SLAG CONTROL FOR IMPROVED STEELMAKING COMPETITIVENESS

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ABSTRACT

During the latter half of the 20th century, when considering steelmaking competitiveness, attention was generally focused on improved metal yields, consistent quality products and optimum production costs. As we move through the first decade of the twenty-first century, it is becoming increasingly evident that in addition to these important factors, we must also give serious consideration to strategies for minimizing the various wastes generated during the steel manufacturing processes thus saving raw materials and at the same time reducing the impact on the environment. With these incentives in mind, this paper provides several examples of innovative processing technologies where the emphasis is placed on the following aspects:

- *Heterogeneous fluxes to minimize slag volume*
- *Custom design of slags for desulphurization.*

HETEROGENEOUS FLUXES TO MINIMIZE SLAG VOLUME AND ELIMINATE FLUORSPAR

Normally the basic oxygen process for steelmaking generates slags at a rate of 120 to 150 kg/ton of steel [1]. The actual composition of BOF slags will vary significantly, depending upon a number of factors, e.g. the sulfur and phosphorus levels required in the final product. Chemical composition, specifically the phosphorus content, is a critical consideration in establishing the amount of BOF slags which can be recycled. The dephosphorization reaction can be represented as follows:

$$2\,\{P\}_{Fe} + 5\,\{FeO\}_{slag} = \{P_2O_5\}_{slag} + 5\{Fe\} \qquad (1)$$

Hereafter Kubaschewski-Alcock notation is used. Reaction (1) is essentially exothermic, hence favored by lower temperature. In order to take advantage of lower temperature, attention has been, particularly in Japan, focused on phosphorous removal from hot metal rather than molten steel.

When phosphorus removal by Reaction (1) with homogeneous liquid slag proceeds towards equilibrium, the activities of FeO and P_2O_5, respectively, decreases and increase, as shown schematically in Figure 1(a). Table 1 shows the compositions of industrial slags taken from the final stages of hot metal processing and the corresponding hot metal temperature and phosphorus levels [3]. In spite of relatively high FeO concentrations in initial fluxes, the FeO concentrations, at the final stages, decreased to 1.1 to 2.5 mol pct (1 to 3 pct by weight), while the P_2O_5 contents increased to 1.1 to 3.4 mole pct (1 to 3 pct by weight), in conforming to schematic illustration given in Figure 1(a). If lower phosphorus levels are required, then FeO has to be added in order to increase FeO activities and/or CaO addition would be necessary to lower the P_2O_5 activities. Clearly, such additions would result in an increase in slag volume.

On the other hand, according to the Condensed Phase Rule, when three phases coexist in a 3-component system, there is only one degree of freedom. This implies that for a given temperature, there is zero degree of freedom; the activities of FeO and P_2O_5 are fixed and therefore independent of the bulk slag composition. If phosphorus removal was conducted with such heterogeneous slags, the FeO and P_2O_5 activities remain constant even though the bulk concentrations of FeO and P_2O_5 are decreasing and increasing, respectively. A schematic representation of the phosphorus removal process under these conditions is shown in Figure 1(b). Thus heterogeneous slags would not require further additions of CaO and FeO in order to sustain the dephosphorization reaction. Hence, the possibility exists for minimizing, or at least lowering, the steelmaking slag volume.

Table 1: Composition of industrial slags taken from the final stages of hot metal processing and the corresponding hot metal temperature and phosphorus levels

Sample Code	Slag composition (mole pct)			Hot metal				
	CaO	SiO_2	FeO	CaF_2	P_2O_5	Others*	T(K)	[%P]
#1**	53.0	32.2	1.7	6.8	1.1	5.3	1548	0.112
#2**	57.3	28.3	2.5	5.6	1.8	4.5	1548	0.090
#3**	58.3	20.8	2.4	10.4	2.6	5.5	1548	0.057
#4**	58.9	16.1	2.1	11.1	3.2	8.6	1548	0.016
#5**	58.3	11.1	1.6	21.0	3.4	4.6	1573	0.020
#6**	60.0	11.6	1.1	21.5	2.1	3.7	1543	0.030
Initial flux	35- 45	0	50-55	5-15	-	-	-	-

