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THE TREATMENT OF HOT-METAL BY USING CaF_2 CONTAINING LIME-BASED SLAGS

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Synopsis: Sulphur and phosphorus partitioning experiments were performed at 1350°C in graphite crucibles containing carbon-saturated iron and $CaO-SiO_2-Na_2O-CaF_2$ slags. CaF_2 decreases the sulphide capacity of Na_2O containing lime-based slags, as well as the phosphate capacity by lowering the activity coefficient of P_2O_5. Although CaF_2 exerts a negative thermodynamic influence with regard to sulphur and phosphorus removal, these slags possess sufficiently high sulphide and phosphate capacities, as well as low melting points, so that they can be utilized for hot-metal treatment at relatively low temperatures. Only enough CaF_2 should be added to ensure that the slags remain liquid during treatment. Industrial dephosphorization and desulphurization trials were performed successfully utilizing Corex hot-metal and the slags evaluated in this study .

Key Words: desulphurization, dephosphorization, hot-metal, lime-based slags, contribution of CaF_2

1 Introduction

Utilization of lime-based slags provides an inexpensive and efficient manner for the dephosphorization and desulphurization of hot-metal. The ability of lime-based slags to desulphurize and dephosphorize liquid iron can be enhanced [1-7] significantly by small additions of basic oxides such as Na_2O. Furthermore, in order to utilize lime-based slags at relatively low hot-metal temperatures, additions of fluxes such as fluorspar (CaF_2) are required to ensure that the slag remain fluid. It is generally believed that CaF_2 additions do not favour desulphurization from a thermodynamic point of view [8,9], but that dephosphorization [9-12] is enhanced significantly. Turkdogan and Pearson [10] proposed the following empirical relationship between the activity coefficient of P_2O_5, the composition of the slag and the temperature:

$$\log \gamma_{P_2O_5} = -1.12(22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} + 31N_F - 2N_{SiO_2}) - \frac{42000}{T} + 23.58 \quad (1)$$

Additions of CaF_2 (shown as N_F) decreases γP_2O_5 significantly and consequently enhances the thermodynamics of dephosphorization. Tagaya *et. al.* [12] have recently shown that the addition of CaF_2 to dephosphorizing slags stabilizes the compound $3CaO.P_2O_5$ due to the strong interaction between CaF_2 and $3CaO.P_2O_5$, thereby improving dephosphorization.

Although the effect of CaF_2 on the refining capabilities of lime-based slags have been examined extensively [8-12], there is a dearth of thermodynamic data on the ability of slags containing both CaF_2 and Na_2O, to refine hot-metal. Slags in this system are considered for the treatment of Corex hot-metal, which is low in silicon (<0.3%) [13]. Consequently, the purpose of the present study was to determine experimentally the phosphate and sulphide capacities of certain slags in the $CaO-SiO_2-Na_2O-CaF_2$ system.

2 Theoretical considerations

The desulphurization reaction in hot-metal may be represented by:

$$\tfrac{1}{2}S_2(g) + [\underline{O}]_{Fe-C} = \tfrac{1}{2}O_2(g) + [\underline{S}]_{Fe-C} \qquad (2)$$

$$\Delta G^\circ = -17908 + 26.32T\ (J/mol)\ [14] \qquad (2a)$$

where $[\underline{O}]_{Fe-C}$ and $[\underline{S}]_{Fe-C}$ refer respectively to oxygen and sulphur dissolved in carbon containing iron (1 wt per cent standard state). The sulphide capacity is given by:

$$\log C_S = \log \frac{(\%S)}{[\%S]} + \log a_{\underline{O}} + \log K_2 - \log f_S \qquad (3)$$

with $a_{\underline{O}}$ the activity of oxygen dissolved in the metal, K_2 the equilibrium constant for reaction (2) and f_S the Henrian activity coefficient of sulphur dissolved in the metal.

