

SOLUBILITY OF MgO IN CaO-BASED SLAGS

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ABSTRACT

The solubilities of MgO obtained from the data obtained from equilibrium experiments between liquid $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_t\text{O-MnO}$ slags and liquid silver and solid iron in the temperature range of 1703 to 1773 K in a CO/CO_2 gas mixture are analyzed in the current study. The solubilities of MgO decreased with increasing Fe_tO content and the slag basicity, $(\text{mass\% CaO})/(\text{mass\% SiO}_2)$ in the slag basicity less than 2.0 and they were compared with the change of the MgO solubility with increasing MnO concentration in the slags. The present data were temperature-extrapolated to those at 1873 K and compared with the previously reported MgO solubilities in steelmaking slags. The application of the optical basicity resulted in correlation of MgO solubility with COREX process-typed slag compositions.

INTRODUCTION

During the past several decades, many efforts were made to develop reduction processes for iron production that could serve as an alternative and/or complements to the conventional blast furnace ironmaking due to lower grade of iron ores and coals that are unsuitable for the blast furnace. One of the reduction smelting processes, COREX, has drawn much attention and been commissioned due to its commercial viability, long-term prospects of high quality metallurgical coals shortages and increased environmental problems associated with coke ovens, agglomeration plants and other supplementary operations in the blast furnace ironmaking [1].

In order to produce high grade of steels, containing significant amount of manganese content, the direct smelting reduction of manganese ore is being performed in the smelter-gasifier in COREX process. As results, growing concerns are expressed over the lime-based slags containing significant amount of manganese oxide [2, 3, 4, 5]. For smelting reduction of Mn ore in the COREX process, it is necessary to understand the operating and thermodynamic conditions of respective iron and steelmaking processes, as well as the behavior of MnO in slag.

The slag compositions of reduction smelting processes are quite different from those of conventional blast furnace processes. It is of great importance to control the slag properties and to optimize slag/metal reactions in the smelting process to improve the productivity of COREX. In most researches concerning metallurgical slags, MgO crucibles are often used as vessels to hold the metallurgical slags, whose compositions are ultimately saturated with MgO. In practice, MgO containing dolomite is charged into a converter to minimize the lining wear, resulting in forming MgO-saturated slags [6]. It has been also known that MgO additions have great influences on the slag refining capacity and physical properties, consequently, on the ultimate steel productivity with high demand for high-performance usage. Accordingly, this study aims to elucidate the effects of slag composition and temperature on the MgO solubility in the lime-based slags containing MnO for smelting reduction process and to correlate the MgO solubility with optical basicity.

EXPERIMENTAL

Thermodynamic Consideration

The Fe_tO in slags is in equilibrium with solid Fe, which was used together with liquid silver in the temperature range investigated in order to determine the activity of Fe_tO as follows.



$$\Delta G_f^\circ = 273,440 - 208.0T \text{ (J/mol)} \quad [7] \quad (2)$$

The activity of Fe_tO , $a_{\text{Fe}_t\text{O}}$, is calculated by Equation 3 using the equilibrium constant of equation (1), K_1 since the activity of solid Fe is unity in the experimental temperatures investigated. The activity of Fe_tO is with respect to pure liquid iron oxide in equilibrium with pure δ iron in Equation 3. As can be expected from Equation 3, the activity of Fe_tO will increase with increasing the partial pressure ratio of CO_2 to CO, that is, with increasing the oxygen partial pressure in the current system.

$$a_{\text{Fe}_t\text{O}} = (p_{\text{CO}_2} / p_{\text{CO}}) \cdot K_1 \quad (3)$$

Experimental Procedure

A schematic of experimental apparatus is shown in Figure 1, and a SiC-resistor furnace with a mullite tube (72 mm-OD, 66 mm-ID, and 1000 mm-Length) were used for the experiments. A Pt-Pt/13 pct Rh thermocouple mounted outside the mullite tube was employed for the temperature measurements. A PID controller was used to control the temperature within the range of $\pm 2\text{K}$. The slag components of reagent grades were uniformly mixed by agatar mortar. The CaCO_3 was calcined for 2 hours at 1273 K, and a cylindrical (Diameter: 8 mm, length: 14 mm) electrolytic iron weighing 5.5 g and Ag chips weighing 20 g along with 16 g of slag powder were charged into a MgO crucible (25 mm-ID and 50 mm-Length).