* Others means CaS + MgO + MnO + Al_2O_3

** At temperatures above 1623 K, these industrial slags occurred at liquid state

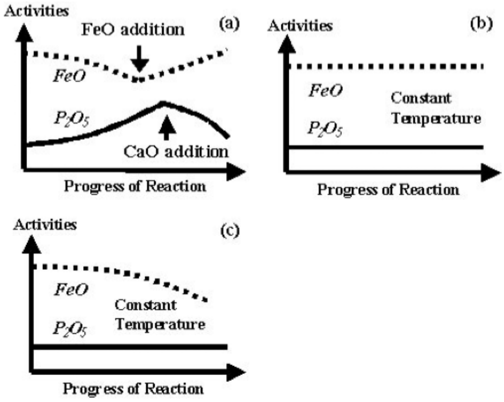

Figure 1: Schematic diagram of dephosphorization reaction; (a) homogeneous liquid slag; (b) heterogeneous slag with zero degree of freedom; (c) heterogeneous slag in which the degree of freedom is greater than unity, saturated with <CaO> + <4CaO·P_2O_5>.

Alternatively, consider, for example, 5-component slags that consist of three phases, i.e., liquid phase + <CaO> + <$Ca_4P_2O_9$>, or liquid phase + <$Ca_4P_2O_9$> + <$Ca_3P_2O_8$>. Hereafter, the following abbreviations will be used; C_4P = 4CaO·P_2O_5 = $Ca_4P_2O_9$, and C3P = 3CaO·P_2O_5 = $Ca_3P_2O_8$. The freedom degree is not unity in such heterogeneous slags. Hence the FeO activities are not fixed. Nevertheless, the P_2O_5 activities are fixed through the following reactions,

$$4 \langle CaO\rangle + (P_2O_5) = \langle Ca_4P_2O_9\rangle \quad (2)$$

$$3 \langle Ca_4P_2O_9 \rangle + (P_2O_5) = 4 \langle Ca_3P_2O_8\rangle \quad (3)$$

Thus one can still anticipate a possibility of minimizing slag volume, and this sequence corresponds to Figure 1(c).

Based upon these considerations, the present authors have measured the activities of FeO and P_2O_5 within a number of heterogeneous slags. Attention is first focused on the CaO-P_2O_5-FeO system. Figure 2(A) shows the iso-thermal section of the phase diagram for this system, while Figure 3 illustrates schematically the experimental set-up used for FeO activity measurements [2]. The technique is based upon electrochemical cell incorporating zirconia electrolyte. For the details of such measurements reference should be made on the authors' previous publications [3]. The activities of FeO and those of P_2O_5 derived through Gibbs-Duhem integrations, respectively, along liquidus lines or phase boundaries are given in Figure 2(B), and Figure 2(C). In these Figures, points *B* and *C* correspond to 3-phase assemblages of CaO + C_4P + Liquid and C_4P + C_3P + Liquid, respectively. Very low P_2O_5 activities within such 3-phase assemblages should be acknowledged.

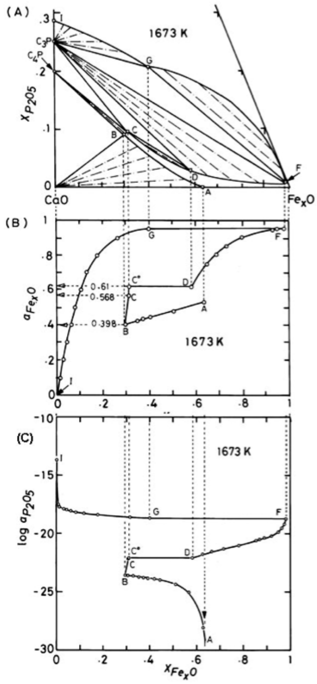

Figure 2: (A) Iso-thermal section of the phase diagram for the system CaO-P_2O_5-FeO. (B) Activities of FeO in CaO-P_2O_5-FeO slags along liquidus line. (C) Activities of P_2O_5 in CaO-P_2O_5-FeO slags along phase boundaries