The equilibrium phosphorus distribution between liquid iron and slag can be formulated as follows:

$$\frac{1}{2}P_2(g) + \frac{5}{4}O_2(g) + \frac{3}{2}O^{2-}(slag) = PO_4^{3-}(slag) \qquad (4)$$

The phosphate capacity ($C_{PO_4^{3-}}$) can be expressed as:

$$\log C_{PO_4^{3-}} = \log L_P + \log \frac{(MM_{PO_4^{3-}})}{MM_P} - \log f_P - \log a_{\underline{O}}^{5/2} + \log K \qquad (5)$$

with L_P the equilibrium phosphorus distribution coefficient, ($MM_{PO_4^{3-}}/MM_P$) the ratio of the molar masses of phosphate and phosphorus, f_P the activity coefficient of phosphorus in liquid iron (1 wt per cent standard state) and K is the combined equilibrium constant for the behaviour at infinite dilution of P_2 and O_2 in liquid iron.

3 Experimental

The experimental apparatus and method have been described previously [15]. Briefly, slag (2g) and carbon-saturated iron (4g) were equilibrated in graphite crucibles in a silicon-carbide resistance-heated tube furnace at 1350 °C under a carbon monoxide atmosphere (1 atm). The temperature was controlled by a Pt/Pt-10%Rh thermocouple at 1350 ±4 °C. At the end of each experimental run the crucible was quenched in a stream of argon gas. The slag and metal phases were crushed and analysed chemically.

4 Results and discussion

It was shown previously [16] that it can not necessarily be assumed that the activity of carbon is unity when an Fe-C alloy is contained in a graphite crucible under a Na_2O-containing slag. The actual carbon activity in the melt must be calculated before the prevailing oxygen activity, as well as the sulphide and phosphate capacities, can be determined by the use of equations (3) and (5). Such a procedure was followed in this study. The sulphur and phosphorus distributions between carbon-saturated iron and CaO-SiO_2-Na_2O-CaF_2 slags, are summarized in Tables 1 and 2.

Table 1 Experimental results for the desulphurization trials

Exp	Na_2O	SiO_2	CaO	CaF_2	(S)	[S]	Exp	Na_2O	SiO_2	CaO	CaF_2	(S)	[S]
1	17.4	33.7	40.3	8.6	0.36	.003	**23**	8.9	31.6	42.2	17.4	1.77	.026
2	17.3	33.7	40.4	8.6	0.42	.0031	**24**	8.6	32.0	42.0	17.4	1.12	.020
3	16.5	33.6	40.3	9.6	1.68	.011	**25**	5.8	28.7	38.9	26.6	0.46	.010
4	16.3	33.9	40.2	9.6	1.35	.0119	**26**	5.9	28.5	39.1	26.5	0.36	.0076
5	15.5	29.5	36.8	18.2	0.35	.002	**27**	8.3	27.9	39.3	24.6	1.92	.034
6	15.6	29.4	36.8	18.2	0.37	.0019	**28**	8.3	27.4	39.7	24.6	1.71	.024
7	15.6	29.4	37.3	17.7	1.83	.012	**29**	5.2	24.3	36.3	34.1	0.50	.009
8	15.5	29.3	37.4	17.8	1.42	.009	**30**	5.0	25.1	35.8	34.1	0.35	.0079
9	14.4	26.1	33.4	26.1	0.34	.001	**31**	8.1	24.0	37.0	30.9	1.69	.021
10	14.4	26.3	33.3	26.1	0.35	.0024	**32**	16.7	36.5	38.0	8.8	0.42	.0073
11	14.7	25.8	32.8	26.7	1.82	.001	**33**	17.0	36.8	37.9	8.3	2.43	.042
12	15.0	25.4	33.2	26.4	1.68	.0083	**34**	15.2	36.5	38.4	9.9	2.12	.031
13	12.7	22.3	30.5	34.6	0.36	.003	**35**	13.0	31.8	37.5	17.7	0.38	.003
14	12.6	21.9	31.2	34.3	0.45	.0031	**36**	13.0	32.1	37.1	17.8	0.28	.0040
15	14.1	21.8	30.5	33.6	1.80	.004	**37**	13.0	32.2	36.5	18.4	2.20	.049
16	14.0	21.8	30.5	33.7	1.79	.0079	**38**	13.1	31.7	37.8	17.5	1.52	.013
17	6.9	35.9	46.9	10.4	0.50	.012	**39**	11.8	27.6	34.0	26.6	0.40	.004
18	7.0	35.7	47.0	10.4	0.40	.0081	**40**	11.7	28.0	33.6	26.8	0.33	.0047
19	9.2	34.9	45.9	10.1	1.89	.033	**41**	12.5	27.9	32.7	26.9	2.04	.028
20	9.1	35.2	45.7	10.1	1.39	.032	**42**	12.3	28.4	32.5	26.8	1.63	.034
21	6.6	33.3	42.6	17.5	0.50	.008	**43**	9.2	24.4	29.1	37.3	0.36	.0055
22	6.8	33.3	42.1	17.8	0.38	.0075	**44**	9.5	23.9	31.5	35.1	2.08	.017

