Evaporation Kinetics of the Molten PbCl_2 – ZnCl_2 System from 973 to 1 073 K

Canguo WANG,¹⁾ Xiaojun HU,²⁾ Hiroyuki MATSUURA³⁾ and Fumitaka TSUKIHASHI⁴⁾

1) Department of Ferrous Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083 China.

2) Department of Physical Chemistry, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083 China.

3) Center for Iron and Steelmaking Research, Department of Materials Science and Engineering, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, PA 15213 USA.

4) Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561 Japan.

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The clarification of chlorides evaporation behavior from chloride or oxychloride melts is quite important for the treatment and recycling of fly ash generated from incineration processes of municipal solid waste. In the present study, the evaporation rate of the molten PbCl_2 – ZnCl_2 binary chloride system was measured at 973, 1 023 and 1 073 K. The effects of temperature, composition of the melt and the oxygen partial pressure of atmosphere on the evaporation rate of molten chloride were investigated. The ZnCl_2 in chloride melt evaporated preferentially, but the evaporated amount of PbCl_2 was negligibly small. Calculated activation energy of ZnCl_2 evaporation was 194 ± 4 kJ/mol and that evaporation rate was smaller than that estimated from ZnCl_2 activity for the PbCl_2 – ZnCl_2 system. Therefore, the evaporation is considered to be controlled by the slower chemical reaction step than the interfacial evaporation reaction. The evaporation rate increased with increasing oxygen partial pressure in the atmosphere, which might be due to the effect of oxychloride formation.

KEY WORDS: evaporation kinetics; zinc chloride; lead chloride; municipal solid waste; incineration; fly ash; recycling; oxychloride formation.

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 treat-

ment 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 Tsukihashi^{6–8)} 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 the chlorination

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 the 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 $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb}) = 0.1$ 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

Fig. 1. Schematic diagram of experimental apparatus.

Table 1. Initial compositions of the PbCl_2 – ZnCl_2 system for each experimental condition.

$(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})$ ratio	Initial ZnCl_2 content (mass%)
0.1	13.4
0.44	40.5
1.0	60.8
2.0	75.6
3.0	82.3

$(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb}) = 3.0$. **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 3.43×10^3 to 1.67×10^4 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),

$$r_{\text{ZnCl}_2}^{\text{eva}} = \frac{W_{\text{ZnCl}_2}^{\text{eva}}}{t} \quad \text{.....(1)}$$

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 ,

Table 2. Experimental conditions and results for evaporation rate measurement of the $\text{PbCl}_2\text{--ZnCl}_2$ system.

Exp. No.	Temperature (K)	(mass%Zn)/(mass%Pb) (-)	Gas	Time (min)	Weight loss (g)	ZnCl ₂ content (mass%)
01-1	973	3.0	Ar	10	0.1525	83.02
01-2				20	0.3422	81.30
01-3				30	0.5300	79.74
01-4				40	0.6496	78.72
02-1	1023	0.1	O ₂	10	0.0673	10.21
02-2				15	0.1208	9.07
02-3				20	0.1444	8.91
03-1	1023	0.44	Ar	10	0.0655	45.01
03-2				15	0.1503	41.76
03-3				20	0.2248	35.79
04-1	1023	0.44	O ₂	10	0.1538	42.42
04-2				15	0.2151	37.54
04-3				20	0.3435	33.09
05-1	1023	1.0	Ar	10	0.1997	60.78
05-2				20	0.6204	52.50
05-3				30	0.8555	47.93
05-4				40	1.0714	41.61
06-1	1023	1.0	O ₂	10	0.1440	59.29
06-2				15	0.3084	56.26
06-3				20	0.4690	53.90
07-1	1023	2.0	Ar	10	0.3506	72.64
07-2				20	0.7165	67.86
07-3				30	1.3340	60.30
07-4				40	1.8204	46.87
08-1	1023	3.0	Ar	10	0.2242	80.64
08-2				20	0.9554	75.21
08-3				30	1.5606	66.91
08-4				40	2.0401	50.55
09-1	1023	3.0	air	10	0.2392	78.67
09-2				15	0.4347	77.08
09-3				20	0.9730	76.34
10-1	1023	3.0	O ₂	10	0.1652	80.94
10-2				15	0.4185	79.21
10-3				20	0.7485	76.44
11-1	1073	3.0	Ar	10	1.5301	68.43
11-2				20	2.5644	-
11-3				30	2.7107	-

