Removal of Zn and Pb from $\text{Fe}_2\text{O}_3\text{--ZnFe}_2\text{O}_4\text{--ZnO--PbO}$ Mixture by Selective Chlorination and Evaporation Reactions

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Selective chlorination and evaporation reactions could become one of the useful methods for the treatment of steelmaking dust containing zinc and lead. In the present study, chlorination rate of $\text{Fe}_2\text{O}_3\text{--ZnFe}_2\text{O}_4\text{--ZnO--PbO}$ mixture with $\text{Ar--Cl}_2\text{--O}_2$ gas ($P_{\text{Cl}_2}=0.5\times 10^4$ to 2.0×10^4 Pa, $P_{\text{O}_2}=1.0\times 10^4$ to 5.1×10^4 Pa) has been measured at 1 073 K by gravimetry and the effects of partial pressures of chlorine and oxygen on the chlorination and evaporation rates have been investigated. Zinc oxide and lead oxide contained in the oxide mixture were selectively chlorinated and zinc and lead chlorides evaporated to gas phase, while iron oxide remained as oxide in a chlorinated residue. By chlorinating with Ar--Cl_2 gas, over 99 % of zinc and lead could be removed from oxide mixture and approximately 3 % of iron has been lost by chlorination and evaporation reactions simultaneously. To decrease the loss of iron oxide and improve the efficiency of selective chlorination and evaporation reactions, chlorination by using $\text{Ar--Cl}_2\text{--O}_2$ gas has been conducted and the enrichment of oxygen gas effectively depressed the chlorination of iron oxide, while the removal efficiency of zinc and lead was maintained.

KEY WORDS: selective chlorination; evaporation; zinc; lead; zinc ferrite; chloride; steelmaking dust; kinetics; recycling.

1. Introduction

Steelmaking dust generated from electric arc furnace (EAF) contains considerable amount of valuable metals; e.g., 5 to 30 mass% of Zn and 3 to 5 mass% of Pb.¹⁾ The amount of generated EAF dust is estimated at approximately 500 000 tons per year in Japan.²⁾ EAF dust has been treated by electrothermal distillation method, Waelz kiln or MF process by applying reduction and evaporation reactions to recover zinc.³⁾ EAF dust must be treated and utilized as much as possible to reduce the disposal cost of EAF dust, because EAF dust is designated as special management industrial waste and the pretreatment such as chemical treatment and cement solidification must be taken before landfill, which leads to great expense. However, some zinc contained in EAF dust are hard to be recovered due to the existence of low reducible zinc compound, mainly ZnFe_2O_4 . As a result, about 30 % of EAF dust have landfilled annually in Japan,³⁾ and the amount of dumped zinc is estimated to be 30 000 tons, which is considerably large compared to the annual zinc production of about 600 000 tons in Japan. Since EAF dust contains mainly iron oxide as well as zinc and lead oxides, the efficient separation of zinc and lead from EAF dust would enable us not only to utilize the removed and recovered zinc and lead as resources of zinc and lead production but also to use separated iron oxide residues as ironmaking and steelmaking resources. The development of new EAF dust treatment

processes has become an important issue from the viewpoint of the environmental protection and recycling of valuable materials.

These days, the selective chlorination and evaporation processes with the use of waste polyvinyl chloride (PVC) have been proposed by some researchers^{4–11)} for the treatment of EAF dust. **Figure 1** shows the chemical potential diagram of the Fe–Zn–Pb–O–Cl system at 1 073 K which

Fig. 1. Chemical potential diagram of the Fe–Zn–Pb–O–Cl system at 1 073 K. P_{Cl_2} and P_{O_2} are partial pressures of chlorine and oxygen, respectively. P^0 is the atmospheric pressure of 101 325 Pa.

