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ESTIMATING PHOSPHATE CAPACITIES OF MULTI-COMPONENT SLAGS BY MASS TRIANGLE MODEL

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Abstract

Considering the importance of dephosphorization process in ironmaking and steelmaking, this paper attempted to estimate the phosphate capacities of different systems. Mass triangle model could approach the properties of multi-component systems without the parameter for every component. This present work also extended the mass triangle model to multi-component systems application to three systems containing as much as seven components proved the feasibility and accuracy of this model. The calculated contour lines revealed the reasonable trend as experimental results, and calculation results for fixed compositions showed a low error rate. Scattered points calculation obtained more accurate results. Since this model can also evaluate other properties of slag, such as density, viscosity, sulphide capacity etc., this model might shoot light on the understanding of various properties of multi-component slags accurately, and thus offer insight on optimization of ironmaking and steelmaking process.

Keywords: *Phosphate capacities; Mass triangle model; Multi-component system*

1. Introduction

There is an increasingly large demand for clean steel. However, scarcity of high quality resources urges the utilization of high-phosphorus ores. Phosphorus in steel could lead to cold shortness. So the hot metal pretreatment and secondary refining processes are both developed for removal of sulphur and phosphorus. Generally, phosphorus is removed by oxidization and stabilized as phosphate in slag. Phosphate capacity of slags has been widely investigated by numerous studies.

CaO based slag is widely used due to its lower price and high bound ability with phosphate. However, it could elevate the melting point of the flux. Phosphate capacity of some lime-based systems [1-6] has been reported. In the pretreatment process, the temperature is generally low and CaF_2 is usually added to lower the melting point of slag and improve the kinetic conditions [7]. Considering the toxicity of fluorides to the health to human being, it is necessary to clarify the influences of other additives on dephosphorization. For CaF_2-free systems, Al_2O_3, Na_2O, MnO, BaO etc. are added to CaO-base slags with high basicity and high FeO to decrease the melting temperature, increase fluidity and improve the dephosphorization ability of slags [8]. Na_2O has a stronger ability for dephosphorization and a better fluidity, while it would erode the refractory due to its strong basicity [9-10]. Meanwhile, in the process with basic refractory, the slag would be saturated by MgO. CaO-MgO_{sat}-FeO_x-SiO_2 system has been studied commonly concerning dephosphorization capacity [11-12].

Despite various systems that have been studied, experimental data was never enough. Some empirical equations have been derived relating the phosphorus distribution ratio $\log L_P = \log\frac{(\%P)}{[\%P]}$ to slag components, which are shown in Table 1.

Besides, as pointed out by Mori [16], phosphate capacity was reported to relate to the optical basicity at 1600°C, as shown in Eq. (3).

$$\log C_{PO_4^{3-}} = 17.55\Lambda + 5.72 \quad (3)$$

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Table 1. Some previous equations on log L_p

Reseachers	$\log L_P = \log \frac{(\%P)}{[\%P]}$
Healy[13]	$\frac{22350}{T} + 0.08(\%CaO) + 2.5*\log(\%Fe_t) - 16.00$
Suito et al.[14]	$\frac{10.730}{T} + 4.11*\log(\%CaO + 0.3\%MgO + \%CaF_2 - 0.05\%Fe_tO) + 2.5*\log(\%Fe_tO) + 0.05\%*\log(P_2O_5) - 13.87$
Turkodgan[15]	$\frac{21.74}{T} + 0.071*(\%CaO + 0.3\%MgO) + 2.5*\log(\%Fe_tO) - 9.87$

Obtaining an overall knowledge for the performance of a certain slag is very important for hot metal pretreatment since a slag should shoulder various task and be optimized to the best property. In this work, the mass triangle model is employed to make an estimation of phosphate capacity for several multi-component slags, which was proposed by Chou et al [17]. In previous work, satisfactory results were obtained in estimation of density [18], surface tension [19] as well as sulphide capacity [20] in ternary systems with limited solubility. In the present study, another important chemical property of slag, i. e. the phosphate capacity was calculated by the mass triangle model. Meanwhile, the mass triangle model was extended to calculate some multi-component systems.

