with the $\text{Na}_2\text{O}/\text{SiO}_2=1/2$ (wt% ratio). On the other hand, $\log C_S$ in the liquid region of the CaF_2 – CaO system⁸⁾ at 1 500 °C are considerably higher than those in the Na_2O – SiO_2 system⁶⁾ at 1 250 °C.

It is apparent from Fig. 2 that the values for $\log C_P$ increase or decrease with the addition of CaO or CaF_2 to the melt with the $3\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ composition, respectively. The increase in $\log C_P$ with the addition of CaO can be explained by the difference between the values for $\log C_P$ at the $3\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ composition and that in the pure liquid CaO .⁴⁾ Similarly, the decrease in $\log C_P$ with the addition of CaF_2 can also be explained by the difference between the value of $\log C_P$ at the $3\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ composition and that in the pure liquid CaF_2 at 1 500 °C. The logarithms of C_P are expected to increase as a result of the increase in oxygen ion followed by the fluorination reaction: $(\text{Si}-\text{O}-\text{Si})+2\text{F}^-=2(\text{Si}-\text{F})+\text{O}^{2-}$, if fluoride such as CaF_2 is added to the silicate melt with acidic compositions. This is confirmed by Bronson and St. Pierre²⁴⁾ in the experiment of the sulfide capacity measurement at 1 503 °C; that is, $\log C_S$ was observed to increase with the addition of CaF_2 (up to 10 wt%) to the CaO – SiO_2 slags with the CaO/SiO_2 (wt%)=1~1.28. Actually, however, as the present slag composition ($3\text{Na}_2\text{O}\cdot 2\text{SiO}_2$) is basic, no increase in $\log C_P$ was observed with the addition of CaF_2 .

The effect of Na_2O or CaF_2 on $\log C_P$ on mole fraction basis has been studied. The results are shown in Fig. 8, where the CaO equivalencies of Na_2O on the mole fraction basis obtained from the data on phosphorus partitions between MgO -saturated CaO – SiO_2 – Fe_2O – Na_2O (7–13 %) slags and liquid iron are indicated by the hatched area. The CaO -equivalencies of Na_2O on the mole fraction basis obtained in the experiment for the phosphorus distribution between Na_2O – SiO_2 – CaO slags and carbon-saturated liquid iron melts are shown by the open triangles. The CaO -equivalencies of Na_2O are independent of the Na_2O content and considered to be 1.4, although the considerable scatter in the data points was observed. It was found in the previous experiment³⁾ for the MgO -saturated slags containing CaF_2 wt% ≤ 4 , that the CaO -equivalency of CaF_2 was about 0.9,⁴⁾ but in the present experiment of the slags with the high CaF_2 content, the CaO -equivalency of CaF_2 was

Fig. 8. Effect of Na₂O or CaF₂ on log C_P—CaO-equivalencies of Na₂O or CaF₂.

found to decrease with an increase in the CaF₂ content and found to be 0.6 at the pure CaF₂ although with the considerable scatter.

The exchange reactions of fluorides with oxides of difference cations are given as follows:

It can be seen from Figs. 3 and 4 that the values for log C_P in the BaF₂–CaO system are smaller than those in the BaF₂–BaO system and those in the CaF₂–MgO system are also smaller than those in the CaF₂–CaO system. The reasons for this can be explained by the facts that the exchange reactions given by Eqs. (13) and (14) do not occur and that the values for log C_P in the pure oxides decrease in the order of BaO>CaO>MgO.⁴⁾ The fact that the values for log C_P in the CaF₂–BaO system are smaller than those in the CaF₂–CaO system cannot be explained by the difference in the log C_P for the pure oxides. The experimental points of the slag compositions in the CaF₂–BaO system were recalculated from Eq. (13) on the assumption that one mole of CaO was formed from one mole of BaO; that is, about 4 wt% CaO was formed from 10 wt% BaO on the weight percent basis. The values for log C_P plotted against the recalculated slag compositions were found to be in good agreement with those obtained in the CaF₂–CaO system.

Tabuchi and Sano²⁷⁾ have studied the phosphorus distribution between carbon-saturated Ag melts and the CaF₂–CaO slags at 1500 °C under the P_{CO}=0.5 atm (P_{O₂}=4.56×10⁻¹⁷ atm) atmosphere. Their results confirm the existence of P³⁻ ion in addition to P⁵⁺ ion, whose content is about one-fourth of P⁵⁺ ion.

Fig. 9. Comparison with the previous results²⁷⁾ of the present value for log C_P in the CaF₂–CaO system.

Fig. 10. Temperature dependence of log L_P in the CaF₂–CaO and CaF₂–CaO–Al₂O₃ systems.

The values for log C_P calculated from their phosphate content are also shown in Fig. 9, indicating the close agreement with the present results, although their results for log C_P are slightly higher than those in this work.

3. Temperature Dependence of Phosphorus Distribution Ratios

It is often observed in the practical operation that the phosphorus distribution ratios are dependent on the temperature to a considerable degree. Only a few laboratory data on the temperature dependence of L_P have been reported so far. Figure 10 shows the results for the phosphorus distribution ratios between the CaF₂–CaO slags and carbon-saturated iron melts at three different temperatures of 1 430, 1 500 and 1 550 °C. The results for the CaF₂–CaO–Al₂O₃ slags are also shown in Fig. 10. It is seen from Fig. 10 that the temperature dependence of L_P observed in the CaF₂–CaO slag is greater than that observed in the CaF₂–CaO–Al₂O₃ slag.

From the results of the phosphorus distribution between 57% Na₂O–24% SiO₂–18% PO_{2.5}–1% Fe₂O₃ slags and carbon-saturated iron melts, Tsukihashi *et al.*²²⁾ reported the temperature dependence of the phosphorus distribution ratios as log (%P)/[%P]=21 500/T–11.73 (1 200~1 300 °C). As shown in

Fig. 11. Temperature dependence of $\log L_p$ observed in the fluxes for hot metal pretreatment and liquid steel refining.

Fig. 1, no temperature dependence of L_p was observed in the present Na_2O - SiO_2 slags. The previous results for the temperature dependence of L_p in the BOF type slags and the slags in a hot metal pretreatment are summarized in Fig. 11, indicating that the temperature dependence of L_p varies with the slag compositions. In order to obtain the accurate results for the variation of L_p with the slag compositions, further works are necessary.

V. Summary

The results of the phosphorus distribution between the soda- and lime-based fluxes and carbon-saturated iron melts are summarized as follows;

(1) When Na_2O is replaced by MgO , CaO or BaO at a given SiO_2 content in the Na_2O - SiO_2 - MO ($\text{M}=\text{Mg}$, Ca , Ba) ternary system, the phosphorus distribution ratios were found to decrease. The ratios increase with the addition of CaO to the $3\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ composition, while they decrease with the addition of CaF_2 .

(2) The phosphorus distribution ratios in the $\text{MF}_2(\text{MF})\text{-MO}(\text{M}_2\text{O})$ ($\text{M}=\text{Na}$, Ba , Ca , Mg) system decrease in the order of $\text{Na} > \text{Ba} > \text{Ca} > \text{Mg}$.

(3) In the Na_2O - SiO_2 system the phosphorus distribution ratios at 1 250 and 1 350 °C were nearly equal to each other, but in the CaF_2 - CaO (- Al_2O_3) system, they decrease with an increase in the temperature from 1 430 to 1 550 °C. Their temperature dependence in the CaF_2 - CaO system was found to be greater than those in the CaF_2 - CaO - Al_2O_3 system.

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