was calculated by FactSage 5.3 software. Mole ratios are $X_{Zn}/(X_{Fe}+X_{Zn}+X_{Pb})=0.252$ and $X_{Pb}/(X_{Fe}+X_{Zn}+X_{Pb})=0.0159$. These conditions correspond to the Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO oxide mixture containing 20.0 mass% Zn and 4.0 mass% Pb. It is obvious that zinc and lead oxides are converted to chlorides, while iron oxide is stable at high partial pressures of chlorine and oxygen. These metal chlorides show high vapor pressures at low temperatures, or low boiling points; for example, boiling points of $ZnCl_2$ and $PbCl_2$ are 1 004 K and 1 223 K, respectively.¹²⁾ Therefore, zinc and lead oxides could be selectively removed by utilizing selective chlorination and evaporation reactions. To develop the selective chlorination and evaporation process for the treatment of EAF dust, it is quite important to know the kinetics and mechanisms of selective chlorination and evaporation reactions. Until now, authors have clarified the chlorination kinetics and mechanisms of PbO , ZnO and $ZnFe_2O_4$ chlorination reaction with Ar - Cl_2 - O_2 gas in previous studies.¹³⁻¹⁵⁾

Fray⁴⁾ demonstrated the efficient removal of zinc from EAF dust containing considerable amount of zinc ferrite by using air and Cl_2 mixture at 1 023 K. Moreover, Tailoka and Fray⁵⁾ treated some metallurgical dusts by HCl gas generated from incineration of waste PVC. In the case of the treatment of EAF dust containing 21.40 mass% Zn at 1 166 K for 201 min, 78% of zinc was removed as well as 2.2% of iron oxide was lost by chlorination reaction. On the contrary, when the mixture of EAF dust and PVC was heated, 79.3% of zinc and 7.2% of iron were removed. These experiments indicate that oxidizing atmosphere would be important for the selective chlorination reaction.

Zhang *et al.*^{9,11)} and Hirasawa¹⁰⁾ heated the mixture of Fe_2O_3 - ZnO - PVC and $ZnFe_2O_4$ - PVC at 1 000 K, 1 150 K and 1 205 K in argon atmosphere. At all experiments, metallic irons were obtained and the zinc content in the residues were approximately 0.2 mass%. The loss of iron was reported to be about 1% and the efficient selective chlorination has been conducted.

As mentioned above, many valuable results are reported and the possibility of selective chlorination and evaporation reactions for the efficient treatment of EAF dust has been demonstrated. In the present study, chlorination kinetics of Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO oxide mixture with Ar - Cl_2 - O_2 gas has been measured at 1 073 K and the effects of chlorine and oxygen partial pressures on the chlorination rate and selectivity of chlorination and evaporation reactions have been investigated. From obtained results, chlorination and evaporation mechanisms were discussed.

2. Experimental

The chlorination rate of Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO mixture with Ar - Cl_2 - O_2 gas was measured by gravimetry at 1 073 K. **Figure 2** shows the schematic diagram of experimental apparatus. Reagent grade of Fe_2O_3 , $ZnFe_2O_4$, ZnO and PbO powders were used to prepare oxide mixture of Fe_2O_3 -36.87mass% $ZnFe_2O_4$ -12.45mass% ZnO -4.31mass% PbO . These compositions were determined from the average contents of EAF dusts; Zn=20.0 mass%, Pb=4.0 mass% and ZnO: $ZnFe_2O_4$ =1:1 (molar ratio). Two grams of prepared oxide mixture were put in a mullite boat (width

Fig. 2. Schematic diagram of experimental apparatus.

12 mm, depth 9 mm and length 60 mm) and the boat was inserted into a hot zone of an electric furnace. Argon, chlorine and oxygen gases were purified by passing through columns of silica gel and $Mg(ClO_4)_2$, and mixed to control partial pressures of chlorine and oxygen. Gas mixture was introduced in a reaction tube at 600 cm³/min for 1 to 30 min. In each experiment, weight change of specimen between before and after chlorination reaction was measured. Flow rates of reaction gases were controlled by mass flow meter. Measurement with a mullite boat without specimen was conducted at the same experimental conditions and no change of the weight of mullite boat by chlorination reaction was confirmed. After experiments, chlorinated residue was analyzed by chemical analyses, by titration method with potassium dichromate for total iron content and by ICP-AES for zinc and lead contents. Some chlorinated residues were submitted to identify phases by XRD analysis.