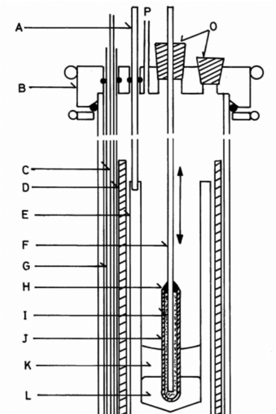

Figure 3: Experimental set-up for the FeO activity measurements. A; Steel rod: B, Water-cooled brass cap: C, Pt-PtRh13 thermocouple: D, Magnesia protection crucible: E, Iron crucible: F, Molybdenum rod: G, Alumina thermocouple sheath: H, Zirconia cement: I, Mo-MoO_2 reference electrode: J, Magnesia stabilized zirconia tube: K, FeO-containing slag: L, Liquid silver: M, Mullite tube: N, Magnesia pedestal: O, Rubber stopper, P, argon outlet, Q, argon inlet: R, Rubber stopper.

Next, consideration is also given on 4-phase assemblages within the system $CaO\text{-}SiO_2\text{-}P_2O_5\text{-}FeO$ system. Needless to say, silica is the major component of steelmaking slag. A schematic illustration of the phase relation in this quaternary system is given in Figure 4, where C_5PS and $<C_3P\text{-}C_2S>ss$, respectively, indicate $<5CaO\cdot P_2O_5\cdot SiO_2>$ and solid solutions between tri-calcium phosphate and di-calcium silicate [6]. The FeO activities were determined for 4-phase assemblages including liquid phases of *L(1)* through *L(4)* as shown in Figures 5 and 6.

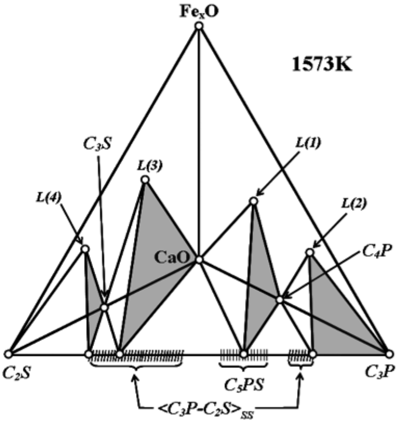

Figure 4: Schematic diagram to illustrate four-phase assemblages within the system $CaO\text{-}SiO_2\text{-}P_2O_5\text{-}FeO$ at 1573 K

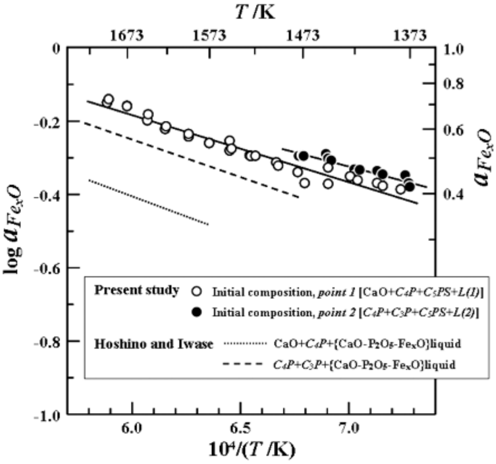

Figure 5: Activities of FeO in 4-phase assemblages containing liquid phase of *L(1)* and *L(2)*

