Influence of Temperature on the Selective Chlorination and Evaporation Reactions of Zn and Pb in EAF Dust

Guodong Sun, Hiroyuki Matsuura and Fumitaka Tsukihashi

Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa 277–8561, Japan

Large amount of dust is produced during ironmaking and steelmaking process and it should be recycled or treated for the sake of environmental protection. Particularly, the dust produced in electric arc furnace (EAF) process is quite special because of its abundance in Zn and Pb, which makes it inappropriate for recycling to the conventional steelmaking process. Chlorination and evaporation method is a possible choice to treat the dust, in which Zn and Pb are selectively chlorinated and recovered as gaseous chlorides while the chlorination of Fe can be prevented in its oxidizing atmosphere. In the present study, the feasibility of the selective chlorination and evaporation reaction of Zn and Pb in EAF dust was confirmed in the mixing atmosphere of Cl_2 and O_2 gas ($P_{\text{O}_2} = 9.0 \times 10^4$ Pa and $P_{\text{Cl}_2} = 1.0 \times 10^4$ Pa). Change of oxide phase with reaction time was also analyzed by XRD measurement. The influence of temperature on the chlorination and evaporation reaction rate and removal fractions of Zn and Pb was investigated by gravimetric method and composition analyses at the temperature range from 923 K to 1073 K. The chlorination and evaporation rate increased with increasing temperature from 923 to 1073 K and the removal fractions of Zn and Pb after 60 min at 1023 or 1073 K reached approximately 98% and 99%, respectively. It was confirmed that small portion of Fe was chlorinated and evaporated from the dust in the present experimental conditions. [doi:10.2320/matertrans.M-M2016835]

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1. Introduction

Dust is one of major by-products during ironmaking and steelmaking process. In Japan 7.477 million tons of dust was generated in 2010.¹⁾ Among them the amount of dust generated from electric arc furnace (EAF) process is estimated to be around 500 kt per year (17 kg/t-steel).²⁾ EAF dust is hard to be directly recycled to the steelmaking process because of its abundance in Zn, Pb and halogen elements since the major raw material in this process is steel scraps, especially galvanized steel which is coated by zinc and also contains lead mainly as paints and electrical parts. If this dust is reused as raw material in a conventional steelmaking process, it will cause various troubles against the smooth operation of the process and also increase the energy consumption. On the other hand, simple disposal or landfill of EAF dust makes the total EAF process uneconomical because of rigorous environmental protection regulations in many countries³⁾ and it is regarded as a hazardous material because of the leachability of many heavy metals.⁴⁾ The presence of Zn and Pb is not only a problem but also an opportunity for metallurgical industry. If zinc and lead could be efficiently and economically separated from the EAF dust, the separated Zn and Pb bearing material could be a raw material in Zn and Pb industry and the Fe bearing residue could be also recycled in the steelmaking process.

Lots of efforts have been made by researchers, for example, searching for a reasonable way to recycle Zn for further treatment or a method to remove harmful elements contained in EAF dust before disposal. The present methods employed to treat EAF dust mainly include hydrometallurgy, pyrometallurgy and stabilization methods³⁾. The most widely used industrial process is Waelz kiln process, in which zinc is reduced, produced zinc evaporates from EAF dust and is oxidized by air.⁵⁾ The product of this process is crude zinc oxide. High zinc content of EAF dust is required for this process. Besides, the presence of ZnFe_2O_4 which is hard to be reduced

leads to the low reduction ratio of Zn in EAF dust. The main composition of residue is iron oxide and zinc ferrite, which still cannot be recycled in steelmaking process.

