

Vapor Pressure of Zinc and Zinc Chloride in the Fe₁O-CaO-SiO₂-Al₂O₃ Slag System

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Vapor pressure of zinc from the Fe₁O-CaO-SiO₂-Al₂O₃ slag system was measured by the Knudsen effusion method under conditions with varying parameters such as temperature, slag compositions, and initial contents of zinc and chlorine. In the thermodynamic estimations using thermodynamic parameters under the experimental temperature range, for slag samples without Cl addition, it suggests that metallic Zn is the only vapor species. In the case of Cl addition, gaseous ZnCl₂ is predominant and the formation ratio of metallic Zn and FeCl₂ can be neglected. In the measurements, the vapor pressures of metallic Zn and ZnCl₂ increase with increasing temperature. For ZnCl₂, the logarithm of vapor pressure ($\ln P$) is a linear function of the reciprocal of temperature ($1/T$), while in the case of gaseous metallic Zn, a non-linear relationship is observed between $\ln P$ and $1/T$. The slag basicity exhibits the different effects on the vapor pressures of metallic Zn and ZnCl₂. The former increases with increasing the slag basicity, while the latter decreases. A high FeO content in the slag tends to increase the vapor pressure of metallic Zn and ZnCl₂. [doi:10.2320/matertrans.47.1341]

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1. Introduction

A large amount of fly ashes are formed in waste incineration processes. Due to the presence of some toxic elements and organic compounds such as Pb and dioxins, most of the fly ashes are classified as hazardous wastes and have to be stored in a safe yard after appropriate treatment. However, due to the increasing costs of such treatment and insufficient knowledge on the long-term stability with respect to the leachability of heavy metals, the future application of these treatments is limited. On the other hand, several more stringent regulations/laws have been enacted in Japan to promote the recycling/reutilization of waste materials, for example, the law for recycling of specified types of home appliances and the law for recycling of automobiles. There is a need to develop an effective process to recover valuable resources, *e.g.*, heavy metals such as zinc and lead from the ashes in a recyclable form.

The smelting process has been accepted as a practical method to treat fly ashes and dust containing heavy metals. The advantages of this process are as follows: (1) volatile metal elements such as zinc and lead can be separated from the residue by evaporation; (2) recovered heavy metals can be reutilized by conventional metallurgical processes; and (3) oxide residue, sometimes referred to as slag, could be inert to the environment. Since toxic organic compounds in wastes are completely destroyed due to a long residence time at high temperatures, permanently safe slag products can be achieved if the heavy metals are appropriately removed.

In order to effectively control the removal process of the heavy metals from fly ashes, a better understanding of their vaporization behaviors from molten materials is required. Chlorine-bearing slag/salts are of particular interest from industrial point of view, since the high temperature behaviors of heavy metals strongly depend on the chlorine content or potential.¹⁾ So far, some experimental researches have been performed on the partitioning of heavy metals under incineration and combustion condition (at 873 K–1273 K),^{2–5)} along with some thermodynamic equilibrium

calculations for the formation of vapor species.^{6,7)} However, the basic thermodynamic knowledge regarding vapor pressures, activities, and interactions in molten slag or salt of these metals is limited due to experimental difficulties.

Several methods have been applied to determine saturated vapor pressures. Knudsen effusion method is one of the most accurate techniques for the measurement of the vapor pressure lower than 100 Pa.^{8,9)} Although this method has rarely been used for metal chlorides, it has long been employed for measurements of organic compounds.^{10–12)}

In this study, the vapor pressure of zinc for the slag system Fe₁O-CaO-SiO₂-Al₂O₃ with and without chlorine was measured under varying conditions of the parameters such as temperature, slag compositions, and initial contents of zinc and chlorine.

2. Experimental

2.1 Sample preparation

The FeO-CaO-SiO₂-Al₂O₃ system was employed as the slag sample since it has the common composition of the matrix in the waste incineration ashes.¹³⁾ Three compositions were chosen as the slag samples and they are located at the edges of the liquid-stable region at low temperature (1150°C) in the phase diagram of FeO-CaO-SiO₂ system (Fig. 1). The slag samples selected are as follows, F-slag with the highest FeO content, C-slag with the highest CaO content, and S-slag with the highest SiO₂ content. Their chemical compositions are shown in the phase diagram of the FeO-CaO-SiO₂ system (Fig. 1). For each slag sample, the Al₂O₃ content is set at 5%. These slag samples are prepared in the same manner as that described in the previous report.¹⁴⁾ The chemical compositions of the produced slag are listed in Table 1.

