1. Introduction

In Japan, the municipal solid waste is mainly treated by incineration process from the viewpoint of volume reduction for reclamation, sanitation, minimization of the environmental load and so on. The amount of the incinerated municipal solid waste is up to 42 012 kt, and 5 112 kt of incineration residue is generated from the incineration processes in financial year 2003.1) Incineration residue consists of bottom ash and fly ash. In the case of stoker type incineration furnace, discharged amount of each ash is 60 to 170 kg/t-waste for bottom ash and 10 to 50 kg/t-waste for fly ash.2) On the other hand, fluidized bed type furnace discharges 60 to 110 kg/t-waste of fly ash and no bottom ash.2) Bottom ash is mainly composed of Al, Ca, Fe, K, Na and Si in stable oxides,3) and contains some heavy metals such as Cd, Cr, Cu, Pb and Zn.4) On the contrary, fly ash contains considerable amount of metal chlorides. Especially, heavy metals such as lead and zinc easily react with chlorine in the incineration process, and evaporate and condensate as chlorides and oxychlorides. Since heavy metal chlorides exhibit high toxicity and environmental load, fly ash is classified as special management industrial waste and the special treatment such as cement solidification and chemical treatment must be conducted for fly ash stabilization before reclamation, which causes the expensive cost for waste treatment processes.

However, those heavy metals contained in fly ash could become valuable metal resources if the efficient separation processes are developed. The ratio of reserves to production is estimated to be 20 and 22 years for lead and zinc from world reserves and mine production in 2005, respectively.5) Therefore, effective recycling of these valuable metals is an important and urgent issue. Lead and zinc chloride show high vapor pressures and low boiling points at relatively low temperature. Therefore, it is considered that the evaporation method is the efficient recycling process for separation and recovery of lead and zinc from fly ash, and evaporation kinetics of these chlorides is the important knowledge.

Present authors have investigated the chlorination and evaporation behaviors of these metals. Son and Tsukihashi6–8) clarified the oxychloride formation of PbOCl and ZnOCl for lead and zinc from the vapor pressure measurement of these chlorides at oxidizing atmosphere. Matsuura et al.9–12) measured the chlorination and evaporation rates of these oxides at chlorinating and oxidizing atmosphere. Increase of oxygen partial pressure increased with increasing oxygen partial pressure in the atmosphere, which might be due to the effect of oxychloride formation.
rate of zinc oxides due to the formation of oxychlorides, while it was not so effective for lead oxide chlorination. From the previous studies, it is considered that change of atmosphere intensively affects the evaporation behavior of these chlorides.

In the present study, the evaporation kinetics of PbCl$_2$ and ZnCl$_2$ from PbCl$_2$–ZnCl$_2$ melt has been measured and the effects of temperature, composition of the melt and the oxygen partial pressure of atmosphere have been investigated. Based on the measured results, the evaporation mechanism and the application for the recovery process of metals from fly ash have been discussed.

2. Experimental

Figure 1 shows the schematic diagram of experimental apparatus. A mullite reaction tube (O.D. 60 mm, I.D. 52 mm and Height 1000 mm) was set in an electric furnace, and a ceramic supporter was placed inside a hot zone. Reagent grade of PbCl$_2$ and ZnCl$_2$ were weighed and mixed in a mullite crucible (O.D. 21 mm, I.D. 17 mm and Height 100 mm) to prepare 3 g of samples. That prepared crucible was inserted into a heated electric furnace, and the measurement started at that time. Experimental temperature was measured by an R-type thermocouple inserted from the bottom of a furnace. Since the decline in the temperature by approximately 30 K was observed when the crucible was put in the supporter, temperature of the furnace was kept at higher temperature by 30 K than experimental temperature and the setting temperature was changed to originals immediately after the crucible was inserted. Temperature in a hot zone returned to prescribed ones within 3 min after the beginning of experiments. Argon, air or pure oxygen gases were introduced on the specimen through a gas lance with gas flow rate of 600 cm$^3$/min. At the end of each experiment, the crucible was taken out from the furnace quickly and quenched by flushing argon gas. Weight of the crucible was measured before and after each experiment. The chloride specimen in the crucible was taken out and the contents of zinc and lead were analyzed by ICP-AES. All treatments such as preparation of samples and weight measurements were conducted in a glove box purged by dried argon gas due to the strong hygroscopicity of zinc chloride.