The reaction experiments with Ag, Fe, and slag were carried out in the temperature range of 1673 to 1773 K. The oxygen partial pressure was controlled by the ($p_{\text{CO}}/p_{\text{CO}_2}$) ratio of a CO/CO₂ gas mixture using a gas mixing pump (DIGAMIX 2M200), and CO and CO₂ were dried by H₂SO₄ and silica gel in advance. The gas mixture was blown at a total flow rate of 500 mL/min. The flow of Ar gas was maintained before influxing a mixture of CO/CO₂ from the top of the reactor. A preliminary experiment indicated that 18 hours was required for the equilibrium to be reached. After the equilibrium, the crucible was quickly withdrawn from the furnace and rapidly quenched in an Ar gas stream. The compositions of slag samples (CaO, SiO₂, Fe_tO, Al₂O₃, MnO, MgO) were determined using the X-ray Fluorescence spectrometer.

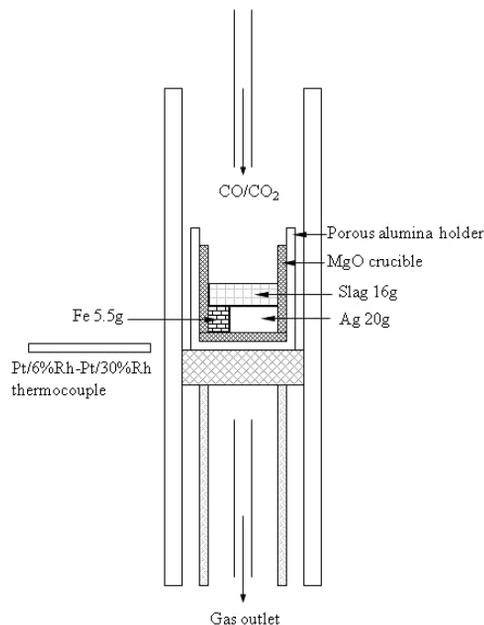


Figure 1: Schematic diagram of the experimental apparatus

RESULTS AND DISCUSSION

Effect of Slag Compositions on MgO Solubility

The solubilities of MgO were measured over the wide composition range of (mass% Fe_tO) = 3.2 ~ 21.4 and CaO/SiO₂=1.0 ~ 1.2, and the results are plotted in Figures 2 to 4. As previously mentioned, the oxygen partial pressure was controlled by CO/CO₂ gas mixture to

change the activity of Fe_tO , which made it possible to adjust the Fe_tO content in the slags investigated. Thus, the Fe_tO content increased from 3.2 to 21.4 mass% with increasing the oxygen partial pressure from 1.8×10^{-12} to 3.7×10^{-10} atm in Figure 2. As can be seen in Figure 2, the MgO solubility decreases from 18.2 to 12.0 mass% at 1723 K as the slag basicity, $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$, increases. Furthermore, it showed a similar tendency as those measured for steelmaking slags by Shim and Ban-ya [8] and Suito and Inoue [9] although their measurements were made at 1873 K. That is, the MgO solubility rapidly decreases with increasing slag basicity in the lower basicity, however, the values slightly decreased and fell into less than 10 mass% MgO as the slag basicity exceeded 2.0. In practice, the slag composition of $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2) = 1.9$ corresponds to the stoichiometric composition of dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$) above which the MgO solubility lies between 5 to 8 mass%. This was previously pointed out by Shim and Ban-ya [8].

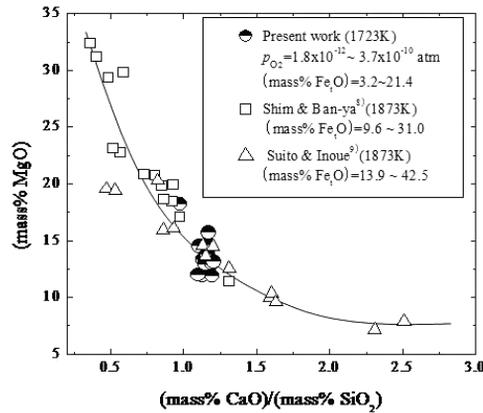


Figure 2: Variation of MgO solubility as a function of slag basicity, $(\text{mass}\% \text{CaO})/(\text{mass}\% \text{SiO}_2)$ in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}_{\text{sat}}\text{-Fe}_t\text{O-MnO}$ at 1723 K