Table 2 Experimental results for the dephosphorization trials

Exp.	Na_2O	SiO_2	CaO	CaF_2	(P)	[P]	Exp	Na_2O	SiO_2	CaO	CaF_2	(P)	[P]
1	16.0	36.0	34.7	8.9	0.27	0.12	**13**	6.5	33.4	39.2	20.2	0.02	0.19
2	15.6	35.7	38.2	8.4	0.46	0.13	**14**	6.6	33.2	40.0	18.9	0.02	0.32
3	14.6	33.4	36.7	13.7	0.22	0.17	**15**	5.2	25.8	35.1	32.6	0.02	0.25
4	15.0	32.9	36.5	13.5	0.40	0.14	**16**	11.3	37.6	40.2	9.5	0.15	0.22
5	14.8	31.2	33.8	17.9	0.20	0.12	**17**	11.3	37.3	39.8	9.1	0.15	0.26
6	14.7	30.3	34.0	19.5	0.37	0.12	**18**	10.2	35.0	38.2	14.8	0.13	0.17
7	12.3	22.7	30.0	34.1	0.14	0.14	**19**	10.2	34.6	38.4	15.0	0.19	0.18
8	11.8	22.8	30.0	34.2	0.29	0.15	**20**	8.2	31.5	38.0	21.1	0.03	0.18
9	7.6	38.5	43.5	9.6	0.03	0.18	**21**	8.4	31.2	37.6	20.8	0.17	0.17
10	7.4	38.8	40.1	9.7	0.06	0.29	**22**	8.0	24.2	30.3	36.8	0.02	0.24
11	7.0	36.1	44.3	14.7	0.04	0.11	**23**	8.9	23.9	28.1	37.2	0.12	0.25
12	6.9	36.1	41.4	14.3	0.05	0.24							

Desulphurization:

The relative contributions of CaF_2 and basicity to desulphurization were separated by the construction of a nomogram shown in Fig. 1. In this nomogram the CaF_2 content is represented by the fluorine ratio ($\%CaF_2/[\%CaO + \%CaF_2]$) and optical basicity is used as a measure of the basicity. However, following Duffy [17], CaF_2 was excluded in the calculation of the optical basicity. Fig. 1 clearly shows that the sulphide capacity of the slags under investigation increases with an increase in basicity, but decrease when CaF_2 is added to the slag.

Although additions of CaF_2 do not enhance desulphurization from a thermodynamic point of view, the sulphide capacities are high enough to ensure efficient sulphur removal from hot-metal.

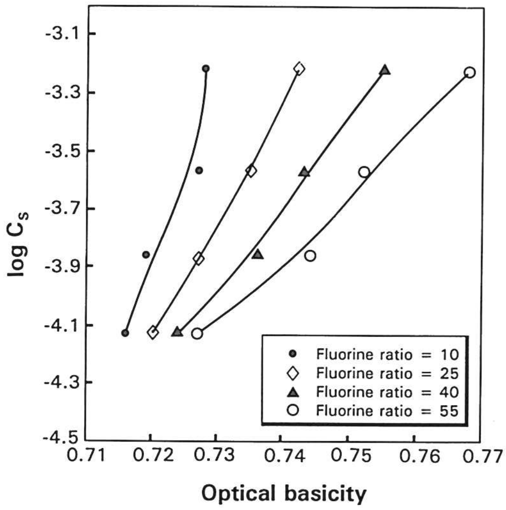

Fig. 1 Sulphide capacities of CaO-Na_2O-SiO_2-CaF_2 slags at 1350°C.