The slag samples are crushed and ground into powder and then mixed with chemical reagents of ZnO. For most of the experiments in which the slag samples without chlorine are used, the initial ZnO content is fixed at 10%. In the case of chlorine addition, the ZnO content is kept at 5% and CaCl₂ is then added at a specified molar ratio of CaCl₂:ZnO. In some

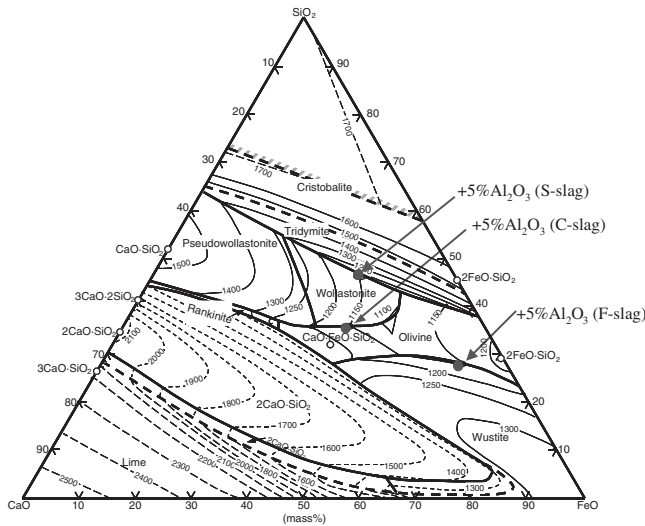


Fig. 1 The phase diagram of FeO-CaO-SiO₂ system and composition of slag used for the experiment.

Table 1 Chemical composition of produced slag.

Slag sample	CaO (%)	FeO (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	Fe ²⁺ /Fe ³⁺	Basicity (CaO/SiO ₂)
F-slag	6.96	54.41	24.35	9.7	4.58	6.20	0.29
C-slag	21.27	13.96	31.91	28.2	4.66	0.55	0.67
S-slag	17.87	17.80	44.19	15.19	4.95	1.30	0.40

cases, iron powder, Fe₂O₃ and SiO₂ are added to control FeO content, Fe²⁺/Fe³⁺ ratio and basicity (CaO/SiO₂), in order to examine their effects in detail.

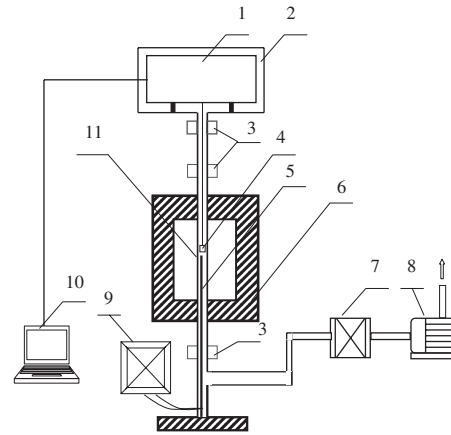
2.2 Experimental apparatus and procedures

A schematic diagram of the apparatus is shown in Fig. 2. A cylindrical cell made of pure platinum with equal height and diameter ($D = H = 10$ mm) is used. The cell comprises of two parts, upper and lower pans. The upper pan has an orifice with a diameter of 0.2 mm. The sample powder is placed as a thin layer at the bottom of the lower pan. The lids of the two pans are press-sealed. The cell is then hung at the center of the reaction tube at the hook of the precision balance by a platinum wire. The balance yields a minimum accuracy of 0.01 mg. A high vacuum condition (lower than 10^{-2} Pa) is maintained by a turbo molecular pump and a rotary pump. The temperature of the sample is controlled by a regulated electric furnace. The weight loss of the sample is continuously recorded by a data acquisition system.