3. Results and Discussion

In the present study, the evaporation rate of the molten PbCl$_2$–ZnCl$_2$ system was measured at 973, 1023 and 1073 K with the initial content of (mass%Zn)/(mass%Pb) = 0.1 to 3.0. Initial content of PbCl$_2$–ZnCl$_2$ melts are shown in Table 1.

Evaporation rate measurements were conducted for 10 to 40 min with the same experimental condition. All experimental conditions and results are shown in Table 2. In some measurements at 1073 K, chloride melts evaporated very fast and the amounts of experimental residue were too little to analyze.

3.1. Effect of Temperature

The effect of temperature on the evaporation rate was investigated from 973 to 1073 K in Ar atmosphere with (mass%Zn)/(mass%Pb) = 3.0. Figure 2 shows the change of weight loss of specimen with time. The weight loss increased almost linearly with time at 973 and 1023 K. On the other hand, in the case of evaporation of chloride melt at 1073 K, evaporation rate drastically decreased after 20 min because over 80% of specimen already evaporated at 20 min and the amount of melts decreased.

Figure 3 shows the change of the ZnCl$_2$ content of molten chloride with time. The ZnCl$_2$ content in PbCl$_2$–ZnCl$_2$ melt decreased with evaporation time, which means that ZnCl$_2$ evaporates preferentially from PbCl$_2$–ZnCl$_2$ melt. Boiling point of ZnCl$_2$ is 1004 K, while that of PbCl$_2$ is 1223 K and the vapor pressure of pure PbCl$_2$ is from 3.43×10$^5$ to 1.67×10$^6$ Pa from 973 to 1073 K.$^{13}$ It is considered that these differences in physicochemical properties cause the different evaporation rates of these chlorides.

Both of evaporated amounts of PbCl$_2$ and ZnCl$_2$ could be calculated from mass balance calculations for each element. Figure 4 shows the change of the evaporated amounts of PbCl$_2$ and ZnCl$_2$ with time. From this figure, it is obvious that the evaporated amount of PbCl$_2$ is negligibly small compared to that of ZnCl$_2$. Therefore, the evaporation rate of PbCl$_2$–ZnCl$_2$ melt would be almost same as that of ZnCl$_2$ at these temperatures and it is considered that ZnCl$_2$ could be separated by evaporation process. Since evaporated amount of ZnCl$_2$ linearly increased with time, the evaporation rate of ZnCl$_2$ was defined as Eq. (1),

\[
r_{\text{ZnCl}_2}^{\text{eva}} = \frac{W_{\text{ZnCl}_2}^{\text{eva}}}{t}
\]

where, \(r_{\text{ZnCl}_2}^{\text{eva}}\) (g/min) is the evaporation rate of ZnCl$_2$, \(W_{\text{ZnCl}_2}^{\text{eva}}\) (g) is the evaporated amount of ZnCl$_2$, and \(t\) (min) is the evaporation time, respectively. Therefore, the evaporation rate is represented as a slope of lines in Fig. 4. Obtained evaporation rates by linear regression were 0.0157±0.001,
The evaporation rate constant was defined by Eq. (2),

\[
K_{\text{eva}} = \frac{r_{\text{eva}}}{A}
\]

where \(K_{\text{eva}}\) (g/cm\(^2\)·min) is the ZnCl\(_2\) evaporation rate constant.

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\]

where \(K_{\text{eva}}\) (g/cm\(^2\)·min) is the ZnCl\(_2\) evaporation rate constant.

The evaporation rate constant was defined by Eq. (2),

\[
K_{\text{eva}} = \frac{r_{\text{eva}}}{A}
\]

where \(K_{\text{eva}}\) (g/cm\(^2\)·min) is the ZnCl\(_2\) evaporation rate constant.
stant and $A$ (cm$^2$) is the reaction surface area (2.27 cm$^2$). Figure 5 shows the temperature dependence of evaporation rate constant of ZnCl$_2$. The logarithm of evaporation rate constant has a linear relationship with reciprocal temperature and the slope of line is calculated to be $-10130\pm220$ obtained by the linear regression of Arrhenius plot. The activation energy of ZnCl$_2$ evaporation was 194 kJ/mol. Bockris et al.\textsuperscript{14) reported the activation energies of self diffusion of zinc and chloride ions in pure ZnCl$_2$ melt. Activation energies drastically decreased with increasing temperature above the melting point of ZnCl$_2$ and were 23 and 24 kJ/mol for zinc and chloride ions at 873 K, respectively. The present result was measured not for pure ZnCl$_2$ but for PbCl$_2$–ZnCl$_2$ melt, which initial PbCl$_2$ content is only 9.5 mol% and temperature is at least 100 K higher than 873 K. Therefore, the activation energy of ZnCl$_2$ diffusion would be extremely lower than the obtained value of 194 kJ/mol and it is considered that the diffusion of ZnCl$_2$ is not the rate determining step. This conclusion is consistent with the fact that the evaporation rate is not affected by the change of chemical composition of chloride melt as shown in Fig. 4.