These years the chlorination method of EAF dust has been studied by many researchers.^{6–11)} Chlorides of Zn and Pb have relatively low boiling points (ZnCl_2 : 1004 K, PbCl_2 : 1223 K),¹²⁾ which can be employed to extract noble metals from EAF dust. Many chlorine bearing materials such as hydrochloric acid, chlorine gas and calcium chloride were used as chlorinating agents for the reaction. One of the critical problems in the practice of chlorination method is the simultaneous chlorination of Fe. In previous researches,^{13–15)} the effects of partial pressures of Cl_2 and O_2 in Ar- Cl_2 - O_2 atmosphere and reaction temperature on chlorination reaction were studied by using the mixture of reagent grade ZnO - ZnFe_2O_4 - Fe_2O_3 - PbO as an experimental raw material. It was confirmed that higher partial pressure of O_2 would drastically decrease the iron loss. It is essential to confirm the role of O_2 and investigate the influence of various factors such as temperature or atmosphere on the selective chlorination evaporation behaviors of real EAF dust because the composition of EAF dust is complicated and thus the mechanisms of its chlorination reactions may be much unpredictable. Therefore, it is necessary to study the reaction behavior further and confirm the feasibility of the chlorination process. In the present study, the feasibility of selective chlorination of EAF dust was studied in the Cl_2 - O_2 atmosphere ($P_{\text{O}_2} = 9.0 \times 10^4$ Pa and $P_{\text{Cl}_2} = 1.0 \times 10^4$ Pa) and the influence of temperature at temperature range from 923 K to 1073 K on chlorination and evaporation reactions was investigated.

2. Experimental

The EAF dust used in this research was provided by a steelmaking company in Japan. The composition of original EAF dust is shown in Table 1.

The major phases of EAF dust are spinels (Franklinite and

Table 1 Composition of original EAF dust (mass%).

Element	Zn	Fe	Pb	Cu	Al	Mg	Ca	C	Si	P	H ₂ O
Concentration	37.26	18.18	1.53	0.16	0.28	0.24	0.78	5.05	1.36	0.04	4.95

Fig. 1 X-ray diffraction pattern of the original EAF dust; 1: ZnFe₂O₄, 2: ZnO and 3: Zn(OH)₂.

Fig. 2 Schematic diagram of experimental apparatus.

Magnetite) and Zincite according to the literatures.^{16–18)} The X-ray diffraction pattern of the sample used in this research shown in Fig. 1 indicates the existence of ZnFe₂O₄, ZnO and Zn(OH)₂ phases.

Diffraction peaks regarding Fe₃O₄ phase were overlapped by those of ZnFe₂O₄ and thus the presence of Fe₃O₄ could not be assured. It was confirmed by chemical analysis that there was little Fe²⁺ in the sample. Therefore, it is concluded that iron was present only in the form of ZnFe₂O₄.

Schematic diagram of the experimental apparatus employed in the present study is shown in Fig. 2. The homogeneous EAF dust sample of about 1 g was put in a mullite boat (width 16 mm, height 12 mm, length 80 mm) and the boat was put into the center of an alumina or a mullite tube (25 mm O.D., 20 mm I.D. and 1000 mm length). Chlorine, oxygen and argon gases passed through silica gel columns for moisture absorption and ball flow meters were used to control the flow rate of gases. Experimental temperatures are 923, 973, 1023 and 1073 K. Before and after each experiment, argon gas passed through the tube for 3 min. The mixture of Cl₂ and O₂ gases (O₂: 450 cm³/min, Cl₂: 50 cm³/min) was provided in the reaction tube during prescribed reaction time. The EAF

dust sample and the residue after the experiment were weighed and their compositions were analyzed by ICP-OES. The XRD analysis was employed for the phase detection.

3. Results and Discussion

Possible chlorination reactions of components in EAF dust around 1023 K are expressed as reactions (1) to (4).

From the standard Gibbs energy change of chlorination reactions, it can be seen that the chlorination reaction of zinc and lead is easy to take place around 1023 K while the iron chloride is hard to form in the standard condition, which can be clearly seen by the chemical potential diagram in our previous study.¹³⁾ However, if no oxygen is supplied and $P_{\text{Cl}_2}/P_{\text{O}_2}$ value is too high, the chlorination reaction of iron oxide proceeds forward, which leads to the result of iron loss as reported by some researches^{11,13,14)}. In order to chlorinate zinc and lead while preventing chlorination of iron, high partial pressure of oxygen is essential.