Since the diameter of orifice is very small, an apparent equilibrium condition can be maintained inside the cell. The saturated vapor pressure of the sample can be obtained by eq. (1), which has been derived by Knudsen¹⁵⁾ based on the kinetic theory of gas.

$$P_e = \frac{1}{K_c A_0} \cdot \frac{\Delta W}{t} \cdot \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where P_e (Pa) represents the saturated vapor pressure of the sample, A_0 (m²) is the area of the orifice, M (kg/mol) is the molecular weight of the effusing vapor, t (s) is the experimentation time, ΔW (kg) is the weight loss of the



1. Balance
2. High vacuum room
3. Water cooling
4. Knudsen cell
5. Thermocouple
6. Electric furnace
7. Turbo molecular pump
8. Rotary pump
9. Temperature controller
10. Data acquisition system
11. Reaction tube

Fig. 2 Schematic drawing of apparatus for the Knudsen effusion measurement.

sample, T (K) is the temperature, and R (8.314 J/mol·K) is the gas constant. K_c is a coefficient reflecting the transmission probability of gas molecules throughout the orifice, since some molecules which enter the orifice will not escape but will strike the wall of the orifice and return to the cell. For a typical orifice of cylindrical shape, K_c can be evaluated by the orifice length (thickness of the cell) L and its radius r ,⁹⁾ shown as follows.

$$K_c = \frac{1 + \frac{0.4L}{r}}{1 + \frac{0.95L}{r} + 0.15 \left(\frac{L}{r}\right)^2} \quad (2)$$

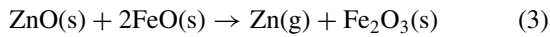
Equation (1) holds when there are no collisions between the molecules either in the cell or near the orifice and when the escaped molecules do not disturb the equilibrium between the vapor and the condensed phases. These conditions are established when the mean free path of the molecule λ , which is determined by the vapor pressure and temperature, is larger than the diameter of the orifice d and when the surface area of the condensed phase A_s is sufficiently larger than the orifice area A_0 . Generally, it was recommended^{8,9,16)} that eq. (1) is accurate when $\lambda/d > 1-10$ and $A_0/A_s < 100$. The reliability of this apparatus have been introduced in the previous literature.¹⁷⁾

3. Results and Discussion

3.1 Case for the slag system without chlorine addition

3.1.1 Vapor species

The possible vapor species of zinc formed in the present slag system have been estimated by the thermodynamic code FactSage¹⁸⁾ together with the "F*A*C*T" solution database, with the principle of Gibbs free energy minimization. The results indicates that in such cases only metallic Zn vapor is formed at the temperature range between 1073 to 1873 K, and the related reaction can be expressed as follows:



Within the experimental temperature range between 1273 and 1573 K, the standard Gibbs free energy change of the reaction (3) is positive. However, under the actual condition it could be negative and the reaction proceeds to the right side because of the relatively low partial pressure of metallic Zn.

3.1.2 Effect of temperature on the vapor pressure of metallic Zn

The Knudsen effusion method is reasonably applicable when the vapor pressure is lower than 100 Pa. On the other hand, a certain weight loss is necessary to assure the accuracy of the weight measurement. The measurement temperature range (1383–1583 K) has been determined considering these conditions. Figure 3 shows the temperature dependency of the vapor pressure of metallic Zn over different samples—90%slag+10%ZnO. For C- and S-slag samples, the vapor pressure of metallic Zn increases significantly with temperature. On the other hand, in case of F-slag, a strong temperature dependency has not been observed. This can mainly be attributed to the following two reasons, (1) reduction atmosphere led by the higher FeO content and Fe²⁺/Fe³⁺ ratio (see Table 1) results in sufficient driving force to form metallic Zn at low temperature, (2) preliminary loss of zinc during the preheating operation. Figure 4 shows the heating profile of the sample cell. In order to obtain a stable vacuum condition and to stabilize the weight readings, the sample has been held at 1073 K for a certain period of time and the temperature is then raised to a target value

(1383–1583 K) in 30 min. The weight loss of the sample during the holding period at 1073 K can be neglected since extremely small quantity of metallic Zn is formed. During the heating period from 1073 K to the specified temperature, a small quantity of zinc is vaporized. Therefore, the ZnO content of the sample is lower than the initial value (10%) at the starting time of the measurement. Considering the above fact, the authors suggest to correct the temperature dependency for F-slag. The actual vapor pressure data for the sample (90%F-slag+10%ZnO) are estimated as the broken line in Fig. 3, indicating that the pressure increases with an increase in temperature. Due to their lower FeO content and lower Fe²⁺/Fe³⁺ ratio, the weight loss of C- and S-slag samples can be neglected until the starting time of the measurement.