3.2. Effect of Composition

The effect of the chemical composition on the evaporation rate of PbCl$_2$–ZnCl$_2$ melt was investigated at 1 023 K with initial (mass%Zn)/(mass%Pb)=3.0 in Ar atmosphere. Figure 6 shows the change of the amount of evaporated ZnCl$_2$ obtained from mass balance calculation in the evaporation system. One of the calculated results from the experimental data represented a minus value due to the experimental and analytical error. Since the linear relationships were observed for the experimental results of (mass%Zn)/(mass%Pb) ratios between 1.0 and 3.0, evaporation rates of ZnCl$_2$ were calculated by the linear regression analyses. On the contrary, obvious linear relationship was not observed in the case of (mass%Zn)/(mass%Pb) ratio of 0.44. It is considered that the evaporation rates at the beginning of experiments were lower than expected at the experimental temperature because the heating of specimen takes time lag. Therefore, the evaporation rate of ZnCl$_2$ for the PbCl$_2$–ZnCl$_2$ of (mass%Zn)/(mass%Pb) 0.44 was calculated using the data at 20 min of evaporation duration by Eq. (1). Moreover, the evaporation rate of pure ZnCl$_2$ was also measured at the same condition for comparison. The experimental conditions and results are shown in Table 3 and Fig. 6. However, the relationship between evaporated amount of ZnCl$_2$ and time is considerably different from others, which result is also due to the heating of ZnCl$_2$ at the initial stage of measurement. Assuming that the specimen is sufficiently heated to the experimental temperature after 15 min, the evaporation rate of ZnCl$_2$ was calculated from two measured results of 15 and 20 min of evaporation duration, which is shown as a slope of a straight line in Fig. 6.

Figure 7 shows the dependence of the evaporation rate of ZnCl$_2$ on the ZnCl$_2$ content of PbCl$_2$–ZnCl$_2$ melt in Ar atmosphere at 1 023 K. Error bars in ZnCl$_2$ contents repre-
sent the changes in composition of chloride melts. It is observed that the increase in initial ZnCl₂ content drastically increases the evaporation rate of ZnCl₂ and the composition dependence of the evaporation rate shows the large negative deviation from the linear relationship between the evaporation rate and ZnCl₂ content. Since the reaction of ZnCl₂ evaporation is expressed as Eq. (3), the evaporation rate of ZnCl₂ could be estimated from the activity of ZnCl₂ assuming that the evaporation rate is expressed as a function of the activity of ZnCl₂ in the melt as Eq. (4),

\[
\text{ZnCl}_2 \text{(in melt)} \rightarrow \text{ZnCl}_2 \text{(g)} \quad \text{(3)}
\]

\[
\frac{r_{\text{eva}}}{k_{\text{eva}}} = A \cdot k_{\text{eva}} \cdot \alpha_{\text{ZnCl}_2} \quad \text{(4)}
\]