3. Results and Discussion

3.1. Effect of Chlorine Partial Pressure

Chlorination reactions of each component of oxide mixture are expressed as Eqs. (1) to (4) at the present experimental temperature of 1 073 K,

From above Gibbs free energy changes, chlorination reaction of Fe_2O_3 is thermodynamically hard to proceed, and zinc and lead contained in oxide mixture are considered to be selectively chlorinated. Moreover, since vapor pressure of pure $PbCl_2$ is 1.67×10^4 Pa at 1 073 K,¹²⁾ $PbCl_2$ would easily evaporate. Therefore, it is thermodynamically expected that zinc and lead contained in the oxide mixture are removed by selective chlorination and evaporation reactions.

The effect of partial pressure of chlorine on the chlorination rate of oxide mixture with Ar - Cl_2 gas was investigated between 0.5×10^4 Pa and 2.0×10^4 Pa of chlorine partial

Table 1. Experimental conditions and results for chlorination of $\text{Fe}_2\text{O}_3\text{--ZnFe}_2\text{O}_4\text{--ZnO--PbO}$ mixture with Ar--Cl_2 gas at 1 073 K.

Exp. No.	$P_{\text{Cl}_2} \times 10^{-4}$ (Pa)	Time (min)	Weight change (g)	T.ZnO content (mass%)	PbO content (mass%)	T. Fe_2O_3 content (mass%)
101	0.5	1	−0.07586	25.47	1.66	73.97
102	0.5	2	−0.12335	23.04	1.19	75.59
103	0.5	3	−0.16291	22.38	1.09	77.19
104	0.5	6	−0.26532	17.61	0.78	81.56
105	0.5	10	−0.36964	13.24	0.65	86.32
106	0.5	15	−0.45775	8.71	0.47	91.06
107	0.5	20	−0.54002	4.17	0.24	95.49
108	0.5	25	−0.59034	1.26	0.10	98.42
109	0.5	30	−0.62212	0.12	0.03	99.44
110	1.0	2	−0.15938	22.32	0.85	77.72
111	1.0	4	−0.25411	18.32	0.67	81.55
112	1.0	5	−0.30124	16.55	0.52	83.38
113	1.0	6	−0.32882	15.12	0.62	84.98
114	1.0	8	−0.39786	11.68	0.41	88.38
115	1.0	10	−0.48468	7.34	0.09	92.68
116	1.0	12	−0.50654	6.26	0.27	93.88
117	1.0	14	−0.55178	3.62	0.17	96.31
118	1.0	15	−0.58762	1.53	0.10	98.51
119	1.0	16	−0.58835	1.49	0.09	98.95
120	1.0	18	−0.62107	0.18	0.04	99.57
121	1.0	20	−0.62951	0.15	0.03	99.80
122	1.0	25	−0.65752	0.11	0.03	100.0
123	2.0	1	−0.14057	23.19	0.83	76.09
124	2.0	2	−0.21320	20.23	0.69	79.00
125	2.0	3	−0.27949	17.51	0.52	81.69
126	2.0	5	−0.38333	12.61	0.40	86.71
127	2.0	8	−0.52255	5.05	0.19	94.45
128	2.0	11	−0.60383	0.67	0.05	98.98
129	2.0	14	−0.62901	0.19	0.03	99.21
130	2.0	17	−0.65388	0.15	0.03	99.16

pressure at 1 073 K. Experimental conditions and results are shown in **Table 1**. It is considered that zinc is contained as ZnO or ZnFe_2O_4 in the chlorinated residue. However, compositions of ZnO and ZnFe_2O_4 were not analyzed in the present work. Therefore, zinc content was presented as total ZnO. Fe_2O_3 content was described as total Fe_2O_3 because of the same reason. Summations of analyzed contents were from 99.34 to 101.1 mass%, that would be due to the analytical error.