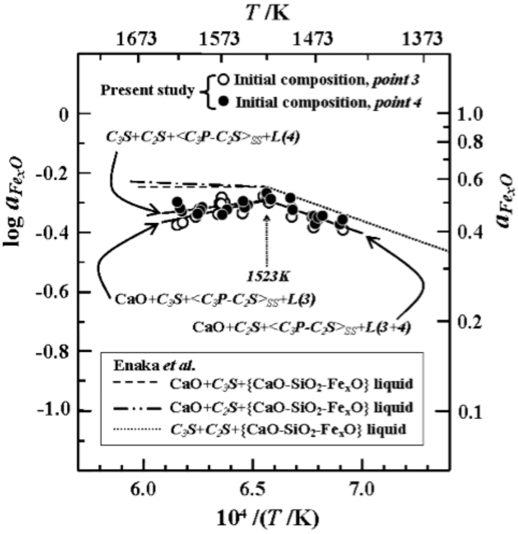

Figure 6: Activities of FeO in 4-phase assemblages containing liquid phase of *L(3)* and *L(4)*. Below 1523K, *L(3)* joins *L(4)*

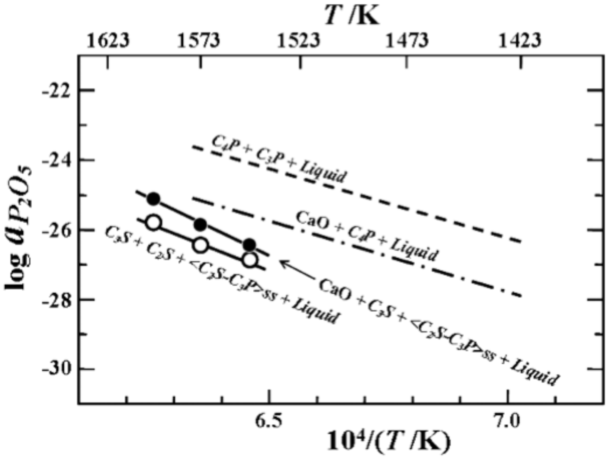

Figure 7: The P_2O_5 activities in various heterogeneous slags

The P_2O_5 activities were also determined for 4-phase assemblages within the system CaO-SiO_2-P_2O_5-FeO as shown in Figure 7. The details of experimental technique are reported by [5, 10].

As can be seen from Equation (1), by knowing the FeO and P_2O_5 activities, the phosphorous levels in hot metal can now be estimated. Such estimated values for [%*P*] are expressed by a hatched area in Figure 8 in comparison with the [%P] values obtained with slags of #1 through #6 of Table 1 at the final stages of hot metal processing. Thus feasibilities for very low phosphorous levels are evident. Based upon basic considerations given in this paper, slag volume of 50 kg/ton-steel has been realized at a steel works in Japan.

CUSTOM-DESIGNED SLAGS FOR HOT METAL SULFUR REMOVAL

Based upon compilation of the literature data on sulfide capacities, C_S, of various homogeneous liquid slags, Sosinsky and Sommerville [7] derived the following empirical relationship between CS and optical basicity, Λ.

$$\log C_S = (22{,}690 - 54{,}640\,\Lambda) / T + 43.6\Lambda - 25.2 \tag{4}$$

Needless to say, the sulfide capacities are related to sulfur partition ratio between slag and metal. By using Equation (4), hence, one can derive the following formula;

$$\log L_s = \log C_S + \log f_S - (1/2) \log PO_2 - 7055/T + 1.224 \tag{5}$$

where f_S is the Henrian activity coefficient of sulfur in liquid iron, and Ls is sulfur partition ratio.

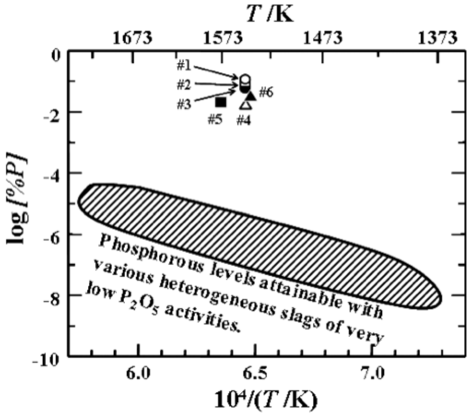

Figure 8: Phosphorous levels attainable with heterogeneous slags in comparison with those observed with industrial slags, #1 through #6 of Table 1