Additionally, Fig. 3 suggests that due to higher FeO content and higher Fe²⁺/Fe³⁺ ratio the vapor pressure of metallic Zn over F-slag sample is much higher than those over S- & C-slag sample even at the same temperature. However, the difference among those decreases with an increase in temperature. It clearly shows that for a sample having lower reduction atmosphere, an increase in temperature is more effective to promote the evaporation of metallic Zn.

3.1.3 Effect of initial content of ZnO

Figure 5 shows the vapor pressure of metallic Zn at 1483 K as a function of the initial content of ZnO in the samples. The vapor pressure increases with an increase of the initial ZnO content. As mentioned above, the content of ZnO in the F-slag sample at the starting time of the measurement is less than the original value. Therefore, the vapor pressure of metallic Zn is corrected, and the results are shown as the broken line in Fig. 5(a). There is a good relationship between

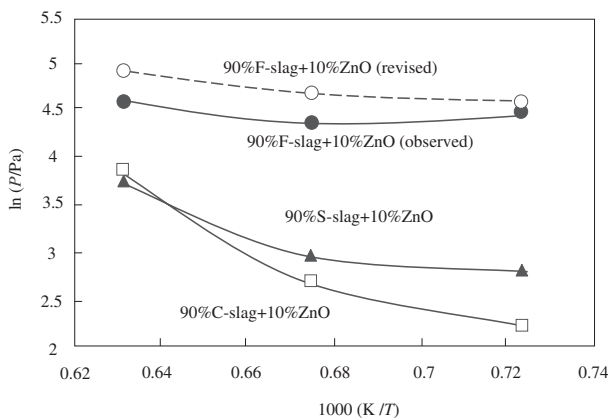


Fig. 3 Relationship between Ln P and 1/T.

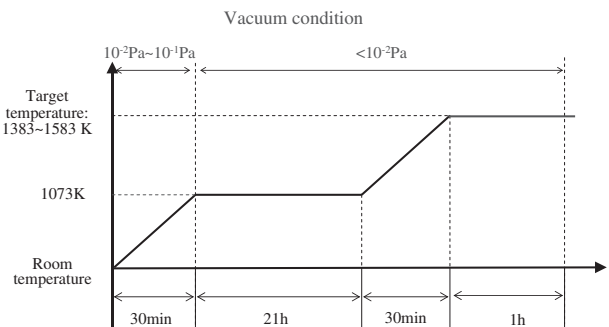


Fig. 4 Temperature profile for sample heating.

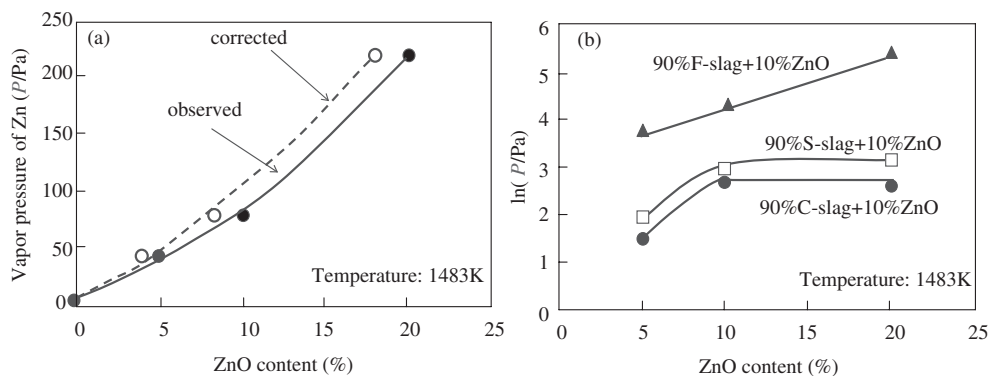


Fig. 5 Effect of ZnO content in the slag on the vapor pressure.