Figure 3 shows the weight change of specimen with chlorination time. The broken line represents the theoretical weight change of specimen in the ideal case (−0.5842 g) that zinc and lead contained in 2 g of specimen have been completely removed by chlorination and evaporation reactions, while the whole of iron has remained as oxide. Weight of sample decreased with time in all partial pressures of chlorine and the rate of chlorination reaction increased with increasing chlorine partial pressure.

A solid layer which color is different from the original oxide mixture was observed on the surface of chlorinated residue and the thickness of this layer increased with chlorination time. Diffraction patterns of chlorinated residue were measured by powder XRD to identify the mineralogical phase of this observed layer. **Figure 4** shows the diffraction patterns of residues after chlorination with Ar--Cl_2 gas of $P_{\text{Cl}_2} = 1.0 \times 10^4$ Pa together with reported peak positions of each pure oxide in JCPDS data.¹⁶⁾ It is considered that

Fig. 3. Effect of chlorine partial pressure on the weight change of specimen with time for $\text{Fe}_2\text{O}_3\text{--ZnFe}_2\text{O}_4\text{--ZnO--PbO}$ chlorination with Ar--Cl_2 gas at 1 073 K.

the residue after 25 min of chlorination is almost converted to Fe_2O_3 . The results of chemical analyses as shown in **Table 1** show that the summations of total ZnO, PbO and total Fe_2O_3 are almost 100 mass% in all specimens. From these facts, it could be concluded that the chlorination reactions of each oxide are expressed as Eqs. (2) to (4) and there is no other solid phase such as FeOCl other than Fe_2O_3 . In addition, diffraction peaks corresponding to

Fig. 4. XRD patterns of specimens after Fe_2O_3 - ZnFe_2O_4 - ZnO - PbO chlorination with Ar-Cl_2 gas of $P_{\text{Cl}_2}=1.0 \times 10^4$ Pa at 1073 K. Times on the right side of each pattern represent the chlorination duration.

$\text{PbCl}_2(\text{l})$ were not observed. Since PbO content of specimen was low, it is considered that PbCl_2 was immediately evaporated after PbO was chlorinated to PbCl_2 . Moreover, it was observed that the peaks corresponding to ZnO disappeared and the intensities of diffraction peaks corresponding to ZnFe_2O_4 increased in the chlorinated residue of 2 min chlorination duration. It seems that ZnFe_2O_4 is easily formed from ZnO and Fe_2O_3 at 1073 K.

Figure 5 shows the changes of total ZnO and PbO content, and of Zn and Pb removal ratio with time. Total ZnO content monotonically decreased with time and behaviors of Zn removal were almost same as those of ZnFe_2O_4 investigated in the previous study,¹⁵⁾ which is consistent with the rapid formation of ZnFe_2O_4 as shown in Fig. 4. Total ZnO content decreased to approximately 0.1 mass% with all chlorine partial pressures. On the other hand, the chlorination reaction of PbO is fast and about 80% of Pb was removed for 1 to 2 min of chlorination. This observation is consistent with the comparison of the chlorination rates of ZnO and PbO in the previous report.¹³⁾ After the initial stage of chlorination reaction, the chlorination rate of PbO rapidly decreased and PbO was gently removed. Final content of PbO was 0.03 mass% and the further removal could be impossible.

The excess weight losses from the theoretical weight loss were observed as shown in Fig. 3. These results indicate that some of Fe_2O_3 are also chlorinated together with zinc and lead as expressed by Eq. (1). As previously mentioned, since the Gibbs free energy change of Fe_2O_3 chlorination reaction is positive at 1073 K, FeCl_3 is thermodynamically hard to be produced. Partial pressure of FeCl_3 in the gas phase equilibrated with pure solid Fe_2O_3 could be estimated to be 1.39×10^3 Pa at 1073 K and $P_{\text{Cl}_2}=1.0 \times 10^4$ Pa from Eq. (1). The partial pressure of FeCl_3 would be actually lower than that value due to the lower partial pressure of chlorine gas by the formation of FeCl_3 . However, the present measurements were conducted in the flow system and the produced gaseous FeCl_3 is continuously exhausted to the outside of the chlorination system. Therefore, chlorination of Fe_2O_3 would slightly proceed. From experimental and analytical results of chlorinated residues, chlorinated