Dephosphorization:

The effects of the fluorine ratio and optical basicity on the phosphorus partition ratio and phosphate capacity respectively, are illustrated in Fig. 2a and b.

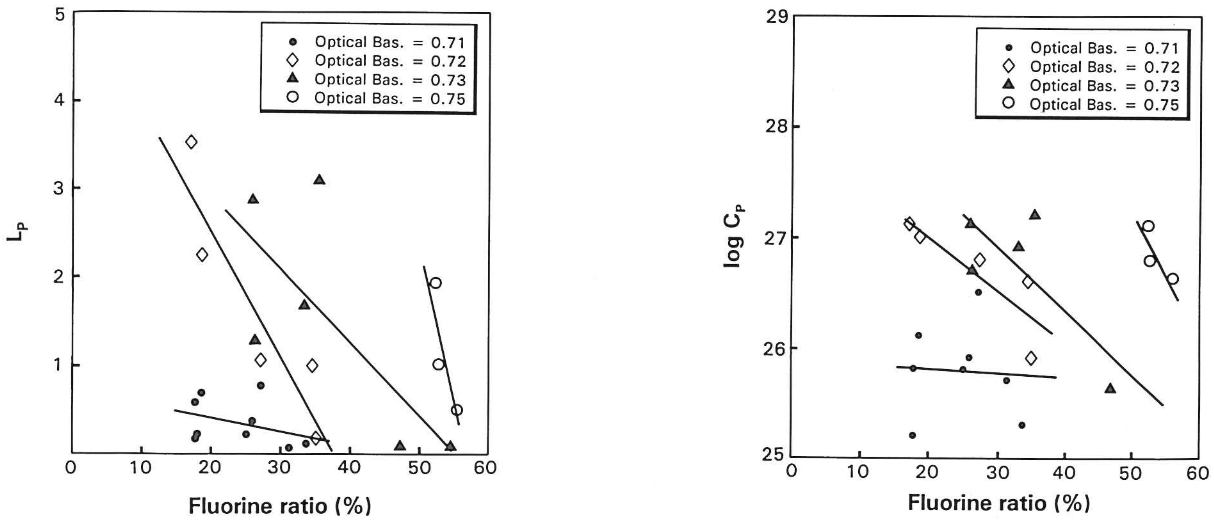

Fig. 2 Influence of optical basicity and fluorine ratio on (a) the phosphorus partition ratio and, (b) phosphate capacities of lime-based slags at 1350 °C.

It follows from Fig. 2 that CaF_2 decreases the partition ratio and phosphate capacity of these slags. For example: The logarithm of the phosphate capacity of a slag with an optical basicity of 0.73 decreases from 28 to 26.5 with an increase in fluorine ratio from 10% to 40%. These results are in agreement with those of Ito and Sano [18], who also reported a decrease in the phosphate capacity of a CaO-CaF_2-SiO_2 slag at 1300 °C, with an increase in CaF_2 contents. Elliott *et. al.* [19] also proposed that the ability of a slag to dissolve phosphorus will be hindered by the presence of fluorine ions.

In order to explain the effect of CaF_2 on the phosphate capacity, the activity coefficient of P_2O_5 (γP_2O_5) was determined. The phosphorus equilibrium between slag and metal can be represented in its simplest form by the following equation:

$$2[\underline{P}]_{Fe} + 5[\underline{O}]_{Fe} = (P_2O_5)_{slag} \qquad (6)$$

with

$$\Delta G^\circ = -705456 + 556.5T \ (J/mol) \ [20] \qquad (6a)$$

The equilibrium constant K, for reaction (6), is given by:

$$K = \frac{N_{P_2O_5} \cdot \gamma P_2O_5}{(f_P \cdot \%P)^2 . a_{\underline{O}}^5} = 4.32 \ X \ 10^{-7} \ at \ 1350^\circ C \qquad (7)$$

γP_2O_5 can be calculated from eq. (7) and it is shown in Fig. 3 as a function of the fluorine ratio at constant optical basicity.