2. Model description

To orient the author, the brief introduction of mass triangle model has been given in this section. The detailed information can be found elsewhere [21]. For metallurgical slag, they are usually limited solubility system at certain temperature, which means no intersect point with binary systems. As shown in Fig.1. The area within the boundary represents a homogenous system. O is a composition point within this area. Three lines that parallel to the three sides of the triangle were drawn from O. They intersect with the sides at A, B and C and intersect with the soluble boundary at A', B' and C'. PA', PB' and PC' represent the property data of point A', B' and C' respectively. WA', WB', and WC' refer to the weight factors of these three points. The weight factor of A is determined by area ratios represented in Eq.[4].

$$W_{A'} = \frac{S_{\Delta OB'C'}}{S_{\Delta A'B'C'}} \tag{4}$$

When the property data on the boundary are known, then the property of point O within the area PO could be expressed as the weight summation of properties of A', B' and C', which is shown in Eq.[5].

$$P_O = W_{A'} \cdot P_{A'} + W_{B'} \cdot P_{B'} + W_{C'} \cdot P_{C'} \tag{5}$$

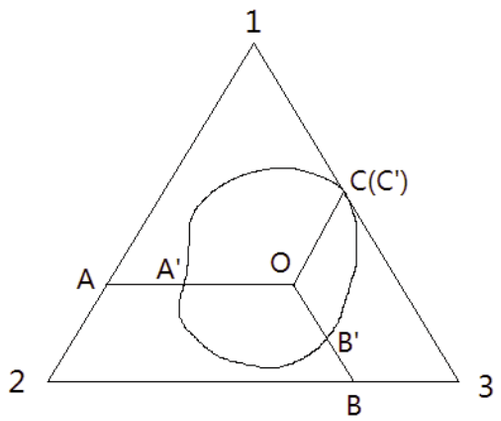

***Figure 1**. Schematic graph of a ternary system with limited solubility*

However, metallurgical slags always have a complex component. For a multicomponent system, it is always asked whether, if the available data points are restricted in some limited discrete points, we can still extract some information from them and if so, how we can do that. Chou et al. has developed a general method for calculating properties based on limited data. It is still based on the weight factor of a component point to the system. Detailed description can be drawn from literature [22].

3. Application to various systems and discussion

In this work, we will deal with three multicomponent systems concerning dephosphorization. In one way, the system will be approached as a pseudo-ternary system based on a certain principle. First, the contents of basic oxides, like CaO, MgO and Na_2O, will be added together to make a basic angle. Similarly, SiO_2 and Al_2O_3 will make a acid angle. Second, the content of iron oxides, which means FeO and Fe_2O_3, will be added together. In another way, discrete component point will be calculated based on other known data according to the method described in literature [22].

3.1 Estimation of various systems by pseudo-ternary method

3.1.1 Phosphate capacity of CaO-MgO-SiO_2-FeOx system

Suito [11] studied the phosphorous distribution ratio of CaO-MgO-SiO_2-FeO_x system in a magnesia crucible, which led to saturation of MgO in the slag. The temperature range was 1550℃~1650℃. Logatirhm value of phosphate capacity of this system was calculated and the contour lines were shown through Fig. 2(a) to Fig. 2(c). The interval for two

adjacent lines is 0.4 for each figure.

It can be seen clearly from the figures that dephosphorization is favored by relative low temperature. Besides, with increase of basic oxides, the phosphate capacity also elevates notably. Suito mentioned that the effects of silica and iron oxides on the capacity were close and substituting CaO with MgO would cause the phosphate capacity to drop obviously.The effect of FeO on the dephosphorization is complex. On one hand, the FeO could release more O^{2-}, which can help form PO_4^{3-}. On the other hand, FeO could bond PO_4^{3-} with and form an instable compound $3FeO{\bullet}P_2O_5$. Furthermore, high FeO contents diluted the concentration of CaO, which performs a main role in dephosphorization. Therefore too much FeO will hinder the dephosphorization process. The total effect of FeO depends on the basicity of slag and there should exist an optimum value. The phenomenon was also observed by Li [11] and Pak [9].