The results shown in Figure 2 can be also supported by Equations 4 to 7. The solubility limit of a component in the slag system is influenced by the actual saturation phase. It is well known that magnesiowustite, a solid solution of FeO in MgO in equilibrium with liquid slag, was formed at the slag/ MgO crucible interface [8]. In particular, the MgO solubility is related to the MgO activity in magnesiowustite phase and the activity of O^{2-} , slag basicity, as shown in Equation 7. The MgO solubility could be inversely proportional to the O^{2-} activity, slag basicity, for some range of Fe_tO content assuming that the equilibrium constant of Equation 4, $K_{\text{Mg}^{2+}}$, and the activity coefficients of Mg^{2+} , $f_{\text{Mg}^{2+}}$, are constant in the slag compositions investigated:



$$K_{\text{Mg}^{2+}} = \frac{a_{\text{Mg}^{2+}} \cdot a_{\text{O}^{2-}}}{a_{\text{MgO}}} \quad (5)$$

$$(\text{mass}\% \text{Mg}^{2+}) = a_{\text{MgO}} \cdot \frac{K_{\text{Mg}^{2+}}}{f_{\text{Mg}^{2+}} \cdot a_{\text{O}^{2-}}} \quad (6)$$

$$(\text{mass\% MgO}) = (\text{mass\% Mg}^{2+}) \frac{MW_{\text{MgO}}}{MW_{\text{Mg}}} = a_{\text{MgO}} \frac{K_{\text{Mg}^{2+}}}{f_{\text{Mg}^{2+}} a_{\text{O}^{2-}}} \frac{MW_{\text{MgO}}}{MW_{\text{Mg}}} \quad (7)$$

where MW_i is the molecular weight of component i . In Figure 3, the MgO solubility decreases from 18.2 to 12.0 mass% as the Fe_tO content increases from 3.2 to 21.4 mass% with the slag basicity maintained between 1.0 and 1.2, which was resulted from increasing the activity of Fe_tO by increasing the oxygen partial pressure. Thus, increasing the Fe_tO activity also increased that in magnesiowustite, which resulted in decreasing the activity of MgO by the Gibbs-Duhem equation.

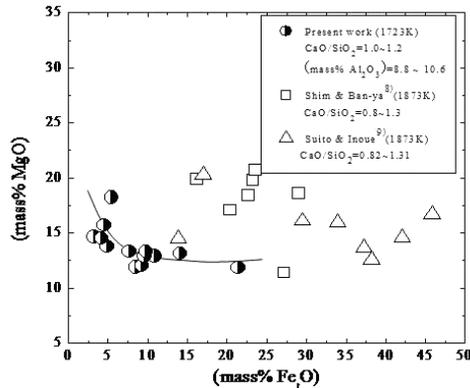


Figure 3: The solubility of MgO as a function of Fe_tO content in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3(9\text{-}10 \text{ mass\%})\text{-MnO}(4\text{-}5 \text{ mass\%})\text{-Fe}_t\text{O-MgO}$ in contact with molten iron at 1723 K

Thus, in Equation 7, increasing the Fe_tO activity decreased the MgO activity, which ultimately contributed to lowering the MgO solubility with increasing the Fe_tO content. According to Shim and Ban-ya [8], the MgO solubility was influenced by Fe_tO and slag basicity in the slag basicity less than 2.0. That is, the MgO solubility decreased with increasing Fe_tO content since Fe_tO behaved as basic oxide in the low basicity range. Furthermore, the values from the present results are lower than those [8, 9] measured at 1873 K, which can be easily explained considering that the general dissolution of solid phase into liquid slag is endothermic.