Table 2 shows the weight of dust samples before and after experiments and based on these data, the weight loss of samples at various temperatures is calculated as shown in Fig. 3. Because the dust weights of EAF samples were more or less different around 1 g, in order to eliminate the influence of sample weight difference on the experimental result, weight loss ratio was calculated to show the experimental results. The weight loss ratio was defined as $W_{\text{weight loss by reaction}}(\text{g})/W_{\text{before reaction}}(\text{g})$. The removal fractions of Zn, Pb and Fe were calculated and shown in Table 3.

Figure 4 shows the weight loss ratio of the dust sample with time at various temperatures. The weight continuously decreased with time and the final weight loss ratios were affected by reaction temperature. The chlorination and evaporation reaction rate is defined as weight loss ratio (%) / reaction time (min). When the temperature was higher than 1023 K, the evaporation almost completed before 30 min and there was little difference in both the chlorination and evaporation reaction rate and the final weight loss ratio. At such temperatures, the maximal weight loss ratio was 58.9%, which is close to the expected weight loss ratio in the case of complete chlorination and evaporation of Zn and Pb and no chlorination of Fe in EAF dust.

As can be seen from the XRD analysis results in Fig. 5, ZnO was firstly chlorinated and vanished after 5 min, and then ZnFe₂O₄ was chlorinated continuously. After 20 min, any peak regarding Zn-containing phase was not detected, which is in accordance with the results in Table 3. Meanwhile, diffraction peaks for Fe₂O₃ phase became significant.

Table 2 Weight change of EAF dust sample after experiment.

No.	Temperature (K)	Gas composition	Time (min)	EAF dust Sample (g)	Residue after experiment (g)	Weight loss (g)	Weight loss ratio (%)
1-1	923	10%Cl ₂ -90%O ₂	3	1.026	0.992	0.034	3.31
1-2			5	1.062	1.064	-0.002	-0.19
1-3			8	1.061	1.035	0.026	2.45
1-4			15	0.972	0.887	0.085	8.74
1-5			30	1.022	0.808	0.214	20.94
1-6			40	1.006	0.751	0.255	25.35
1-7			60	0.994	0.634	0.36	36.22
2-1	973	10%Cl ₂ -90%O ₂	3	1.0081	1.0309	-0.0228	-2.26
2-2			5	1.0203	1.0072	0.0131	1.28
2-3			8	1.0157	0.896	0.1197	11.78
2-4			10	0.9963	0.8116	0.1847	18.54
2-5			15	0.984	0.7465	0.2375	24.14
2-6			30	0.9779	0.6315	0.3464	35.42
2-7			40	1.0072	0.5988	0.4084	40.55
2-8			60	1.0372	0.5366	0.5006	48.26
3-1	1023	10%Cl ₂ -90%O ₂	3	1.0196	0.7936	0.226	22.17
3-2			5	1.0035	0.6657	0.3378	33.66
3-3			8	1.097	0.6658	0.4312	39.31
3-4			10	1.0996	0.6118	0.4878	44.36
3-5			20	0.9459	0.4164	0.5295	55.98
3-6			30	1.0037	0.4174	0.5863	58.41
3-7			60	0.9617	0.3952	0.5665	58.91
4-1	1073	10%Cl ₂ -90%O ₂	3	1.151	0.872	0.279	24.24
4-2			5	1.125	0.735	0.39	34.67
4-3			8	1.087	0.594	0.493	45.35
4-4			10	1.0996	0.5668	0.5328	48.45
4-5			15	1.06	0.502	0.558	52.64
4-6			20	0.985	0.439	0.546	55.43
4-7			30	0.958	0.45	0.508	53.03
4-8			40	0.96	0.436	0.524	54.58
4-9			60	0.991	0.425	0.566	57.11

Table 3 Removal fractions of Zn, Pb and Fe.

