Chloride Capacities of CaO–SiO$_2$–Al$_2$O$_3$ (–FeO, MgO, MnO) Slags and Their Application in the Incineration Processes

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Thermodynamic properties of chlorine in the CaO–SiO$_2$–Al$_2$O$_3$–FeO, MgO, MnO) and CaO–SiO$_2$–FeO slags have been investigated. The experiments were carried out under relatively high oxygen partial pressure, using gas–slag equilibrium, controlling both $P_{O_2}$ and $P_{H_2S}$ simultaneously ($P_{O_2}=10^{-5}$–$10^{-10}$ atm, $P_{H_2S}=10^{-7}$–$10^{-10}$ atm at 1 673 K) by flowing gas mixture of $H_2$, $CO_2$, $HCl$ and $Ar$ gases, and the solubility of chlorine in the 40mass%CaO–40mass%SiO$_2$–20mass%Al$_2$O$_3$ slag was found to vary in proportion to $P_{O_2}^{-1/4}$ and $P_{H_2S}^{1/2}$, which was the same relationship observed in the reducing conditions. Accordingly, chloride capacity ($C_{Cl^-}$) is used to evaluate ability of slags to absorb chlorine. The $C_{Cl^-}$ values were observed to increase with increasing slag basicity, and showed a reasonable relationship with that of $C_{SO_2}^-$. Based on the result obtained in the present study, chlorine distribution during incineration with slags was predicted quantitatively.

KEY WORDS: iron- and steelmaking slags; gas–slag equilibrium; chlorine; solubility of chlorine; chloride capacity; sulfide capacity; slag basicity; incineration.

1. Introduction

Ecological problems have recently been treated in iron- and steelmaking processes, as is seen in the development of waste plastic injection into a blast furnace. However, we have to consider more effective utilization of such a high temperature mass production system as iron- and steelmaking processes for the waste management. In the near future, even the waste containing chlorine such as polyvinyl chloride (PVC) should be treated, but we have to overcome the problem of dioxine and HCl generation. In order to predict the generation of such toxic gases, the behavior of chlorine in high temperature furnaces must be predicted and the evaluation of chlorine gas absorption into slags becomes very important. From this viewpoint, Hirosumi and Morita clarified that chlorine dissolves into the slag as $Cl^-$ ion in low oxygen partial pressure, and they defined the ability of slags to capture chlorine as follows.

$$C_{Cl^-} = \frac{(mass\%Cl^-)P_{O_2}^{1/4}}{P_{H_2S}^{1/2}}$$

However, the previous research was conducted under strongly reducing conditions where oxygen partial pressure is much lower than that of waste incineration. Seeing that sulfur exists as sulfate at higher oxygen partial pressure for instance, chlorine could dissolve as oxochloride such as ClO$^-$, ClO$_2^-$, etc.

In the present study, by measuring the chlorine concentrations at various compositions of the CaO–SiO$_2$–Al$_2$O$_3$ (–FeO, MgO, MnO) and CaO–SiO$_2$–FeO slags in comparatively high oxygen partial pressure ($P_{O_2}=10^{-5}$–$10^{-13}$ atm), the dissolution mechanism of chlorine into molten slags has been clarified and the ability of slags to capture chlorine has been evaluated in terms of chloride capacity, $C_{Cl^-}$.

Finally, based on the result obtained in this study, chlorine distribution during incineration with slags was predicted quantitatively.

2. Experimental

A SiC resistance furnace with a fused mullite tube (53 mm ID and 1 000 mm length) was employed and experimental temperature (1 673 K) was controlled by a proportional-integral differential (PID) controller and kept within ±1 K with a Pt–6%Rh/Pt–30%Rh thermocouple. Schematic sketch inside the furnace is drawn in Fig. 1.

During experiments, the atmosphere was controlled by flowing a gas mixture of $CO_2$, $H_2$ and $HCl$ at a rate of 50–100 Ncm$^3$/min. $P_{O_2}$ was controlled by fixing initial $P_{CO_2}$ and $P_{H_2}$ according to Eqs. (1) and (2), as shown their final $P_{CO_2}$ equals to $P_{H_2O}$. On the other hand, $P_{H_2S}$ was controlled by the final $P_{HCl}$ and $P_{H_2}$ according to Eqs. (3) and (4), when Eq. (1) is in equilibrium state.

$$CO_2(g) + H_2(g) = CO(g) + H_2O(g) \quad (1)$$  
$$\Delta G_f^o = 33 500 – 29.4 T [\text{J/mol}] \quad (2)$$  
$$HCl(g) = \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \quad (3)$$  
$$\Delta G_f^o = 94 200 + 6.41 T [\text{J/mol}] \quad (4)$$

In order to control partial pressures of gas species precisely, capillary mass flow units were used. In the gas pu-
rification system, H$_2$SO$_4$ and Mg(ClO$_4$)$_2$ were used to re-
move H$_2$O, and soda lime were used to remove CO$_2$.