where, \( \alpha_{\text{ZnCl}_2} \) is activity of ZnCl₂ in the melt. Muromtsev and Nazarova\(^{15}\) reported the activities of PbCl₂ and ZnCl₂ in the PbCl₂–ZnCl₂ binary chloride melt at 973 K. The evaporation rate was estimated by Eq. (4) using their reported data as shown in Fig. 7. Here, the evaporation rate of pure ZnCl₂ melt was applied to obtain the evaporation rate constant \( k_{\text{eva}} \) (0.0343 g/cm²·min). Though the estimated evaporation rate of ZnCl₂ also shows a slight negative deviation, the measured evaporation rate of ZnCl₂ were much lower than that estimated from the activity of ZnCl₂ comparing at the same composition. In the present study, the gas flow rate was determined to be 600 cm³/min by the effect of gas flow rate on the evaporation rate in our previous study\(^{16}\) about the evaporation behavior of the FeCl₂–ZnCl₂ system with the same experimental setup, in which the evaporation rate was independent of the gas flow rate. In the meantime, the evaporation rate is not controlled by the diffusion of ZnCl₂ in the chloride melt as explained in the previous section. Therefore, the evaporation of ZnCl₂ is controlled by the interfacial chemical reaction step. Nevertheless, the evaporation rate estimated from the activity of ZnCl₂ in the melt is larger than the observed one. This result indicates that ZnCl₂ evaporation expressed as Eq. (3) is not the rate determining step. In fact, it is well known that the PbCl₂–ZnCl₂ melt is the ionic melt and ZnCl₂ exists as ZnCl₂⁻, ZnCl⁻ or further polymerized species as well as Zn²⁺ and Cl⁻, while PbCl₂ exists only Pb²⁺ and Cl⁻ in the melt.\(^{17}\) Moreover, authors calculated the structure of PbCl₂–ZnCl₂ melt by utilizing molecular dynamics simulation and the formation of polymeric network structures was clarified.\(^{18}\) Consequently, Eq. (3) is divided into several elementary reactions such as ZnCl₂⁻→ZnCl⁻⁺Cl⁻, ZnCl₁⁻→ZnCl₂⁺Cl⁻ and it is considered that one of these elementary reactions is the rate determining step of the ZnCl₂ evaporation reaction. This consideration is also consistent with the fact that the evaporation rate is scarcely affected by the change of ZnCl₂ content during measurements.

### 3.3. Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure on the evaporation rates of PbCl₂–ZnCl₂ and pure ZnCl₂ melts was investigated at 1 023 K with air and O₂ atmospheres. Figure 8 shows the change of the amount of evaporated ZnCl₂ obtained from mass balance calculation in the evaporation system. The amount of evaporated ZnCl₂ increased with time. However, the relationships between that amount and time were not linear. The reason is considered that temperature of specimen at the initial period was lower than 1 023 K as mentioned in the previous section. Since it is expected that samples are sufficiently heated to the experimental temperature at 15 min, the evaporation rates of ZnCl₂ at each experimental condition were calculated from the results between 15 and 20 min.

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Fig. 7. Dependence of the evaporation rate of ZnCl₂ on ZnCl₂ content of PbCl₂–ZnCl₂ melt in Ar atmosphere at 1 023 K.

Fig. 8. Change of evaporated amount of ZnCl₂ with time for the evaporation of PbCl₂–ZnCl₂ and pure ZnCl₂ melts in air and O₂ atmospheres at 1 023 K.

Fig. 9. Dependence of the evaporation rate of ZnCl₂ on ZnCl₂ content of PbCl₂–ZnCl₂ melt in Ar atmosphere.
Figure 9 shows the relationship between evaporation rate of ZnCl₂ and ZnCl₂ content in PbCl₂–ZnCl₂ melt, together with that measured in Ar atmosphere. The evaporation rate of ZnCl₂ in the oxidizing atmosphere was larger than that in Ar atmosphere at the whole composition range. Especially, the evaporation rate from pure ZnCl₂ melt increased approximately twice with changing atmosphere from Ar to O₂, which means that the evaporation of ZnCl₂ is accelerated by adding oxygen gas. On the contrary, the obvious change of PbCl₂ evaporation rate with changing oxygen partial pressure was not observed. The effect of oxygen partial pressure on the chlorination and evaporation rates was also investigated for PbO and ZnO chlorination in the previous studies, and the effect of oxygen partial pressure depresses the evaporation of some elements such as zinc, which is converted to oxide, and accelerates that of some elements such as chromium and vanadium due to the volatile oxychloride formation. Therefore, the adequate condition must be selected based on the physical and chemical properties of resources.

4. Conclusions

The evaporation rate of the PbCl₂–ZnCl₂ binary chloride melt was studied at 972, 1 023 and 1 073 K, and the applicability of selective evaporation process for the recycling of PbCl₂–ZnCl₂ mixture was demonstrated. Conclusions are summarized in the followings.

(1) The ZnCl₂ evaporated preferentially from PbCl₂–ZnCl₂ melt, but the evaporated amount of PbCl₂ was negligibly small.

(2) Calculated activation energy of ZnCl₂ evaporation was 194 ± 4 kJ/mol and extremely higher than the activation energy of ZnCl₂ diffusion.

(3) Composition dependence of ZnCl₂ evaporation rate
deviated negative and more than that estimated from the activity of ZnCl$_2$ in the melt.

(4) Increase in oxygen partial pressure accelerated the evaporation rate of ZnCl$_2$, but it was ineffective for PbCl$_2$ evaporation rate.

REFERENCES