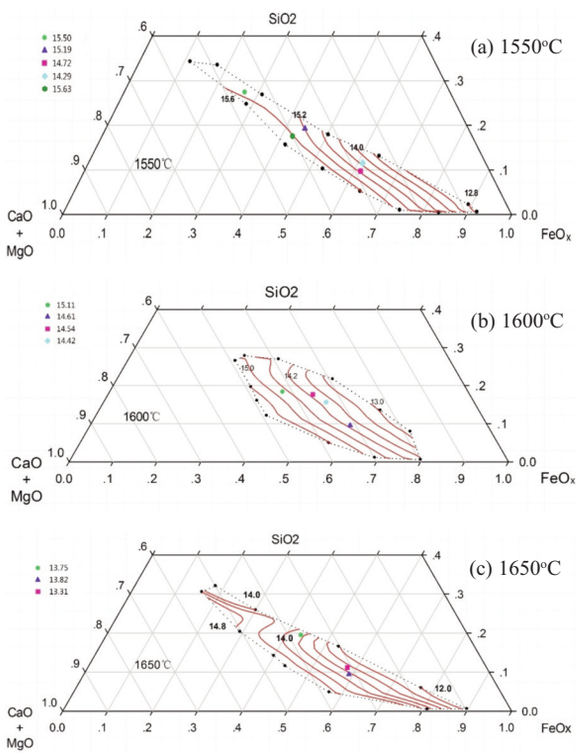

Figure 2. *Phosphate capacity in logarithm of CaO-MgO-SiO_2-FeO_x system*

Table 2. Comparison of experimental and calculated value ($\log C_{PO_4^{3-}}$) of CaO-MgO-SiO_2-FeOx system at different temperature

Composition (mass fraction)			Temperature	Reference	Calculated	Error
SiO_2	CaO+MgO	FeOx	(°C)	Data	Value	Rate
0.27358	0.45699	0.26943	1550	15.61	15.5	0.76%
0.19275	0.36375	0.44351	1550	15.23	15.19	0.28%
0.09736	0.28732	0.61532	1550	15.27	14.72	-3.61%
0.11568	0.27379	0.61053	1550	14.67	14.29	-2.61%
0.17571	0.39994	0.42435	1550	15.55	15.63	0.55%
0.18343	0.42222	0.39434	1600	15.11	14.76	-2.35%
0.09569	0.31253	0.59178	1600	14.61	14.08	-3.58%
0.1771	0.35642	0.46648	1600	14.54	14.09	-3.14%
0.15547	0.33648	0.50806	1600	14.42	14.02	-2.73%
0.19429	0.37172	0.43398	1650	13.75	13.67	-0.58%
0.09412	0.31541	0.59048	1650	13.82	13.31	-3.70%
0.11148	0.31012	0.57839	1650	13.31	12.99	-2.43%

To evaluate the model, some points were calculated and the results are given in Table 1. Eq. (6) is introduced to calculate the mean deviation. In this equation, $K_{i,cal}$ and $K_{i,exp}$ are the calculated and experimental value for the i*th* data point, respectively. N represents the total number of data. The mean deviation Δ between the calculated value and the experimental value is 2.19 pct. The deviation is relatively lower than other empirical equations.

$$\Delta = \frac{1}{N} \cdot \sum_{i=1}^{N} \frac{\left| \kappa_{i,cal} - \kappa_{i,\exp} \right|}{\kappa_{i,\exp}} \qquad (6)$$