No.	Temperature (K)	Gas composition	Time (min)	Weight loss ratio (%)	Removal fraction of Zn (%)	Removal fraction of Pb (%)	Removal fraction of Fe (%)
1-1	923	10%Cl ₂ -90%O ₂	3	3.31	10.15	10.16	7.45
1-2			5	-0.19	9.04	4.88	3.22
1-3			8	2.45	17.22	6.50	6.25
1-4			15	8.74	28.78	9.51	6.32
1-5			30	20.94	57.43	12.37	-14.55
1-6			40	25.35	52.43	14.15	4.42
1-7			60	36.22	53.11	25.49	19.84
2-1	973	10%Cl ₂ -90%O ₂	3	-2.26	21.85	16.62	-1.86
2-2			5	1.28	33.89	18.28	-0.31
2-3			8	11.78	47.39	24.61	-0.25
2-4			10	18.54	54.54	29.21	1.86
2-5			15	24.14	62.45	38.55	2.09
2-6			30	35.42	73.79	63.07	0.34
2-7			40	40.55	78.52	67.47	-5.97
2-8			60	48.26	86.75	83.78	0.57
3-1	1023	10%Cl ₂ -90%O ₂	3	22.17	34.37	43.11	-2.32
3-2			5	33.66	54.72	53.69	1.11
3-3			8	39.31	65.00	59.79	2.10
3-4			10	44.36	72.22	72.73	4.68
3-5			20	55.98	93.23	94.80	3.15
3-6			30	58.41	98.76	99.52	4.05
3-7			60	58.91	97.91	98.48	6.87
4-1	1073	10%Cl ₂ -90%O ₂	3	24.24	35.07	29.3	1.3
4-2			5	34.67	59.23	66.5	-3.9
4-3			8	45.35	81.37	91.40	-5.6
4-4			10	48.45	-	-	-
4-5			15	52.64	97.42	100	-2.8
4-6			20	55.43	97.75	100	13.6
4-7			30	53.03	98.17	100	-2.9
4-8			40	54.58	99.01	100	1.7
4-9			60	57.11	98.09	100	3.1

Fig. 3 Change in the weight loss with reaction time at various temperatures.

Fig. 4 Change in the weight loss ratio with reaction time at various temperatures.

Fig. 5 X-ray diffraction patterns of initial dust and residues reacted at 1023 K.

Fig. 6 Weight change of PbO, ZnO, Fe₂O₃ and others at 1073 K.

Combining the XRD results with measured weight loss and compositions, the weight change of major components in EAF dust with the reaction time at 1073 K was calculated and shown in Fig. 6. ZnO and Fe₂O₃ contents include ZnO and Fe₂O₃ in ZnFe₂O₄, respectively. ZnO and PbO were gradually removed from the dust while the amount of Fe₂O₃ was stable. In the case of other components in EAF dust, there is large weight loss in initial 3 min, which would be the result of the evaporation of water (even though the dust was dehydrated initially, it was confirmed that water was absorbed when open the dust bottles frequently) and chlorides, or the combustion of carbon. It seems that other elements in EAF dust except Zn and Pb are hard to be chlorinated and evaporate.

Fig. 7 Effect of reaction temperature on the removal fraction of Zn in EAF dust.

Fig. 8 Effect of reaction temperature on the removal fraction of Pb in EAF dust.

The removal fractions of Zn and Pb from the sample are shown in Fig. 7 and Fig. 8, respectively. The removal fraction of Zn continually increased with time. As the zinc content in dust decreased, the chlorination and evaporation reaction rates became smaller and the weight loss finally stopped. The chlorination and evaporation reaction rates increased with increasing temperature. The final removal fractions of Zn and Pb also increased with the increase of temperature from 973 to 1023 K. On the contrary, comparing the final removal fractions of Zn and Pb at 1023 and 1073 K, the influence of reaction temperature on the final removal fractions was negligibly small. The final removal fraction of Zn and Pb was around 98% and 99% for 60 min at 1023 or 1073 K, respectively.

Figure 9 shows the change in the removal fraction of Fe with reaction time. It fluctuates around zero and has no obvious relationship with reaction temperature. The fluctuation would be due to the analytical error and the inhomogeneity of EAF dust samples. Considering the present experimental conditions from thermodynamic viewpoint as discussed at the beginning, it is concluded that few portion of Fe was chlorinated and evaporated.