Fig. 2. Change of weight loss of specimen with time for $\text{PbCl}_2\text{--ZnCl}_2$ melt of initial (mass%Zn)/(mass%Pb)=3.0 in Ar atmosphere.

Fig. 3. Relationship between ZnCl_2 content of melt and time for the evaporation of $\text{PbCl}_2\text{--ZnCl}_2$ melt of initial (mass%Zn)/(mass%Pb)=3.0 in Ar atmosphere.

0.0485±0.002 and 0.146 g/min at 973, 1023 and 1073 K, respectively.

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

$$k_{\text{ZnCl}_2}^{\text{eva}} = \frac{r_{\text{ZnCl}_2}^{\text{eva}}}{A} \dots\dots\dots(2)$$

where $k_{\text{ZnCl}_2}^{\text{eva}}$ (g/cm²·min) is the ZnCl_2 evaporation rate con-

Fig. 4. Change of evaporated amounts of PbCl_2 and ZnCl_2 with time for the evaporation of PbCl_2 - ZnCl_2 melt of initial $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})=3.0$ in Ar atmosphere.

Fig. 5. Temperature dependence of the evaporation rate constant of ZnCl_2 for the evaporation of PbCl_2 - ZnCl_2 melt of initial $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})=3.0$ in Ar atmosphere.

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 ± 220 obtained by the linear regression of Arrhenius plot. The activation energy of ZnCl_2 evaporation was $194 \pm 4 \text{ kJ/mol}$. Bockris *et al.*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 1023 K

Fig. 6. Change of evaporated amount of ZnCl_2 with time for the evaporation of PbCl_2 - ZnCl_2 and pure ZnCl_2 melts in Ar atmosphere at 1023 K.

Table 3. Experimental conditions and results for evaporation rate measurement of ZnCl_2 melt.

Exp. No.	Temperature (K)	Gas	Time (min)	Weight loss (g)
12-1	1023	Ar	10	0.0988
12-2			15	0.2565
12-3			20	0.6458
13-1	1023	O_2	10	0.2161
13-2			15	0.5866
13-3			20	1.4175

with initial $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})$ ratios between 0.44 and 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 $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})$ 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 $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})$ 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 $(\text{mass}\%\text{Zn})/(\text{mass}\%\text{Pb})=0.44$ 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 1023 K. Error bars in ZnCl_2 contents repre-

Fig. 7. Dependence of the evaporation rate of ZnCl_2 on ZnCl_2 content of PbCl_2 - ZnCl_2 melt in Ar atmosphere at 1023 K.

sent the changes in composition of chloride melts. It is observed that the increase in initial ZnCl_2 content drastically increases the evaporation rate of ZnCl_2 and the composition dependence of the evaporation rate shows the large negative deviation from the linear relationship between the evaporation rate and ZnCl_2 content. Since the reaction of ZnCl_2 evaporation is expressed as Eq. (3), the evaporation rate of ZnCl_2 could be estimated from the activity of ZnCl_2 assuming that the evaporation rate is expressed as a function of the activity of ZnCl_2 in the melt as Eq. (4),

$$r_{\text{ZnCl}_2}^{\text{eva}} = A k_{\text{ZnCl}_2}^{\text{eva}} a_{\text{ZnCl}_2} \dots\dots\dots (4)$$