Fig. 5. Effect of chlorine partial pressure on the change of (a) total ZnO and PbO content, and (b) Zn and Pb removal ratio with time for Fe_2O_3 - ZnFe_2O_4 - ZnO - PbO chlorination with Ar-Cl_2 gas at 1073 K.

Fig. 6. Effect of chlorine partial pressure on the change of the amount of chlorinated Fe_2O_3 with time for Fe_2O_3 - ZnFe_2O_4 - ZnO - PbO chlorination with Ar-Cl_2 gas at 1073 K. The ordinate of right side corresponds to the fraction of Fe_2O_3 chlorination.

amount of Fe_2O_3 could be obtained from mass balance calculation in the reaction system. Figure 6 shows the change of the amount of chlorinated Fe_2O_3 with time. The ordinate of the right side in Fig. 6 represents a fraction of the amount of chlorinated Fe_2O_3 to the whole amount of Fe_2O_3 . Since the amount of Fe_2O_3 chlorinated in the initial period

Table 2. Experimental conditions and results for chlorination of $\text{Fe}_2\text{O}_3\text{-ZnFe}_2\text{O}_4\text{-ZnO-PbO}$ mixture with $\text{Ar-Cl}_2\text{-O}_2$ gas of $P_{\text{Cl}_2}=1.0\times 10^4$ Pa at 1073 K.

Exp. No.	$P_{\text{O}_2}\times 10^{-4}$ (Pa)	Time (min)	Weight change (g)	T.ZnO content (mass%)	PbO content (mass%)	T. Fe_2O_3 content (mass%)
201	1.0	1	-0.10930	24.23	1.18	74.75
202	1.0	2	-0.15669	22.59	1.04	76.62
203	1.0	3	-0.19161	21.50	0.77	78.15
204	1.0	5	-0.26478	18.39	0.69	81.36
205	1.0	9	-0.38130	12.44	0.60	87.30
206	1.0	13	-0.47976	7.00	0.35	92.39
207	1.0	17	-0.54778	2.83	0.18	96.43
208	1.0	21	-0.58969	0.15	0.04	99.43
209	1.0	25	-0.59288	0.11	0.03	99.25
210	3.0	2	-0.13538	23.10	0.98	76.35
211	3.0	5	-0.23644	18.82	0.77	80.53
212	3.0	9	-0.33171	14.73	0.58	84.92
213	3.0	13	-0.41710	10.15	0.44	89.60
214	3.0	17	-0.49105	6.18	0.27	93.54
215	3.0	21	-0.55299	2.32	0.13	97.25
216	3.0	25	-0.58436	0.28	0.04	99.50
217	5.1	2	-0.16385	22.74	0.69	76.81
218	5.1	5	-0.28112	17.24	0.49	82.17
219	5.1	9	-0.40339	11.13	0.36	88.37
220	5.1	13	-0.48501	6.66	0.26	93.19
221	5.1	17	-0.55359	2.24	0.13	97.63
222	5.1	21	-0.58225	0.22	0.06	99.60
223	5.1	25	-0.58480	0.15	0.05	99.54