3.1.2 Phosphate capacity of CaO-Na_2O-MgO-SiO_2-FeO system

In steelmaking processes to produce high grade steels, the secondary refining is considered to be the very effective for the purpose of dephosphorization. Na_2O-based slags always have good performance in dephosphorization. But Na_2O bring serious corrosion to refractory. Kunisada [10] reported phosphorous distribution between liquid iron and Na_2O-MgO-FeO-SiO_2 containing calcium. Based on similar principle, pseudo ternary system was got and the contour lines for $\log C_{PO_4^{3-}}$ at 1600°C were shown in Fig. 3. It can be concluded that both CaO and Na_2O have a positive effect of dephosphorization. But due to its negative effect, the content Na_2O must be kept low. Table 3 showed the comparison of experimental and calculated values of some selected points in Fig. 3. The mean deviation for this system is 2.08 pct, which also suggests the validity of this model. It is interesting to note that the authors also investigated the relationship between phosphoate capacity and theoretical optical basicity and compared the results for the CaO-based slags. They found that the phosphate capacities of the two slags could not be represented uniquely by the theoretical optical basicity.

3.1.3 Phosphate capacity of CaO-MgO-SiO_2-FeO_x-Na_2O-Al_2O_3 system

Ladle dephosphorization is an alternative to obtain lower phosphorus steel by using special fluxes.

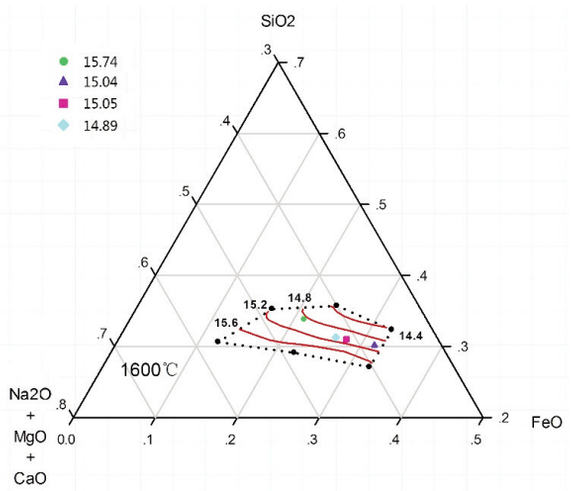

***Figure 3**. Phosphate capacity in logarithm of CaO-Na_2O-MgO-SiO_2-FeO system at 1600℃*

Table 3. Comparison of experimental and calculated value ($\log C_{PO_4^{3-}}$) of CaO-Na_2O-MgO-SiO_2-FeO system at 1600℃

Composition (mass fraction)			Reference Data	Calculated Value	Error Rate
SiO_2	CaO+MgO+Na_2O	FeO			
0.33766	0.44913	0.2132	15.74	14.86	-5.58%
0.30152	0.38178	0.3167	15.04	15.04	-0.02%
0.31016	0.41176	0.27807	15.05	15.03	-0.12%
0.31283	0.42336	0.26382	14.89	15.23	2.28%

Calcium fluoride is commonly added to decrease the melting point and viscosity of slags. But considering the toxicity of fluorides, developing CaF_2-free slag is becoming urgent. Al_2O_3, Na_2O, MnO are usually added into the CaO-based slag. Li [12] has studied phosphate capacity of highly basic CaO based slags saturated with MgO and the effect of Na_2O and Al_2O_3 addition. Fig. 4 presented the calculated phosphate capacity of this complex system.It is important to mention that this study also shown the industrial significance of MgO saturated highly basic CaO-FeO_x-SiO_2 slags, which can be used as a substitution for CaF_2-containing slags. The ideal condition, the final phosphorus content will be about 16 ppm. Therefore, the mass triangle model provides a method to predict whether a multi-component system could have industrial advantage. Since this model can also estimate sulphide capacity of molten slag and good results have been reported by Wang [20], this model is supposed to offer a comprehensive understanding for a certain system. This will certainly bring great convenienceto future optimization of slag component in various ironmaking and steelmaking processes.