where, a_{ZnCl_2} is activity of ZnCl_2 in the melt. Muromtsev and Nazarova¹⁵⁾ reported the activities of PbCl_2 and ZnCl_2 in the PbCl_2 - ZnCl_2 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 ZnCl_2 melt was applied to obtain the evaporation rate constant k_{eva} (0.0343 g/cm²·min). Though the estimated evaporation rate of ZnCl_2 also shows a slight negative deviation, the measured evaporation rate of ZnCl_2 were much lower than that estimated from the activity of ZnCl_2 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 study¹⁶⁾ about the evaporation behavior of the FeCl_2 - ZnCl_2 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 ZnCl_2 in the chloride melt as explained in the previous section. Therefore, the evaporation of ZnCl_2 is controlled by the interfacial chemical reaction step. Nevertheless, the evaporation rate estimated from the activity of ZnCl_2 in the melt is larger than the observed one. This result indicates that ZnCl_2 evaporation expressed as Eq. (3) is not the rate determining step. In fact, it is well known that the PbCl_2 - ZnCl_2 melt is the ionic melt and ZnCl_2 exists as ZnCl_4^{2-} , ZnCl_3^- or further polymerized species as well as Zn^{2+} and Cl^- , while PbCl_2 exists only Pb^{2+} and Cl^- in the

Fig. 8. Change of evaporated amount of ZnCl_2 with time for the evaporation of PbCl_2 - ZnCl_2 and pure ZnCl_2 melts in air and O_2 atmospheres at 1023 K.

Fig. 9. Dependence of the evaporation rate of ZnCl_2 on ZnCl_2 content of PbCl_2 - ZnCl_2 melt in air and O_2 atmospheres at 1023 K, compared with that in Ar atmosphere.

melt.¹⁷⁾ Moreover, authors calculated the structure of PbCl_2 - ZnCl_2 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 $\text{ZnCl}_4^{2-} \rightarrow \text{ZnCl}_3^- + \text{Cl}^-$, $\text{ZnCl}_3^- \rightarrow \text{ZnCl}_2 + \text{Cl}^-$ and it is considered that one of these elementary reactions is the rate determining step of the ZnCl_2 evaporation reaction. This consideration is also consistent with the fact that the evaporation rate is scarcely affected by the change of ZnCl_2 content during measurements.

3.3. Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure on the evaporation rates of PbCl_2 - ZnCl_2 and pure ZnCl_2 melts was investigated at 1023 K with air and O_2 atmospheres. Figure 8 shows the change of the amount of evaporated ZnCl_2 obtained from mass balance calculation in the evaporation system. The amount of evaporated ZnCl_2 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 1023 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 ZnCl_2 at each experimental condition were calculated from the results between 15 and 20 min.

Figure 9 shows the relationship between evaporation rate of ZnCl_2 and ZnCl_2 content in PbCl_2 – ZnCl_2 melt, together with that measured in Ar atmosphere. The evaporation rate of ZnCl_2 in the oxidizing atmosphere was larger than that in Ar atmosphere at the whole composition range. Especially, the evaporation rate from pure ZnCl_2 melt increased approximately twice with changing atmosphere from Ar to O_2 , which means that the evaporation of ZnCl_2 is accelerated by adding oxygen gas. On the contrary, the obvious change of PbCl_2 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,^{9,10)} and ZnO chlorination rate increased with increasing partial pressure of oxygen, while that of PbO did not change. The present result consists with those of the previous studies.

Oxidation reactions of PbCl_2 (l) and ZnCl_2 (l) are described by Eqs. (5) and (6), respectively.

The equilibrium constants of reactions (5) and (6) are 6.41×10^{-6} and 0.0443 , respectively. Therefore, some of ZnCl_2 contained in PbCl_2 – ZnCl_2 melts would be oxidized and dissolved in the melt, while PbCl_2 would be scarcely oxidized. If the addition of ZnO in PbCl_2 – ZnCl_2 melt increases the activity of ZnCl_2 , the evaporation rate of ZnCl_2 could be accelerated. However, it is observed that the dissolution of oxide ion in the molten ZnCl_2 decreases the partial pressure of ZnCl_2 in the previous works.^{7,8)} Accordingly, it is difficult to attribute the increase of evaporation rate of ZnCl_2 to the partial oxidation of ZnCl_2 in the melt.