the vapor pressure and the initial content of ZnO in the F-slag sample at 1483 K, as expressed by the following equation.

$$P_{Zn} = 0.214ZnO\%^2 + 7.90ZnO\% + 2.63 R^2 = 0.997 \quad (4)$$

where P_{Zn} (Pa) represents the vapor pressure of metallic Zn from the F-slag sample at 1483 K and ZnO% represents the initial mass content of ZnO. According to the eq. (3), its equilibrium constant K_{eq} can be represented as follows,

$$\frac{P_{Zn}a_{Fe_2O_3}}{a_{ZnO}a_{FeO}^2} = K_{eq}, \quad (5)$$

where, $a_{Fe_2O_3}$, a_{FeO} , a_{ZnO} are the activities of Fe_2O_3 , FeO and ZnO in the slag, respectively, and p_{Zn} can be expressed as $P_{Zn}(Pa)/103125(Pa)$. Therefore, p_{Zn} should be linearly dependent on ZnO%, when the activity coefficient of ZnO is kept constant for the range of ZnO content. The authors suggest a possible reason for the non-linear relationship for ZnO% in eq. (4) as concentration dependent of the activity coefficient of ZnO.

The results shown in Fig. 5(b) indicate that the vapor pressures for C- and S-slag increase with the increase in the initial content of ZnO, and they remain constant over 10%. This may be attributed to their low FeO content (low Fe^{2+}/Fe^{3+} ratio) resulting in an insufficient driving force to form the metallic Zn vapor (eq. (3)).

3.1.4 Effect of slag compositions on the vapor pressure of metallic Zn

(1) Effect of basicity

The measured vapor pressures of metallic Zn for slag samples having different FeO contents are shown as a function of slag basicity in Fig. 6. It suggests that the vapor pressure increases with an increase in the slag basicity. This could be explained by the fact that the increase in basicity increases the ZnO activity because of a stronger affinity between CaO and other slag components such as SiO_2 and Fe_2O_3 . A similar tendency has been reported by M. A. Abdelatif⁽¹⁹⁾ on the zinc recovery from metallurgical wastes such as the dust of the lead blast furnace after the Cl removal pretreatment at 1673–1773 K. Their results showed that after the heat treatment, the amount of residual zinc has decreased with the increase of slag basicity.

(2) Effect of FeO content and Fe^{2+}/Fe^{3+} ratio

Figure 7 shows the vapor pressure of metallic Zn as a function of FeO content at different values of basicity and

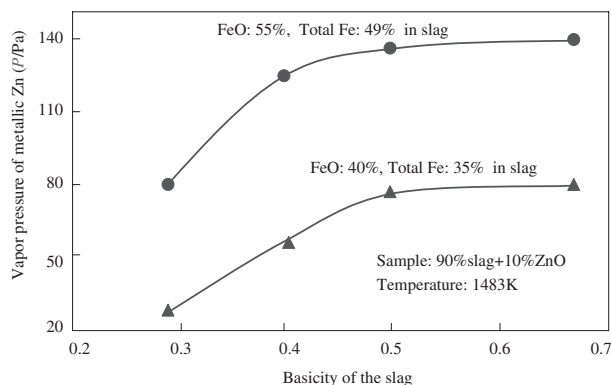


Fig. 6 Vapor pressure of metallic Zn as a function of the basicity of the slag.

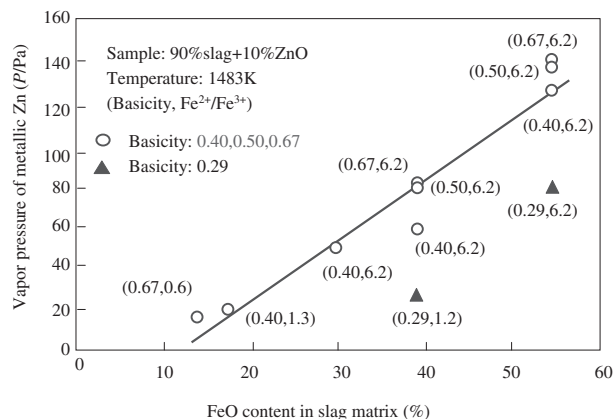


Fig. 7 Vapor pressure of metallic Zn as a function of FeO in slag.