of chlorination is very little, some calculated results represented minus values due to the experimental and analytical errors. Chlorination of Fe_2O_3 has proceeded from the initial stage of chlorination and the chlorination rate has increased with the elapse of chlorination time. The increase of chlorination rate is corresponding to the decrease of the chlorination rates of zinc and lead and this phenomenon was also observed in the case of ZnFe_2O_4 chlorination.¹⁵⁾ It is expected that the increase of oxygen partial pressure depresses the chlorination rate of Fe_2O_3 from Eq. (1). The oxygen gas is generated by chlorination reaction of zinc and lead according to Eqs. (2) to (4) and oxidizing atmosphere around the specimen is formed and maintained, where the chlorination rate of Fe_2O_3 would be small. However, the production rate of oxygen gas decreases with decreasing the chlorination rates of zinc and lead and the partial pressure of oxygen also decreases. Therefore, the chlorination rate of Fe_2O_3 would increase with the decrease of the chlorination rates of zinc and lead. The effect of oxygen partial pressure on the reaction mechanism was discussed in the following section in detail. Fraction of chlorinated Fe_2O_3 was from 3.0 to 3.9% when 99% of zinc and lead was removed, and the chlorination rate increased with increasing partial pressure of chlorine.

3.2. Effect of Oxygen Partial Pressure

The effect of oxygen partial pressure on the chlorination rate of oxide mixture with $\text{Ar-Cl}_2\text{-O}_2$ gas of $P_{\text{Cl}_2}=1.0\times 10^4$ Pa was investigated between 1.0×10^4 Pa and 5.1×10^4 Pa of oxygen partial pressure at 1073 K. Experimental conditions and results are shown in **Table 2**.

Figure 7 shows the effect of oxygen partial pressure on the weight change of specimens with chlorination time. For

Fig. 7. Effect of oxygen partial pressure on the weight change of specimen with time for $\text{Fe}_2\text{O}_3\text{-ZnFe}_2\text{O}_4\text{-ZnO-PbO}$ chlorination with $\text{Ar-Cl}_2\text{-O}_2$ gas of $P_{\text{Cl}_2}=1.0\times 10^4$ Pa at 1073 K.

all partial pressures of oxygen, weight of specimen monotonically decreased with chlorination time. At the initial stage of chlorination, the chlorination rate of oxide mixture was scarcely affected by oxygen partial pressure. On the contrary, the chlorination rate slightly decreased with increasing partial pressure of oxygen at the latter period of chlorination. Moreover, when the weight loss of specimen approached to the theoretical weight loss by zinc and lead chlorination and evaporation reactions, variations of specimen weight diminished, which phenomenon indicates that the chlorination reaction of Fe_2O_3 is inhibited by mixing oxygen gas.

Figure 8 shows the changes of total ZnO and PbO con-

Fig. 8. Effect of oxygen partial pressure on the change of (a) total ZnO and PbO content, and (b) Zn and Pb removal ratio with time for Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO chlorination with $Ar-Cl_2-O_2$ gas of $P_{Cl_2}=1.0 \times 10^4$ Pa at 1073 K.

tent, and of Zn and Pb removal ratio with chlorination time. The chlorination rate of zinc decreased with increasing oxygen partial pressure up to 3.0×10^4 Pa, however it slightly increased again at $P_{O_2}=5.1 \times 10^4$ Pa. This dependence of chlorination rate of zinc on oxygen partial pressure might be due to the formation of gaseous zinc oxychloride such as $ZnOCl(g)$ together with $ZnCl_2(g)$.^{17,18)} In the case of ZnO chlorination, ZnO chlorination rate slightly increased with increasing partial pressure of oxygen.¹⁴⁾ On the other hand, $ZnFe_2O_4$ chlorination rate decreased with increasing oxygen partial pressure due to the interference of chlorination reaction by the occupation of reaction sites with oxygen.¹⁵⁾ In the present work, if ZnO contained in the oxide mixture assumed to be immediately converted to $ZnFe_2O_4$ in the case of atmosphere of $Ar-Cl_2-O_2$ system as mentioned in the previous section, zinc is considered to be contained as $ZnFe_2O_4$. Nevertheless, the increase of oxygen partial pressure decreased the chlorination rate of zinc and slightly increased again. The reason of this behavior on the change of partial pressure of oxygen is not clear at present.