On the other hand, oxychloride formations for lead and zinc were identified in our previous works,^{6–8)} and the formations of $\text{PbOCl}(\text{g})$ and $\text{ZnOCl}(\text{g})$ were reported as Eqs. (7) and (8), respectively.

The equilibrium constants of reactions (7) and (8) are 1.75×10^{-3} and 1.33×10^{-3} , respectively. Hence, $P_{\text{ZnOCl}}/P_{\text{PbOCl}}$ is almost same as $P_{\text{ZnCl}_2}/P_{\text{PbCl}_2}$. Therefore, it is expected that the increase of ZnCl_2 evaporation rate with increasing oxygen partial pressure shows the same tendency as the increase of PbCl_2 evaporation rate. Nevertheless, the evaporation rate of ZnCl_2 was considerably affected by oxygen partial pressure, while that of PbCl_2 was not affected as observed in the present and previous studies.

From above discussion, it is obvious that the increase of the evaporation rate of ZnCl_2 is due to neither the change of the oxide ion content in the melt nor the formation of

gaseous zinc oxychloride $\text{ZnOCl}(\text{g})$. One possible reason is that oxygen gas affects the elementary evaporation reaction directly, like a catalytic effect. As mentioned above, there are many types of ionic species containing zinc in the melt and some of them might have strong affinity with oxide ion. The other possibility is that the other unknown zinc oxychloride species evaporates from the melt. In the present study, the outlet gas was analyzed by a mass spectrometer to find the evaporating species. However, any gaseous species containing zinc was not observed except ZnCl_2 , and the ion current for ZnCl_2 became small in a short time and disappeared. ZnCl_2 easily deposited on the wall of the capillary tube for gas introduction and the tube was choked up by the chloride. The reaction mechanism for the evaporation of ZnCl_2 from the PbCl_2 – ZnCl_2 melt, especially the effect of oxygen gas, is still unknown. These possible reaction mechanisms should be clarified in the future work.

3.4. Recycling Process of Zinc and Lead by Selective Evaporation

From the present experimental results, it could be concluded that the recycling process of zinc and lead by utilizing selective evaporation is efficient. Meyer *et al.*¹⁹⁾ measured the vapor pressures of the PbCl_2 – ZnCl_2 system. They clarified the higher partial pressure of ZnCl_2 compared to that of PbCl_2 and demonstrated the rectification efficiency regarding to molten salt composition. According to their result, for instance, ZnCl_2 is concentrated to 80 mol% from PbCl_2 –20 mol% ZnCl_2 melt by single rectification and to 99 mol% by twice. They concluded that it is possible to separate the mixture of PbCl_2 – ZnCl_2 melt by simple rectification. The present results also clarified the prior evaporation of ZnCl_2 from PbCl_2 – ZnCl_2 mixture from the kinetic viewpoint. In addition, it was also indicated that the efficiency of rectification process would be improved by selecting the appropriate oxygen partial pressure. Especially, the control of the oxidizing atmosphere may be quite important in the practical process because zinc chloride is extracted not from pure binary PbCl_2 – ZnCl_2 melt but from the multi component system. It is expected that the increase in oxygen partial pressure depresses the evaporation of some elements such as iron which is converted to oxide, and accelerates that of some elements such as chromium^{20–27)} and vanadium^{28–30)} 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 PbCl_2 – ZnCl_2 binary chloride melt was studied at 972, 1 023 and 1 073 K, and the applicability of selective evaporation process for the recycling of PbCl_2 – ZnCl_2 mixture was demonstrated. Conclusions are summarized in the followings.

- (1) The ZnCl_2 evaporated preferentially from PbCl_2 – ZnCl_2 melt, but the evaporated amount of PbCl_2 was negligibly small.
- (2) Calculated activation energy of ZnCl_2 evaporation was $194 \pm 4 \text{ kJ/mol}$ and extremely higher than the activation energy of ZnCl_2 diffusion.
- (3) Composition dependence of ZnCl_2 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.

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