Vapor Pressure of Zinc and Zinc Chloride in the FeO-CaO-SiO$_2$-Al$_2$O$_3$ Slag System

Yanling Zhang, Etsuro Shibata, Eiki Kasai and Takashi Nakamura

**Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan**

Vapor pressure of zinc from the FeO-CaO-SiO$_2$-Al$_2$O$_3$ 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 ZnCl is predominant and the formation ratio of metallic Zn and FeCl$_2$ can be neglected. In the measurements, the vapor pressures of metallic Zn and ZnCl$_2$ increase with increasing temperature. For ZnCl$_2$, 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 ZnCl$_2$. 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 ZnCl$_2$. [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. So far, some experimental researches have been performed on the partitioning of heavy metals under incineration and combustion condition (at 873 K–1273 K) along with some thermodynamic equilibrium calculations for the formation of vapor species. 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. Although this method has rarely been used for metal chlorides, it has long been employed for measurements of organic compounds.

In this study, the vapor pressure of zinc for the slag system FeO-CaO-SiO$_2$-Al$_2$O$_3$ 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-SiO$_2$-Al$_2$O$_3$ system was employed as the slag sample since it has the common composition of the matrix in the waste incineration ashes. 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-SiO$_2$ 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 SiO$_2$ content. Their chemical compositions are shown in the phase diagram of the FeO-CaO-SiO$_2$ system (Fig. 1). For each slag sample, the Al$_2$O$_3$ content is set at 5%. These slag samples are prepared in the same manner as that described in the previous report. 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 CaCl$_2$ is then added at a specified molar ratio of CaCl$_2$:ZnO. In some
cases, iron powder, Fe$_2$O$_3$ and SiO$_2$ are added to control FeO content, Fe$^{2+}$/Fe$^{3+}$ ratio and basicity (CaO/SiO$_2$), in order to examine their effects in detail.

### Table 1 Chemical composition of produced slag.

<table>
<thead>
<tr>
<th>Slag sample</th>
<th>CaO (%)</th>
<th>FeO (%)</th>
<th>SiO$_2$ (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>Al$_2$O$_3$ (%)</th>
<th>Fe$^{2+}$/Fe$^{3+}$</th>
<th>Basicity (CaO/SiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-slag</td>
<td>6.96</td>
<td>54.41</td>
<td>24.35</td>
<td>9.7</td>
<td>4.58</td>
<td>6.20</td>
<td>0.29</td>
</tr>
<tr>
<td>C-slag</td>
<td>21.27</td>
<td>13.96</td>
<td>31.91</td>
<td>28.2</td>
<td>4.66</td>
<td>0.55</td>
<td>0.67</td>
</tr>
<tr>
<td>S-slag</td>
<td>17.87</td>
<td>17.80</td>
<td>44.19</td>
<td>15.19</td>
<td>4.95</td>
<td>1.30</td>
<td>0.40</td>
</tr>
</tbody>
</table>

#### 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 Knudsen$^{[5]}$ 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, $A_0$ (m$^2$) is the area of the orifice, $M$ (kg/mol) is the molecular weight of the effusing vapor, $t$ (s) is the experimentation time, $\Delta W$ (kg) is the weight loss of the 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 $r$ 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 $\lambda$, 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$^{[8,16]}$ that eq. (1) is accurate when $\lambda/d > 10$–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 FactSage$^{[18]}$ together with the “Fe+Al+Ca+Si+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:
ZnO(s) + 2FeO(s) → Zn(g) + Fe₂O₃(s) \( (3) \)

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. 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.

### 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 the ZnO content and the corrected 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.

\[ P_{Zn} = 0.214ZnO\%^2 + 7.90ZnO\% + 2.63 R^2 = 0.997 \] (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,

\[
\frac{P_{Zn}a_{Fe_2O_3}}{a_{ZnO}a_{FeO}} = K_{eq}
\] (5)

where, \( a_{Fe_2O_3}, a_{FeO}, a_{ZnO} \) are the activities of Fe\(_2\)O\(_3\), 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\(_2\)O\(_3\). A similar tendency has been reported by M. A. Abdel-latif\(^{19}\) 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 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:

\[ P_{Zn}(Pa) = 2.96FeO\% - 35.67 R^2 = 0.943 \] (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, 95%F-slag+5%ZnO+CaCl\(_2\) (ZnO:CaCl\(_2\) = 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\(_2\)O\(_3\), CaO, SiO\(_2\), Al\(_2\)O\(_3\), ZnO, and CaCl\(_2\) 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 \times 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, ZnCl\(_2\), and FeCl\(_2\), are dominant in the present system at temperatures between 773 and 1873 K. The proposed chemical forming reactions of metallic Zn and ZnCl\(_2\) are expressed by eq. (3) and (7). FeCl\(_2\) vapor can mainly be obtained by eq. (8) and partly by eq. (9).

\[
\begin{align*}
\text{ZnO(l)} + \text{CaCl}_2(l) &\rightleftharpoons \text{CaO(l)} + \text{ZnCl}_2(g) \\
\text{FeO(l)} + \text{ZnCl}_2(g) &\rightleftharpoons \text{ZnO(l)} + \text{FeCl}_2(g) \\
\text{FeO(l)} + \text{CaCl}_2(l) &\rightleftharpoons \text{CaO(l)} + \text{FeCl}_2(g)
\end{align*}
\] (7, 8, 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, ZnCl\(_2\) is the main species of the vapor (>90\%) and the ratios of metallic Zn and FeCl\(_2\) (<10\%) could be neglected. A considerably
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, \( P_{\text{ZnCl}_2} \), 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 effect of FeO content of slag on the vapor pressure. 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.

(2) Effect of basicity

Figure 11 shows the effect of slag basicity on the vapor pressure of ZnCl₂. 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.

\[
\ln \left( \frac{P_{\text{ZnCl}_2}}{103125} \right) \cdot \frac{a_{\text{CaO}}}{a_{\text{ZnCl}_2}} = - \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]  

On the other hand, in the case without chlorine addition,
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 Fe\(^{2+}/Fe^{3+}\) 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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