In order to further confirm the above results, the exhaust

Fig. 9 Effect of reaction temperature on the removal fraction of Fe in EAF dust.

Table 4 Recovery ratio of elements by water.

Element	Zn	Fe	Pb
Yield (%)	20.19	0.04	21.90

Table 5 Experimental conditions of previous¹³⁾ and present study.

	Previous study ¹³⁾	Present study
Temperature (K)	1073	1073
Sample composition (mass%)	Zn: 20 Pb: 4 Fe: 50 Mixture of reagents	Zn: 37.3 Pb: 1.5 Fe: 18.2 Real EAF dust
Sample weight (g)	2	1
Atmosphere	10%Cl ₂ -10%O ₂ -50%Ar	10%Cl ₂ -90%O ₂
Flow rate (cm ³ /min)	600	500

gas was rinsed by water for 60 min when the chlorination reaction of EAF dust was conducted at 1023 K (Exp. 3-7). The solution composition was analyzed by ICP-OES. The yield of Zn, Fe or Pb was defined by eq. (5) and calculated results are shown in Table 4.

$$\text{Yield (\%)} = \frac{W_{\text{Element in water (g)}}}{W_{\text{Element in dust (g)}}} \times 100 \quad (5)$$

Though most of the produced chlorides condensed at the end of the reaction tube, more than 20% of Zn and Pb were recovered while Fe yield was significantly small. This result provides another evidence about the thermodynamic stability of Fe₂O₃ against the chlorination reaction at highly oxidizing condition.

In previous research,¹³⁾ the chlorination experiments were conducted using the mixture of reagent grade ZnO-ZnFe₂O₄-Fe₂O₃-PbO as an experimental raw material. The experimental conditions of previous and present experiments are compared in Table 5. Note that the sample composition in previous experiment was 20 mass%Zn, 4 mass%Pb and

Fig. 10 Comparison of the removal fraction between present and previous¹³⁾ results.

50 mass%Fe while that in present experiment is 37.3 mass%Zn, 1.5 mass%Pb and 18.2 mass%Fe. Sample weights in previous and present experiments are 2 g and 1 g, respectively.

Content of Zn is different but the weight of Zn is very close (previous study: 0.40 g, present study: 0.37 g). It could be known from Fig. 10 that the removal ratio curves of Zn are close and the chlorination and evaporation reaction rate of present experiment is a little higher than that of previous experiment in initial stage even though in previous experiment Cl₂ of higher flow rate was used. That was because the reactivity of ZnFe₂O₄ with Cl₂ gas was lower than that of ZnO in the present study and the weight of ZnFe₂O₄ was smaller than that in previous study while the weight of ZnO was larger.

For the element of Pb, the chlorination and evaporation reaction rate of previous experiment before 8 minutes was much larger than present result. Pb content of dust in previous experiment was much higher than that in present experiment, the reason why the chlorination and evaporation reaction rate was much higher remains unclear.

Tiny amount of Fe was lost during the chlorination reaction in previous and present studies. The removal ratio of Fe fluctuates around zero in the present study while that of previous result is much smaller, which is because of the inhomogeneity of real EAF dust.

4. Conclusions

In this research, the chlorination and evaporation reaction of EAF dust in the atmosphere of 10% Cl₂-90% O₂ was studied at the temperature between 923 K and 1073 K. The summary of the experimental results are as follows:

- (1) In the atmosphere of high oxygen partial pressure, zinc and lead were chlorinated and evaporated from EAF dust while iron remained in the form of iron oxide at the present temperature range. The feasibility of selective chlorination of Zn and Pb in EAF dust was fulfilled.
- (2) Zinc oxide was chlorinated and vanished from the residue prior to zinc ferrite.
- (3) The increase of reaction temperature from 923 K to 1073 K raised the chlorination and evaporation reaction rate.

- (4) The removal fractions of Zn and Pb after 60 min at 1023 or 1073 K were about 98 and 99%, respectively.

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