The contour lines predicted that the phosphate capacity would increase with the basicity. Besides, the addition of Na_2O would improve the dephosphorization process, while the addition of Al_2O_3 would probably hinder it. The scattered points were also calculated by mass triangle model. Table 4 gives the results. The mean deviation for this complex system is 0.74 pct. It can be concluded that for systems which contained as much as seven components in this case, this model was pretty competitive in predicting properties of molten slags.

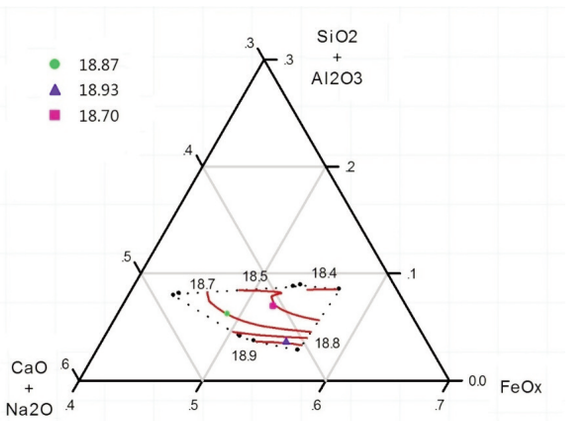

***Figure 4**. Phosphate capacity in logarithm of CaO-MgO-SiO_2-FeO_x-Na_2O-Al_2O_3system at 1600℃*

3.2 Estimation of various systems by discrete component point

In the first method, we get a pseudo-ternary based on the property of component. However, the difference of two kinds of basic oxides or acid oxides has not been disclosed. To solve this problem, the mass triangle was extended to multi-component systems and the comparison of calculated and experimental results is shown in Fig. 5. The mean deviation is 1.03 pct.

Table 4. Comparison of experimental and calculated value of $\log C_{PO_4^{3-}}$ CaO-MgO-SiO_2-FeO_x-Na_2O-Al_2O_3 system at 1600℃

Composition (mass fraction)			Reference Data	Calculated Value	Error Rate
SiO_2+Al_2O_3	CaO+MgO+Na_2O	FeOx			
0.06175	0.4482	0.49005	18.87	18.7	-0.91%
0.0359	0.41395	0.55014	18.93	18.88	-0.27%
0.06992	0.40791	0.52217	18.7	18.51	-1.03%

For slag at 1600ºC, the values are also estimated by the optical basicity. The results are given in Table 5. It can be seen obviously that the calculation results obtained by optical basicity have a much larger

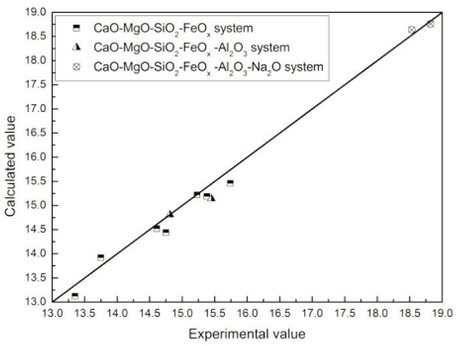

***Figure 5**. Comparison of experimental and calculated value* $\log C_{PO_4^{3-}}$ *for various multi-component systems*

deviation than present work. As pointed by Kunisada [10], the phosphate capacity or the apparent equilibrium constant for some slag would not always conform to Eq. (3). One of the reason may be that the interactions among slag components are not taken into consideration in the theoretical optical basicity determined arithmetically. In the present work, the mass triangle model avoid the problem and provide a more convenient and accurate way for estimation.

4. Conclusions

Dephosphorization is a very important process in steelmaking. To gain a better understanding of phosphate capacities of molten slags, it is necessary to make modeling according to the limited experimental data. Due to insufficiency of the phosphate capacity model, mass triangle model was employed in this work.