The slag samples were prepared by mixing CaO calcined
from CaCO$_3$, reagent grade SiO$_2$, Al$_2$O$_3$, FeO, MgO and
MnO. About 3 g of slags were charged into crucibles, then
kept in a hot zone of the furnace. The materials of crucible
were selected according to the slag systems and the atmo-
sphere of experiment. Iron crucible was used for FeO con-
taining slags, and Ni crucible was used when oxygen partial
pressure was less than 10$^{-11}$ atm, while platinum crucibles
in the other cases. The experimental time was determined
to be 24 h, which were confirmed enough for the equilibri-
um attainment by the preliminary experiments. Just before
taking out the samples, the experimental gas mixture was
switched to Ar gas for 1 min. The samples were withdrawn
and quenched in the flushing Ar gas and subjected to chemi-
ical analyses.

The Ca, Al, Fe, Mg and Mn contents of the slags were
determined by inductively coupled plasma (ICP) emission
spectrometry at the wavelengths of 318, 396, 238, 279 and
258 nm, respectively, while SiO$_2$ and total chlorine contents
by gravimetry and silver nitrate titration.

The slag compositions were corrected so that the total of
contents of CaO, SiO$_2$, Al$_2$O$_3$, FeO, MgO and MnO may be-
come 100 mass%. Namely, the chlorine contents are ex-
cluded in representing the slag compositions after the ex-
periments.

3. Results and Discussion

3.1. Chlorine Dissolution into Molten Slag

In order to investigate the behavior of chlorine in mol-
ten slags in comparatively high oxygen partial pressure,
the relationship between the solubility of chlorine in the
slag, (mass%Cl), and $P_{Cl_2}$, as well as that between
(mass%Cl) and $P_{O_2}$ was investigated. The 40mass%Cao-
40mass%SiO$_2$–20mass%Al$_2$O$_3$ slag was selected with $P_{Cl_2}$
and $P_{O_2}$, ranging from approximately $10^{-10}$ to $10^{-7}$ atm
and $10^{-13}$ to $10^{-7}$ atm, respectively at 1673 K. Experimental
conditions and results are summarized in Table 1.

As seen in Fig. 2, there is a linear relationship between
log $P_{O_2}$, and log(mass%Cl$^-$)/$P_{Cl_2}^{1/2}$, and the slope of the line
is close to $-1/4$. Accordingly, the solubility of chlorine in the
slag is considered to be in proportion to $P_{O_2}^{-1/4}$ and $P_{Cl_2}^{1/2}$.
Based on this result, the dissolution mechanism of chlorine
into the slag at the present experimental condition can be
described as Eq. (5) and the dissolution mechanism of chlo-
rine is the same as that under the reducing conditions re-
ported by Hirosumi et al.2)

$$\frac{1}{2} Cl_2(g) + \frac{1}{2} O^2-(slag) = Cl^-(slag) + \frac{1}{4} O_2(g) \quad (5)$$

This means that chlorine also dissolves into the slag as Cl$^-$
ion and oxychloride ions may not be stable in such high
oxygen partial pressures. Henceforth, chloride capacity $C_{Cl^-}$
defined by Hirosumi et al.2 as Eq. (6) are brought into use
as an ability of chlorine absorption in the present work.

![Fig. 1. Schematic cross section of the experimental apparatus.](image)

![Fig. 2. Relationship between oxygen partial pressure, chlorine partial pressure and concentration of chlorine in the slag at 1673 K.](image)
Here, $K_5$ is the equilibrium constant of Eq. (5), $a_{\text{O}_2}/\text{H}_2\text{O}$ is the activity of oxide ion, and $f_{\text{Cl}}/\text{H}_2\text{O}$ is the activity coefficient of chloride ion in the slag, respectively.