Equations (4) and (5) can be used for custom design of slags. Consider, for example, removal of sulfur from hot metal from 0.10% to 0.005% with slag volume of 50kg-slag/ton-hot metal at 1673 K. Based upon mass balance for sulfur, this sequence corresponds to $L_s = 380$. The oxygen partial pressures, PO_2, at the interface between molten slag and carbon-saturated liquid iron were determined by the present authors, and the results indicate $\log PO_2 = -15.1 \pm 0.6$ at 1673 K. For normal hot metal chemistry, we have $\log f_S = 0.7$. By putting these values for L_s, f_S, T and PO_2 into Equation (5), then we have, $\log C_S = -2.9$. Through Equation (4), this value of $\log C_S = -2.9$ gives $\Lambda = 0.8$. Theoretically, any slag with an optical basicity of 0.80 can be used to treat hot metal and achieve the objective defined above. The slag compositions with $\Lambda = 0.8$ are given in Table 2.

Table 2: Slag compositions with $\Lambda = 0.8$

	CaO	Na_2O	K_2O	Al_2O_3	SiO_2	CaF_2
No. 1	55			45		
No. 2	45			25		30
No. 3	43	5		49	3	
No. 4	50	4.8	2.4	30.5	12.3	

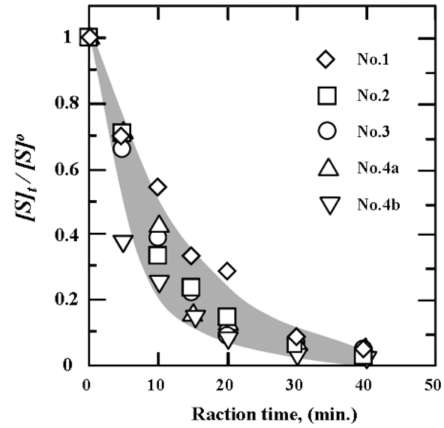

Figure 9: Variation of $[S]_t/[S]^o$ with time with various slags of Λ = 0.8 at 1673 K

Slag No. 1 is a typical calcium aluminate slag near the eutectic point of CaO-Al_2O_3 binary system, Calcium aluminate flux Al_2O_3 contents of 53 to 60% is shipped from the cement industry and then is mixed with CaO to make the composition close to slag No. 1. Flux No. 2 is the mixture of CaO, Al_2O_3 and CaF_2, which was used for ladle slag for many years. The composition of slag No. 3 is close to that of white mud, which is the by-product of alumina industry. [8, 9, 11]. Slag No.4 is the mixture of CaO, Al_2O_3 and nepheline. It is expected that nepheline can be used as additive to replace CaF_2 in CaO-based fluxes.

It is noted again that these slags have the identical optical basicity value of 0.8. However, as can be seen from the comments given below, it is quite likely that the local market price of these fluxes differ from one to another.

These four slags of difference compositions were tested through crucible experiments under substantially identical conditions. Namely, carbon-saturated Fe-C alloys with 0.10% sulfur was melted in a graphite crucible at 1673 K under a stream of argon, and samples were withdrawn at an interval of 5 or 10 minutes after 50 g of slags per 1 kg was added on the molten metal surface. Thus, following to the concept of slag custom-design described above, the final sulfur content obtainable with these four slags should be the same. The experiments using slag No. 1 and No. 3 were conducted in a 10 kHz high frequency induction furnace at the University of Toronto, while those with slag No. 2 and No. 4 were at Kyoto University using the similar induction furnace. Figure 9 shows variation $[S]t / [S]^o$ with reaction time, t; $[S]t$ and $[S]^o$ are the sulfur contents in pct by weight at $t = t$ and $t = 0$, and $[S]o \approx 0.1$. As shown in this Figure, despite the difference in slag compositions, desulphurization behaviour was very similar; $[S]t / [S]^o$ became 0.05 within 40 minutes.

CONCLUSIONS

- By using heterogeneous slags, there is a possibility to minimize the volume of BOF slags
- The correlation of optical basicity with sulfide capacity of molten slag can be used to design a slag for hot metal sulfur removal.

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