Fe^{2+}/Fe^{3+} ratio. The vapor pressure shows a strong dependency on the FeO content. Further, when the basicity is above 0.40, there is a linear relationship between the vapor pressure and the FeO content independent of the Fe^{2+}/Fe^{3+} ratio. This relationship can be expressed by the following equation:

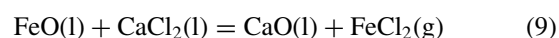
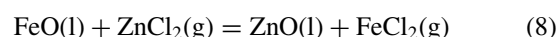
$$P_{Zn}(Pa) = 2.96FeO\% - 35.67 R^2 = 0.943 \quad (6)$$

where FeO(%) represents the FeO content in the slag. It indicates that FeO mainly behaves as a basic compound, since the vapor pressure of metallic Zn significantly increases due to the increase in ZnO activity with increasing in FeO content. On the other hand, the Fe^{2+}/Fe^{3+} ratio gives smaller effect on the vapor pressure of metallic Zn.

3.2 Case for the slag system with Cl addition

3.2.1 Vapor species

Major vapor species formed from the sample, 95F-slag+5%ZnO+CaCl₂ (ZnO:CaCl₂ = 1:1 in mol), has been estimated by the calculation using FactSage⁽¹⁸⁾ based on the principle of Gibbs free energy minimization. The considered reactants are FeO, Fe_2O_3 , CaO, SiO_2 , Al_2O_3 , ZnO, and CaCl₂ with the same compositions as that of experimental sample. The masses of the formed products have been then calculated under the experimental temperature range between 673 and 1873 K in a pure Ar atmosphere with the total pressure of 1.01×10^5 Pa. The details are introduced in the previous literature⁽¹⁴⁾ and the results are shown in Fig. 8. Three types of vapor species, metallic Zn, ZnCl₂, and FeCl₂, are dominant in the present system at temperatures between 773 and 1873 K. The proposed chemical forming reactions of metallic Zn and ZnCl₂ are expressed by eq. (3) and (7). FeCl₂ vapor can mainly be obtained by eq. (8) and partly by eq. (9).



From the estimation that zinc chloride gives much higher vapor pressure than metallic Zn, the temperature range of the measurement is set at between 973 and 1058 K. Figure 8 indicates that within this temperature range, ZnCl₂ is the main species of the vapor (>90%) and the ratios of metallic Zn and FeCl₂ (<10%) could be neglected. A considerably

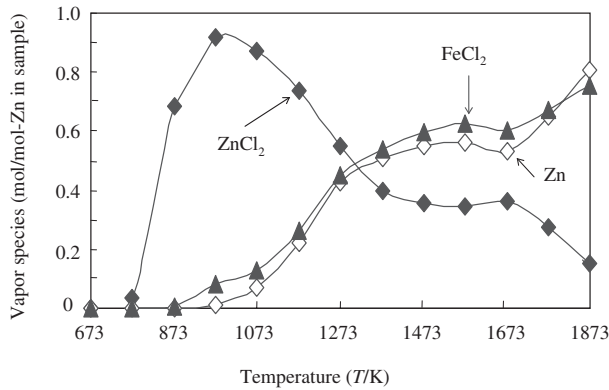


Fig. 8 Calculation results for the vapor species formed from the sample of 95%F-slag+5%ZnO+CaCl₂ (ZnO:CaCl₂ = 1:1 in mol).

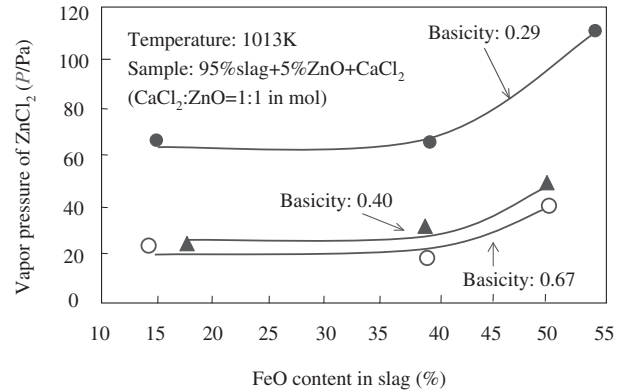


Fig. 10 Effect of FeO content of slag on the vapor pressure.