3.2. Effects of FeO, MgO and MnO Addition on $C_{\text{Cl}}/\text{H}_2\text{O}$

The effects of FeO, MgO and MnO addition to the 40mass%CaO–40mass%SiO$_2$–20mass%Al$_2$O$_3$ slag on its $C_{\text{Cl}}$ at 1 673 K were investigated. Experimental conditions and results are summarized in Table 2. Figure 3 shows the change in $C_{\text{Cl}}$ values with FeO, MgO and MnO content of the final slags. They slightly increased by FeO, MgO and MnO addition because of the increase in the slag basicity, although they increased drastically when Na$_2$O was added. However, the extent of the effect also implies the change in activity coefficient of chlorine in the slags seeing that MgO addition showed the smallest effect.

3.3. CaO–SiO$_2$–FeO Slag System

For the CaO–SiO$_2$–FeO system, Fe crucibles were used to determine the activity of iron oxide according to Eq. (7). Hence, the FeO content of the slag was controlled by changing oxygen partial pressure.

The activities of iron oxide calculated from the above equation ($a_{\text{FeO}}$ Calculation) were compared with those estimated from the experimental slag composition and the values at 1 873 K after Ban-ya and Hino ($a_{\text{FeO}}$ Experiment) as shown in Fig. 4. Regular solution approximation was employed in extrapolating their data to those at 1 673 K, which would be reasonable according to their findings. Since both values were in good agreement, the reaction between Fe–FeO was considered to be in an equilibrium state. Slight discrepancy at higher FeO activity could be explained by the error in the temperature extrapolation or the effect of dissolved OH$^-$ ion due to the higher partial pressure of H$_2$O.

The obtained values for $C_{\text{Cl}}$ are listed in Table 3 and iso-capacity contours are drawn in the isothermal cross section of the CaO–SiO$_2$–FeO slag system at 1 673 K (Fig. 5). As seen in the figure, $C_{\text{Cl}}$ increases as the CaO and FeO content increases, and decreases with the SiO$_2$ contents. Herewith, the effect of slag composition on the $C_{\text{Cl}}$ value was investigated using some indexes in order to reproduce the experimental results as precisely as possible. Although

### Table 2. The $C_{\text{Cl}}$ values for the CaO–SiO$_2$–Al$_2$O$_3$–FeO, MgO, MnO slags together with gas compositions at 1 673 K.

| No. | Temp.(K) | HCl (atm) | H$_2$ (atm) | CO$_2$ (atm) | Ar (atm) | P$_{\text{FeO}}$ (atm) | P$_{\text{MgO}}$ (atm) | P$_{\text{MnO}}$ (atm) | Slag composition (mass%) | $C_{\text{Cl}}$ |
|-----|----------|-----------|-------------|--------------|--------|-------------------|-------------------|-------------------|-----------------------|--------|
| 2-1 | 1675     | 0.056     | 0.128       | 0.336        | 0.480  | 9.46E-09          | 6.82E-09          |                   | CaO 38.8             | 0.3   |
| 2-2 | 1675     | 0.056     | 0.119       | 0.343        | 0.482  | 1.18E-08          | 7.99E-09          |                   | SiO$_2$ 40.9         | 0.3   |
| 2-3 | 1673     | 0.022     | 0.731       | 0.054        | 0.192  | 1.46E-12          | 1.86E-12          |                   | Al$_2$O$_3$ 20.0     | 0.3   |
| 2-4 | 1673     | 0.022     | 0.752       | 0.039        | 0.188  | 6.76E-13          | 1.74E-10          |                   | FeO 39.5             | 0.3   |
| 2-5 | 1673     | 0.039     | 0.561       | 0.060        | 0.339  | 3.20E-12          | 6.67E-10          |                   | MgO 39.5             | 0.3   |
| 2-6 | 1673     | 0.020     | 0.265       | 0.540        | 0.175  | 5.01E-09          | 4.73E-10          |                   | MnO 39.5             | 0.3   |
| 2-7 | 1673     | 0.028     | 0.054       | 0.690        | 0.229  | 3.38E-07          | 1.44E-07          |                   | Cl 39.9             | 0.3   |
| 2-8 | 1673     | 0.025     | 0.059       | 0.707        | 0.209  | 2.95E-07          | 1.03E-07          |                   | 39.9                 | 0.3   |
| 2-9 | 1673     | 0.041     | 0.075       | 0.343        | 0.341  | 1.00E-07          | 1.29E-07          |                   | 36.6                 | 0.3   |
| 2-10| 1673     | 0.029     | 0.089       | 0.646        | 0.236  | 9.80E-08          | 5.13E-08          |                   | 37.1                 | 0.3   |
| 2-11| 1673     | 0.030     | 0.081       | 0.639        | 0.250  | 1.19E-07          | 6.87E-08          |                   | 36.2                 | 0.3   |
| 2-12| 1673     | 0.031     | 0.249       | 0.464        | 0.256  | 3.97E-09          | 5.11E-09          |                   | 38.4                 | 0.3   |
| 2-13| 1673     | 0.032     | 0.244       | 0.460        | 0.264  | 4.09E-09          | 5.63E-09          |                   | 38.5                 | 0.3   |
| 2-14| 1673     | 0.028     | 0.255       | 0.486        | 0.231  | 4.19E-09          | 4.17E-09          |                   | 37.5                 | 0.3   |
| 2-15| 1673     | 0.028     | 0.258       | 0.484        | 0.230  | 4.02E-09          | 4.02E-09          |                   | 36.1                 | 0.3   |
| 2-16| 1673     | 0.031     | 0.248       | 0.463        | 0.258  | 3.99E-09          | 5.24E-09          |                   | 36.5                 | 0.3   |