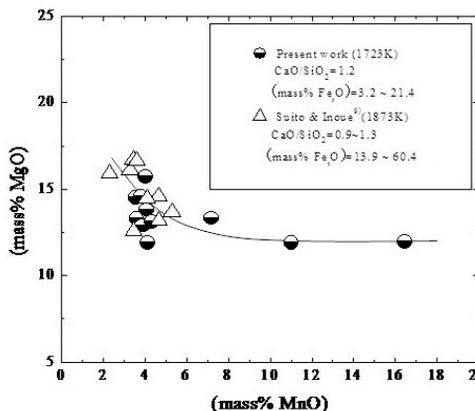


Figure 4: The solubility of MgO as a function of MnO content in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3(10 \text{ mass\%})\text{-MnO}(3\text{-}16 \text{ mass\%})\text{-Fe}_t\text{O}(10 \text{ mass\%})$ slag saturated with MgO and molten iron at 1723 K

In Figure 4, the MgO solubility decreases from 15.7 to 12.0 mass% as the MnO content increases from 3.5 to 16.5 mass% with the slag basicity maintained between 1.0 and 1.2. The results also indicate that the degree of decreasing MgO solubility with increasing MnO is considerably smaller than that with increasing slag basicity. This proves that the CaO-equivalent of MnO is lower than that of MgO, which can be explained by the relative basicity of oxides in terms of optical basicity, which will be described in the subsequent discussion [10].

Effect of Temperature on MgO Solubility

The temperature dependence of MgO solubility was investigated for the slags containing about 3 to 4 mass% MnO with slag basicity of 0.9 to 1.2 at an oxygen partial pressure of 5.1×10^{-9} atm. As shown in Figure 5, the MgO solubility increases from 5 to 11 mass% as the temperature increases from 1703 to 1773 K and their temperature dependence can be formulated by Equation 8:

$$\log(\text{mass\%MgO}) = -\frac{3,330}{T} + 3.09 \quad (8)$$

This can be understood by Equation 7. That is, the MgO solubility increased since the equilibrium constant of Equation 4, K_{Mg_2} , for a constant slag basicity at higher temperatures increases and the dissolution reaction of MgO into liquid slags is endothermic in Equation 4. Furthermore, higher temperatures will accelerate the dissolution of MgO into liquid slags with improved slag fluidity.

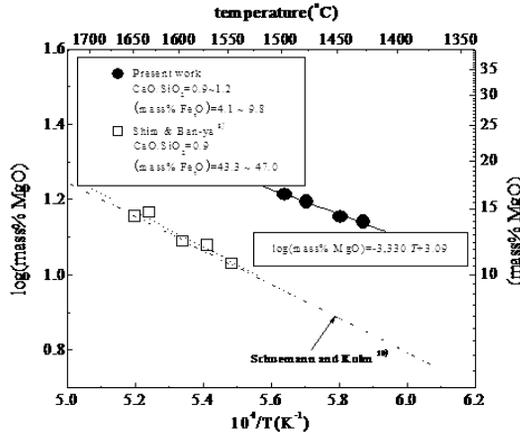


Figure 5: Temperature dependence of the solubility of MgO in CaO-SiO₂-Al₂O₃ (10mass%)-MnO (4 mass%)-Fe₂O₃ (4.1~9.8 mass%) in the temperature range of 1703 to 1773 K

Schueman and Kolm [10] earlier reported the effect of temperature on the solubility of MgO in steelmaking slags in terms of Equations 9 and 10.

$$k_T = \frac{(\text{mass\%MgO})_{\text{sat}}(T)}{(\text{mass\%MgO})_{\text{sat}}(T_0)} \quad (9)$$

$$k_T = \exp\left(5.5478 - \frac{10,391}{T}\right) [10] \quad (10)$$

They evaluated Equation 10 using the results from the previous research and derived the temperature dependence of the MgO solubility in steelmaking slags in reference to that at 1873 K [8, 9, 11, 13]. As shown in Figure 5, the temperature dependence of MgO solubility in complex slags is represented by a straight line using the relations (9) and (10) and Shim and Ban-ya's data [8] at 1873 K as a reference one. As can be noticed, the slope of the regression line by present work is similar to that derived based on Schuemann and Kolm [10]. Thus, the present results measured in the temperature range of 1703 to 1773 K can be temperature-extrapolated to those at 1873 K by applying Equations 9 and 10.