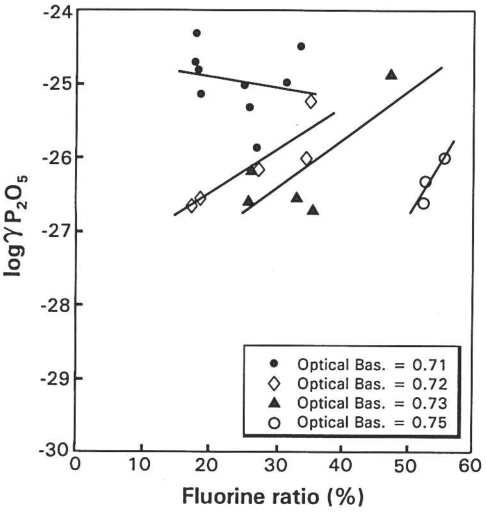

Fig. 3. Activity coefficient of P_2O_5 at 1350°C as a function of the fluorine ratio.

It follows that γP_2O_5 increases when CaF_2 is added to the slag, especially at high basicities. It is of great importance to evaluate the significance of this finding:

CaF_2 increases the activity of the FeO [11,18] in FeO-containing slags thereby favouring dephosphorization. However, it was shown in this study that γP_2O_5 increases with an increase in the fluorine ratio of the slag in the absence of FeO. It seems therefore, that the decrease in γP_2O_5 by the addition of CaF_2, found by previous researchers, was masked by the dominant effect of CaF_2 on the FeO activity. This premise is supported by the findings of Simeonov and Sano [2]. The work of Sommerville and Kay [21] indicates that the activity of SiO_2, at constant SiO_2 content in the CaF_2-CaO-SiO_2 system at 1450 °C, increases with an increase in CaF_2 content. An increase in the activity of SiO_2 will result in a simultaneous increase in the activity of P_2O_5 and consequently, additions of CaF_2 to the slag will increase γP_2O_5.

The impairment of dephosphorization by CaF_2 additions to lime-based slags, can most probably be explained as follows: CaF_2 is less basic in character than CaO and consequently an increase in the CaF_2 content of lime-based slags lowers the basicity and increases the activity of SiO_2. This results in an increase in the activity coefficient of P_2O_5 and a concomitant decrease in the phosphate capacity.

Finally, the lime-based slags evaluated in this study possess high phosphate and sulphide capacities, and because of their low melting points, should be suitable for efficient treatment of hot-metal at a relatively low temperature. Full-scale plant trials were performed at the Pretoria Works of Iscor Ltd. A flow-treated reagent consisting of 60% lime, 25% soda-ash and 15% fluorspar was injected into the Corex hot-metal at ±1310 °C. On average, the sulphur decreased from 0.09% to 0.04% with a reagent consumption of approximately 6.9 kg/ton of hot-metal. A 45% lime, 30% millscale, 10% fluorspar and 15% soda-ash reagent, added to the Corex hot-metal (%Si = ±0.15 and %P = ±0.15) stream during tapping from the torpedo into the transfer ladle, resulted in an average removal of 0.03% phosphorus. The reagent consumption was about 25 kg/ton of hot-metal and it is important to note that it was not injected and no provision was made for temperature losses.

5 Conclusions

- Additions of Na_2O increase the sulphide and phosphate capacities of silicate as well as lime-based slags significantly.
- CaF_2 decreases the sulphide as well as the phosphate capacity of Na_2O containing lime-based slags.
- CaO-SiO_2-Na_2O-CaF_2 slags have high sulphide and phosphate capacities, as well as low melting points, and can consequently be utilized for hot-metal treatment at relatively low temperatures.
- The CaF_2 content in CaO-SiO_2-Na_2O-CaF_2 slags used for the treatment of hot-metal should be restricted and only enough CaF_2 should be added to ensure that the slags remain liquid during the hot-metal treatment.
- Hot-metal treatment was accomplished on industrial scale by using reagents formulated according to this study.

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