Table 5. Comparison of calculated results for various systems at 1600 ℃ by optical basicity and present work

System	Exp. value	Optical basicity		Mass triangel	
		calculated	deviation	calculated	deviation
CaO-MgO-SiO_2-FeOx	14.61	17.01	16.40%	14.52	0.62%
CaO-MgO-SiO_2-FeOx	15.38	17.99	17.00%	15.19	1.23%
CaO-Na_2O-MgO-SiO_2-FeO	14.806	16.9	14.10%	14.81	0.03%
CaO-Na_2O-MgO-SiO_2-FeO	15.45	17.49	13.20%	15.14	2.00%
CaO-MgO-SiO_2-FeO_x-Na_2O-Al_2O_3	18.82	18.69	0.69%	18.76	0.32%

Mass triangle model could solve the problem of multi-component systems by two ways. One is to make a pseudo ternary system and the other is calculated the target point directly. Application to three systems containing as much as seven components was made by both methods. The calculated contour lines revealed the reasonable trend as experimental results, and calculation results for fixed compositions are very close to the experimental data within a low error rate. Scattered points calculation obtained a pretty low deviation. Thus, the results have proved a good reliability and flexibility of the mass triangle model. Since this model can also evaluate other properties of slag, this model might open a door to understand various properties of multi-component slags accurately.

Acknowledgement

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References

[1] R. Inoue and H. Suito:Trans.ISIJ., 25 (2) (1985) 118-126.
[2] K. Ito, M. Yanagisawa and N. Sano:Tetsu-to-Hagane, 68 (2) (1982) 342-344.
[3] M. Muraki, H. Fukushima and Sano N:Tetsu-to-Hagane, 71 (6) (1985) 693-699.
[4] J. Im, K. Morita and N. Sano:ISIJ Inter., 36 (5) (1996) 517-521.
[5] K. Ito and N. Sano:Tetsu-to-Hagane, 69 (15) (1983) 1747-1754.
[6] W. H. Van Niekerk and R. J.Dippenaar:Metall. Mater. Trans. B, 29 (1) (1998) 147-153.
[7] H. Suito and R. Inoue:Trans. ISIJ., 22 (11) (1982) 869-877.
[8] R. Simeonov and N. Sano:Trans. ISIJ., 25 (10) (1985) 1031-1035.
[9] J. J. Pak and R. J.Fruehan:Metall. Trans. B, 22 (1) (1991) 39-46.
[10] K. Kunisada and H. Iwai:Trans. ISIJ., 27 (4) (1987) 263-269.
[11] H.Suito and R.Inoue:Trans ISIJ., 21 (4) (1981) 250-259.
[12] G. Li, T. Hamano and F.Tsukihashi:ISIJ Inter., 45 (1) (2005) 12-18.
[13] G. W. Healy: J Iron Steel Inst., 208 (7) (1970) 664-668.
[14] H. Suito and R.Inoue:Trans ISIJ., 24 (1) (1984) 47-53.
[15] E. T. Turkdogan and J. Pearson:JIron Steel Inst., 175 (1953) 398.
[16] T. Mori: Bull. JapanInst. Metals., 23 (1984) 354–361.
[17] K. C. Chou:CALPHAD, 19 (1995) 315-325.
[18] L. J. Wang, S. L. Chen, K. C. Chou and Y. A. Chang. Computer Coupling of Phase Diagrams and Thermochemistry, 29 (2) (2005) 149.

[19] L. J. Wang, K. C. Chou, S. L. Chen and Y. A. Chang: Z. Matallkd., 96 (8) (2005) 948.

[20] L. J. Wang, Q. Y. Liu and K. C. Chou:J. Mining Metall. Sec. B: Metall., 48 (2) (2012) 219-226.

[21] L. J. Wang, K.C. Chou and S.Seetharaman:CALPHAD, 32 (2008) 49-55.

[22] K. C. Chou and G. H. Zhang:Metall. Mater. Trans. B, 40 (2) (2009) 223-232.