In order to compare the present results measured below 1873 K with those experiments conducted at 1873 K by previous researchers, the similar mathematical treatment as that used by Schuemann and Kolm [10] was carried out. That is, the analytical concentration of each component in the steelmaking slags was normalized by considering the equivalent amount of MnO, P₂O₅ and Al₂O₃ for SiO₂, CaO, Fe_tO and MgO by Equations 11 to 14, and it was designated in terms of (mass% X_iO)^{*}:

$$\begin{aligned} (\text{mass\% SiO}_2)^* &= (\text{mass\% SiO}_2) + k_p \cdot (\text{mass\% P}_2\text{O}_5) \\ &+ k_{Al} \cdot (\text{mass\% Al}_2\text{O}_3) + (1 - k_{Mn}) \cdot (\text{mass\% MnO}) \end{aligned} \quad (11)$$

$$\begin{aligned} (\text{mass\% CaO})^* &= (\text{mass\% CaO}) + k_{Mn} (\text{mass\% MnO}) \\ &+ (1 - k_p) (\text{mass\% P}_2\text{O}_5) + (1 - k_{Al}) (\text{mass\% Al}_2\text{O}_3) \end{aligned} \quad (12)$$

$$(\text{mass\% Fe}_t\text{O})^* = (\text{mass\% Fe}_t\text{O}) \quad (13)$$

$$(\text{mass\% MgO})^* = (\text{mass\% MgO}) \quad (14)$$

where the equivalent factors of P (k_p) and Al (k_{Al}) were reported to be 0.63 and 0.79, respectively [10]. And the equivalent factor of Mn (k_{Mn}) was assumed to be 0.59 considering the optical basicity of MnO [14].

In order to plot the solubility of MgO in the ternary phase diagram of CaO, SiO₂ and Fe_tO at 1873 K, the respective concentration was once again normalized by Equations 15 to 17:

$$(\text{mass\% SiO}_2)^\Delta = (\text{mass\% SiO}_2)^* \cdot 100/[100 - (\text{mass\% MgO})^*] \quad (15)$$

$$(\text{mass\% Fe}_t\text{O})^\Delta = (\text{mass\% Fe}_t\text{O})^* \cdot 100/[100 - (\text{mass\% MgO})^*] \quad (16)$$

$$(\text{mass\% CaO})^\Delta = 100 - (\text{mass\% SiO}_2)^\Delta - (\text{mass\% Fe}_t\text{O})^\Delta \quad (17)$$

In the present work, the solubilities of MgO were measured for the slag composition of (4.1 to 9.8 mass%) Fe_tO and (mass%CaO)/(mass%SiO₂) values of 0.9 to 1.3 and their results were normalized and plotted by the above normalization as shown in Figure 6. The dashed lines in Figure 6 represent the estimated contours of the MgO solubility in the steelmaking slags which are in equilibrium with magnesiowustite by projecting the magnesiowustite saturation surface on the base system, CaO-SiO₂-Fe_tO [10]. As can be seen in Figure 6, the solubilities of MgO in the present slags are lower than those estimated from the dashed contours of MgO solubility for the steelmaking slags by 3 to 5 mass%. This is believed to have occurred due to the temperature extrapolation applied for the present slags and the difference in the original slag compositions and in experimental temperatures influencing the slag fluidity, etc. Furthermore, the equivalent factor of MnO (k_{Mn}) should be corrected to reflect the effect of MnO on the increase of slag basicity.

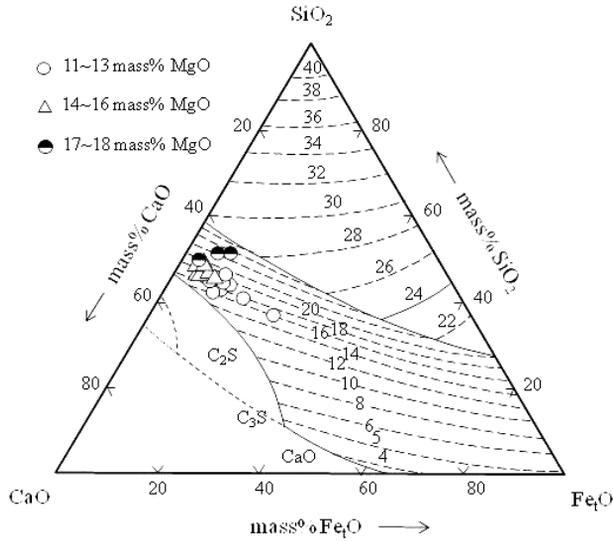


Figure 6: Representation of the solubilities of MgO in CaO-SiO₂-Fe₁O-Al₂O₃-MnO slag in contact with Ag and Fe in the temperature range of 1703 to 1773 K by temperature extrapolation to central projection of the magnesiowustite saturation surface on the base system CaO-SiO₂-Fe₁O [10].