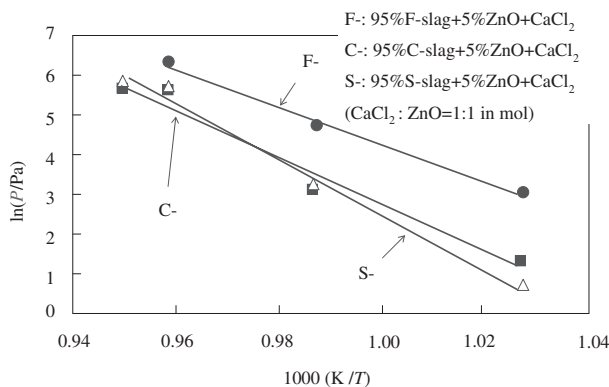


Fig. 9 Temperature dependence of vapor pressure.

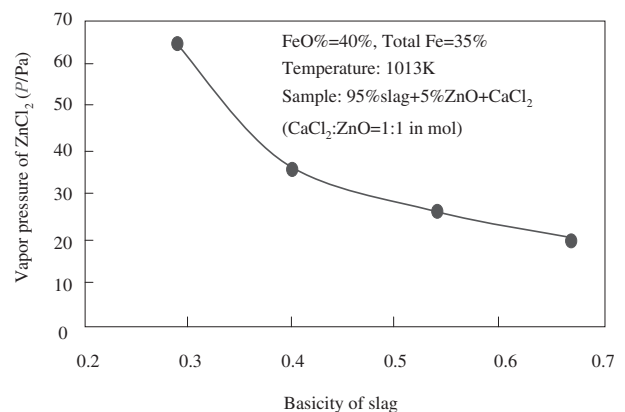


Fig. 11 Effect of slag basicity on the vapor pressure of ZnCl₂.

small amount of the metallic Zn and FeCl₂ vapors is estimated to be produced in C- and S-slag due to their lower reduction atmosphere. Therefore, under the present experimental conditions, it is assumed that ZnCl₂ is the only vapor species and contributes to the total weight loss of the sample. Its vapor pressure can be obtained by using of eq. (1).

3.2.2 Temperature dependency of the vapor pressure of ZnCl₂

Figure 9 shows the temperature dependency of the vapor pressure of ZnCl₂ for the sample 95%slag+5%ZnO+CaCl₂ (CaCl₂:ZnO = 1:1 in mol). The vapor pressure of ZnCl₂, P_{ZnCl_2} (Pa), increases with increasing temperature. The relationships obtained between $\ln P_{\text{ZnCl}_2}$ and $1/T$ are observed to be linear.

3.2.3 Effect of slag compositions

(1) Effect of FeO content

Figure 10 shows the vapor pressure of ZnCl₂ as a function of FeO content in slag for the sample 95%slag+5%ZnO+CaCl₂ (CaCl₂:ZnO = 1:1 in mol) at 1483 K. The present results that vapor pressure of ZnCl₂ increases with the increase of FeO content suggest the increase of zinc activity with the increase of FeO content which leads to further enhancement of the chlorination reaction.

(2) Effect of basicity

Figure 11 shows the effect of basicity on the vapor pressure of ZnCl₂ obtained for the sample 95%slag+5%ZnO+CaCl₂ (CaCl₂:ZnO = 1:1 in mol) at a constant

FeO content of 40%. Unlike the case without chlorine addition, the vapor pressure of ZnCl₂ decreases with the increasing slag basicity. This can be explained by the fact that the resulting large activity of CaO tends to prevent the reaction (7). Further, the previous research^{20,21} has reported that the Cl activity in slag decreases with increasing basicity of the slag system of CaO-SiO₂-FeO/Al₂O₃, which leads to the suppression of the zinc chloride formation.