Fig. 3. Effects of FeO, MgO and MnO addition to the 40mass%CaO–40mass%SiO$_2$–20mass%Al$_2$O$_3$ slag on $C_{\text{Cl}}$ at 1 673 K.

![Fig. 3](image)

Fig. 4. Relationship between $a_{\text{FeO}}$ Calculation and $a_{\text{FeO}}$ Experiment.

![Fig. 4](image)

The activities of iron oxide calculated from the above equation ($a_{\text{FeO}}$ Calculation) were compared with those estimated from the experimental slag composition and the values at 1 873 K after Ban-ya and Hino ($a_{\text{FeO}}$ Experiment) as shown in Fig. 4. Regular solution approximation was employed in extrapolating their data to those at 1 673 K, which would be reasonable according to their findings. Since both values were in good agreement, the reaction between Fe–FeO was considered to be in an equilibrium state. Slight discrepancy at higher FeO activity could be explained by the error in the temperature extrapolation or the effect of dissolved OH$^-$ ion due to the higher partial pressure of H$_2$O.

The obtained values for $C_{\text{Cl}}$ are listed in Table 3 and iso-capacity contours are drawn in the isothermal cross section of the CaO–SiO$_2$–FeO slag system at 1 673 K (Fig. 5). As seen in the figure, $C_{\text{Cl}}$ increases as the CaO and FeO content increases, and decreases with the SiO$_2$ contents. Herewith, the effect of slag composition on the $C_{\text{Cl}}$ value was investigated using some indexes in order to reproduce the experimental results as precisely as possible. Although
the use of a simple basicity index was initially tried, a little
modification brought a better relationship. Accordingly, the
following index with the cross term of $X_{\text{AlO}_{1.5}}X_{\text{FeO}}$ has been
introduced; $\vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots \vdots 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\vdots \vdot...
tween \( C_{\text{Cl}} \) and \( C_{\text{Cl}}^* \) can be derived as Eq. (13).

\[
\log C_{\text{Cl}} = \frac{1}{2} \log C_{\text{Cl}}^* + \log K_s \frac{f_{\text{Cl}}^{1/2}}{f_{\text{Cl}}} \quad \text{...(13)}
\]

Accordingly, if the last term of the right hand side of Eq. (13) is constant regardless of the slag composition, \( C_{\text{Cl}} \) is expected to change in proportion to \( C_{\text{Cl}}^* \).

**Figure 8** shows the relationship between observed \( C_{\text{Cl}} \) and the \( C_{\text{Cl}}^* \) from Fig. 7 in logarithmic scale. Although there is a temperature difference of 150 K, a good linear correlation is observed between \( \log C_{\text{Cl}}^* \) and \( \log C_{\text{Cl}} \) with a slope of approximately 1/2 which was predicted from Eq. (13).

### 3.5. Prediction of Chlorine Distribution during In-cineration with Slags

Based on the result obtained in the present study, the chlorine distribution between gas and slags can be estimated when chlorine containing waste is incinerated with slags. For example, when \( P_{\text{H}_2\text{O}} = 10^{-10} \text{ atm} \), \( C_{\text{Cl}} = 40 \) and \( \text{mass}\% \text{Cl}^- = 1 \), \( P_{\text{Cl}_2} \) becomes \( 10^{-8} \text{ atm} \). In the practical incineration processes, however, chlorine in the gas phase is considered to be oxidized mainly as HCl originating from H\(_2\)O or as chlorides of the heavy metals according to Eqs. (14) and (17), and the equilibrium partial pressures of HCl and PbCl\(_2\) can be derived from Eqs. (16) and (19) as functions of the partial pressure of H\(_2\)O and activity of PbO, respectively.