On the contrary, the chlorination rate of lead was little affected by the change of oxygen partial pressure. This observation is consistent with the chlorination and evaporation behaviors of PbO observed in the previous work.¹³⁾

Figure 9 shows the change of the amount of chlorinated Fe_2O_3 with chlorination time. The Fe_2O_3 loss drastically depressed with increasing partial pressure of oxygen below

Fig. 9. Effect of oxygen partial pressure on the change of the amount of chlorinated Fe_2O_3 with time for Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO chlorination with $Ar-Cl_2-O_2$ gas of $P_{Cl_2}=1.0 \times 10^4$ Pa at 1073 K. The ordinate of right side corresponds to the fraction of Fe_2O_3 chlorination.

Fig. 10. Effect of oxygen partial pressure on the final contents of total ZnO and PbO of chlorinated residue and Fe_2O_3 loss for 25 min of chlorination for Fe_2O_3 - $ZnFe_2O_4$ - ZnO - PbO chlorination with $Ar-Cl_2-O_2$ gas of $P_{Cl_2}=1.0 \times 10^4$ Pa at 1073 K.

0.5% for 25 min of chlorination. Since almost all of zinc and lead have been removed after 20 min as shown in Fig. 8, the specimen is nearly pure iron oxide. The chlorination rate of Fe_2O_3 is pretty different with changing partial pressure of oxygen after 20 min as shown in Fig. 9 and this phenomenon indicates that the chlorination reaction of Fe_2O_3 is controlled by the oxidizing atmosphere. The present result demonstrates that the selectivity of chlorination reaction could be efficiently improved by the enrichment of oxygen gas.

Figure 10 shows the effect of partial pressure of oxygen on the final content of total ZnO and PbO of chlorinated residue, and the fraction of chlorinated Fe_2O_3 for 25 min of chlorination with $Ar-Cl_2-O_2$ gas of $P_{Cl_2}=1.0 \times 10^4$ Pa at 1073 K. The final content of total ZnO and PbO slightly increased and the removal efficiency of zinc and lead deteriorated a little, while the fraction of chlorinated Fe_2O_3 could drastically decrease with increasing partial pressure of oxygen. Considering the industrial utilization of chlorination and evaporation processes for the treatment of EAF dust,

air would be practically used as a resource of oxygen gas. Therefore, oxygen partial pressure of chlorinating gas is supposed to be below 2×10^4 Pa. The Fe_2O_3 loss by chlorination and evaporation reactions could be depressed to about 1% with the enrichment of oxygen gas to be $P_{\text{O}_2} = 1.0 \times 10^4$ Pa.

From the present study, it was demonstrated that the selective chlorination and evaporation reactions could be useful to remove zinc and lead contained in the Fe_2O_3 - ZnFe_2O_4 - ZnO - PbO oxide mixture and the control of oxygen partial pressure as well as chlorine partial pressure plays important roles in the selective chlorination and evaporation reactions of zinc and lead from Fe_2O_3 -based oxide mixture.

4. Conclusions

Chlorination rate of Fe_2O_3 - ZnFe_2O_4 - ZnO - PbO mixture with $\text{Ar-Cl}_2\text{-O}_2$ gas was measured at 1073 K by gravimetry and the efficient selective chlorination and evaporation reactions of zinc and lead from Fe_2O_3 -based oxide mixture was demonstrated. Obtained results have been summarized in the followings.

(1) Zinc oxide and lead oxide were converted to ZnCl_2 and PbCl_2 , and removed from oxide mixture, while iron oxide remained as oxide in the chlorinated residue.

(2) Chlorination rate increased with increasing partial pressure of chlorine in the chlorination with Ar-Cl_2 gas. Zinc and lead oxide could be removed to 0.1 mass% and 0.03 mass%, respectively. In addition, approximately 3% of iron oxide was chlorinated and lost simultaneously.

(3) Chlorination rate of zinc oxide was affected by the oxygen partial pressure, while that of lead oxide was scarcely affected.

(4) Chlorination and evaporation reactions of iron oxide could be efficiently diminished and Fe_2O_3 loss decreased below 0.5% by utilizing $\text{Ar-Cl}_2\text{-O}_2$ gas, while the efficiency of zinc and lead removal was almost maintained.

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