3.2.4 Effect of the admixing ratio of CaCl₂ to ZnO

Figure 12 shows the effect of the mixing ratio of CaCl₂ to ZnO on the vapor pressure of ZnCl₂ for the sample 95%slag+5%ZnO+CaCl₂ at 1483 K. The vapor pressure of ZnCl₂ increases with the increasing molar ratio of CaCl₂/ZnO up to 1.5, while it remains constant above that value.

3.3 Discussions on the temperature dependency of the vapor pressure of zinc

Since the Knudsen cell measurement has been carried out under an equilibrium condition, the corresponding Gibbs free energy should be zero. Therefore, in the case with chlorine addition, the following relation will be assumed.

$$\ln \left(\frac{P_{\text{ZnCl}_2}}{103125} \right) \cdot a_{\text{CaO}} = - \frac{\Delta H_7^0}{RT} + \frac{\Delta S_7^0}{R} \quad (10)$$

On the other hand, in the case without chlorine addition,

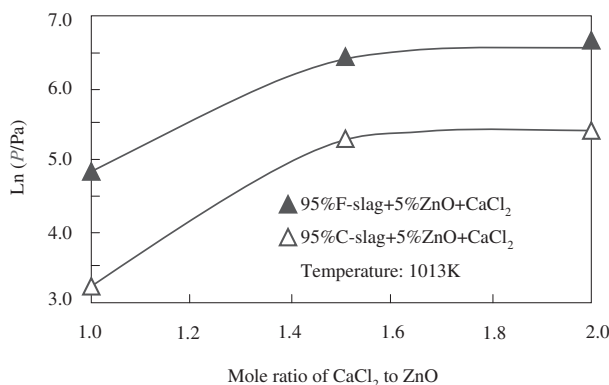


Fig. 12 Effect of admixing ratio of CaCl₂ to ZnO on the vapor pressure of ZnCl₂.

$$\ln \left(\frac{P_{\text{Zn}}}{103125} \right) \cdot a_{\text{Fe}_2\text{O}_3} = -\frac{\Delta H_3^0}{RT} + \frac{\Delta S_3^0}{R} \quad (11)$$

where ΔH_2^0 , ΔS_2^0 , ΔH_7^0 , and ΔS_7^0 represent the standard enthalpies and standard entropies of eq. (3) and (7), respectively, a_{CaO} and a_{CaCl_2} represent the activities of CaO and CaCl₂ in slag, respectively.

According to the measurement results, for the case with chlorine addition, the natural logarithm of ZnCl₂ pressure ($\ln P_{\text{ZnCl}_2}$) is a linear function of the reciprocal of temperature ($1/T$) (Fig. 9). This implies that the ratio of $a_{\text{CaO}}/a_{\text{ZnO}}a_{\text{CaCl}_2}$ is kept at a constant value. In contrast, $\ln P_{\text{Zn}}$ shows highly non-linear dependency on $1/T$ (Fig. 3). The authors suggest a possible reason that the activities of Fe₂O₃ and FeO change with changing temperature.

4. Conclusions

The vapor pressures of metallic Zn and ZnCl₂ for the Fe₁O-CaO-SiO₂-Al₂O₃ slag system have been obtained by the Knudsen effusion method under various conditions such as temperature and slag compositions. The results are summarized as the follows:

- (1) The vapor pressures of metallic Zn and ZnCl₂ increase with increasing temperature. For ZnCl₂, a linear relationship between the logarithm of vapor pressure ($\ln P$) and the reciprocal of temperature ($1/T$) is observed.
- (2) Higher FeO content in slag leads to higher vapor pressures of metallic Zn and ZnCl₂. When the basicity is higher than 0.4, the vapor pressure of metallic Zn gives a linear relationship with the FeO content of slag

regardless of Fe²⁺/Fe³⁺ ratio.

- (3) Basicity of slag shows different effects on the vapor pressure of metallic Zn and ZnCl₂. The former increases while the latter decreases with the increase in the basicity of slag.
- (4) The vapor pressure of ZnCl₂ increases with the increasing molar ratio of CaCl₂ to ZnO (CaCl₂/ZnO) up to 1.5, and levels off above that value.

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