Correlation of MgO Solubility with Optical Basicity

The concept of the optical basicity was introduced and applied to metallurgy by Duffy *et al.* [15]. The values of optical basicities for the pure oxides are directly correlated with the Pauling electronegativity and the equivalent fraction of components and are listed in Table 1 [14].

Table 1: Theoretical optical basicities from Pauling electronegativity of pure oxides

Oxide	CaO	SiO ₂	Fe ₁ O	Al ₂ O ₃	MgO	MnO	P ₂ O ₅
Optical basicity	1.0	0.48	0.51	0.61	0.78	0.59	0.40

In Table 1, the relative basicity of CaO, MgO and MnO are compared in order. Based on the optical basicities in Table 1, it is possible to calculate the optical basicity, Λ , for metallurgical slags of any composition involving these oxides by Equation 18:

$$\Lambda = \sum X_i \Lambda_i \quad (18)$$

where Λ_i is the optical basicity of the pure oxide and X_i is the equivalent cation fraction, i.e. the molar fractions of cations multiplied by the number of oxygens in the respective component.

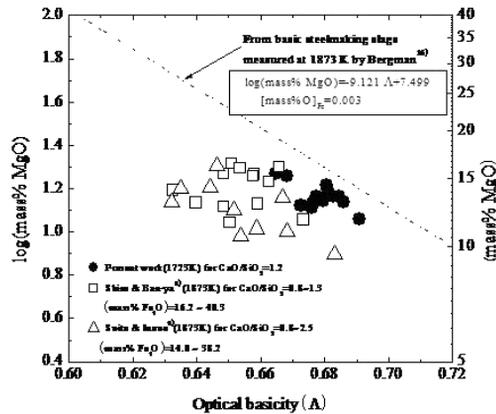


Figure 7: Logarithm of the MgO solubility as a function of the optical basicity of 20 CaO-SiO₂-Fe₂O-Al₂O₃-MnO slags saturated with MgO

The present work plotted together with the results obtained by Shim and Ban-y [8] and Suito and Inoue [9] show similar tendency as shown in Figure 7 although the steelmaking slag-related data have slightly lower MgO solubility. This is because the present slag system has lower iron oxide compared to those for steelmaking slags. In Figure 7, another correlation is shown as a dotted line, which was obtained by Bergman [16] for basic steelmaking slags at 1873 K. Although the current data scatter, they show a similar dependence of MgO solubility on optical basicity as that for steelmaking slags by Bergman [16]. The present results show lower values of MgO solubility than those estimated for steelmaking slags at the identical optical basicities. The reason might be that the correlation derived by Bergmann [16] was based on the assumption that the magnesio-wustite is an ideal solution at 1873 K whereby the activity relation simply is $a_{\text{MgO}} = 1 - a_{\text{FeO}}$.

CONCLUSIONS

Equilibrium experiments were conducted on liquid CaO-SiO₂-Al₂O₃-Fe₂O-MnO slags which was in equilibrium with liquid silver and solid iron in the temperature range of 1703 to 1773 K in a CO/CO₂ gas mixture. The results were analyzed in terms of the MgO solubility, and the following conclusions were obtained from the findings:

- The solubility of MgO decreased with increasing Fe₂O content and the slag basicity, (mass% CaO)/(mass% SiO₂), in the slag basicity less than 2.0
- It was found that the degree of decreasing MgO solubility caused by increasing MnO is considerably smaller than that by increasing slag basicity. This proves that the CaO-equivalent of MnO is lower than that of MgO
- The temperature dependence of the MgO solubility was formulated for the limited range of slag composition, which was used to convert the data to higher temperature such as 1873 K for comparing those with the solubility of MgO in steelmaking slags
- The MgO solubility and optical basicity were correlated and compared to that for basic steelmaking slags. This study proved that the optical basicity can be one of the means to estimate the MgO solubility in the metallurgical slags.

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