\[
\frac{1}{2} \text{H}_2\text{O}(g) + \text{Cl}^- \quad \text{(slag)} = \text{HCl}(g) + 1/2 \text{O}_2(g) \quad \text{(slag)} \quad \text{...(14)}
\]

\[
\frac{1}{2} \text{H}_2\text{O}(g) + 1/2 \text{Cl}_2(g) = \text{HCl}(g) + 1/4 \text{O}_2(g) \quad \text{...(15)}
\]

\[
P_{\text{HCl}} = \left(\frac{\text{mass}\% \text{Cl}^-}{C_{\text{Cl}}} \right) P_{\text{H}_2\text{O}} K_{15} \quad \text{...(16)}
\]

\[
P_{\text{PbCl}_2} = \left(\frac{\text{mass}\% \text{Cl}^-}{C_{\text{Cl}}} \right)^2 a_{\text{PbO}} K_{18} \quad \text{...(19)}
\]

Here, the equilibrium constants \( K_{15} \) and \( K_{18} \) can be derived from the standard Gibbs energies of formation for H\(_2\)O and HCl, and PbO and PbCl\(_2\), respectively.\(^3\) When 1 t of the slag \((C_{\text{Cl}} = 40)\) is equilibrated with 100 Nm\(^3\) of atmospheric gas at 1673 K, chlorine distributions between gas and slag phases can be estimated as shown in **Fig. 9** and **10** as functions of \( P_{\text{H}_2\text{O}} \) and \( a_{\text{PbO}} \) respectively. In **Fig. 10**, \((\text{mass}\% \text{Cl}^-)\) denotes the final chlorine content of the slags and the lower chlorine content of the slag will provide higher fractional distribution of chlorine to slag phase. As seen in the figures, more chlorine is absorbed into the slag with reduction of \( P_{\text{H}_2\text{O}} \) and \( a_{\text{PbO}} \), suggesting that dehydrating pretreatment of waste and prevention of heavy metal contamination are very effective for immobilizing chlorine into slag phase in the incineration processes. This also means that the hydration will distribute most of chlorine to gas phase producing chlorine free slags, followed by HCl recovery from the exhaust gas. Thus, the present results are supportive in predicting the behavior of chlorine between gas and slags during incineration processes quantitatively.

### 4. Conclusions

The solubility of chlorine in the molten CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–(FeO–MgO–MnO) and CaO–SiO\(_2\)–FeO slags have been measured under relatively high oxygen partial pressure by a gas–slag equilibration technique, yielding the following results:

1. The solubility of chlorine in the slag is in proportion to \( P_{\text{O}_2}^{1/4} \) and \( P_{\text{Cl}_2}^{1/2} \), showing that chlorine dissolves into
the slag as Cl\(^-\) ion, and \(C_{\text{Cl}}\) is used to evaluate the ability of chlorine absorption into slags, defined by Hirosumi \textit{et al.} \textsuperscript{23} as;

\[
C_{\text{Cl}} = \frac{\text{mass\%Cl}^-}{P_{\text{Cl}_2}}
\]

(2) The \(C_{\text{Cl}}\) value for the CaO–SiO\(_2\)–Al\(_2\)O\(_3\) slags increases by FeO, MgO and MnO addition.

(3) For the CaO–SiO\(_2\)–FeO slags, the \(C_{\text{Cl}}\) value increases as the CaO and FeO contents increase, and decreases as the SiO\(_2\) content increases.

(4) The \(C_{\text{Cl}}\) values for the CaO–SiO\(_2\)–Al\(_2\)O\(_3\)–FeO slags at 1673 K were approximated in terms of the following empirical equation:

\[
C_{\text{Cl}} = -7.2 + \frac{60X_{\text{CaO}} + 40X_{\text{FeO}}}{X_{\text{SiO}_2} + 0.67X_{\text{AlO}_3} - 5X_{\text{AlO}_3}X_{\text{FeO}}}
\]

(5) The \(C_{\text{Cl}}\) value is less sensitive to the slag composition than that of \(C_{\text{S}^-}\). There is a good linear correlation between log \(C_{\text{S}^-}\) and log \(C_{\text{Cl}}\) with the slope of approximately 1/2 which is consistent with the value predicted from their definitions with an assumption.

(6) Based on the result obtained in the present study, quantitative prediction of chlorine distribution during incineration with slags was performed.

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