Thermodynamic Analysis on the Dust Generation from EAF for the Recycling of Dust

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Recently, in addition to the large interest on the CO$_2$ emission problem, the energy saving and the environmental conservation become more and more important issue. Zero emission campaign is adopted by many companies. In such circumstances, most of steel companies were carrying out the recycling of dust by many ways. There are many aspects on the dust recycling. One of important purpose is the zinc recovery, and other is the utilization as a slag (e.g. roadbed material) by injection. Especially for the dust injection, many troubles such as an accumulation in the filtering system and an increase of the content of harmful elements in the dust will occur. Then, it become very important to understand the mechanism and the thermodynamics of the dust generation and precipitation form EAF to prevent those troubles.

In this study, the dust sampled from the impeller of blower in the dust filtering system of EAF was examined by XRD and XRF. Quite complicated compounds formed in Zn–Fe–Pb–Cr–Mn–O–F system were found in the dust according to the dust injection. Thermodynamic analysis was performed and the equilibrium composition obtained from the calculation was in excellent agreement with the actual composition in the dust. Main constituents in the dust are ZnFe$_2$O$_4$ and Fe$_2$O$_3$. Relatively dominant ones are as follows: Fluorides are FeF$_3$, ZnF$_2$, and PbF$_2$, chlorides are ZnCl$_2$ and PbCl$_2$, and oxides are ZnO and MnO$_2$. The fluorides deposit around 1 000°C from gas phase. And the chlorides ZCl$_2$, PbCl$_2$ and oxides MnO$_2$ form less than 500°C. The partial pressure of chloride gas will become a maximum around 400°C, when there is no moisture.

KEY WORDS: dust; thermodynamic analysis; injection of dust; EAF; chlorides; fluorides; zinc recovery.

1. Introduction

As the dust generated in the ironmaking and steelmaking process includes valuable metals such as zinc, lead and iron, it is an important and secondary resource for industrial society. General purpose of the dust processing from metal industry might be the recovery of zinc. While some of company is carrying out the utilization of EAF (electric arc furnace) slag for the material of a roadbed and so on. In such a case, it would be better to utilize the dust as a slag by injection into the EAF. In the course of dust recycling, as the zinc content in the dust will increase, the added-value of the final dust can increase. However, because of high zinc content in the dust, the reducibility of iron oxide is relatively low. Furthermore, the existence of lead, chlorine and alkali compounds is disturbing the recovery of pure zinc and/or the processing of the dross. Thus, many problems will exist in the recycling of the dust. Moreover, the harmful elements such as the lead, cadmium, hexavalent chromium and fluorine should be utilized by overcoming the environmental problems.

Recently, in addition to the large interest on the CO$_2$ emission problem, the energy saving and the environmental conservation become more and more important issue. Zero emission campaign is adopted by many companies. The dust processing will be one of an effective way for zero emission. In such circumstances, most of steel companies were carrying out the recycling of dust with many ways. Especially, some of the steel companies having EAF carried out the dust injection as the recycle of dust in the plant. It would be very important to understand the mechanism and the thermodynamics of the dust generation or precipitation form EAF to prevent those troubles.

In this study, XRD (X-ray diffraction) and XRF (X-ray fluorescent) analysis of the deposited dust in the filtering system was performed. Thermodynamic analysis was performed and the equilibrium composition obtained from the calculation was in excellent agreement with the actual composition in the dust. Main constituents in the dust are ZnFe$_2$O$_4$ and Fe$_2$O$_3$. Relatively dominant ones are as follows: Fluorides are FeF$_3$, ZnF$_2$, and PbF$_2$, chlorides are ZnCl$_2$ and PbCl$_2$, and oxides are ZnO and MnO$_2$. The fluorides deposit around 1 000°C from gas phase. And the chlorides ZCl$_2$, PbCl$_2$ and oxides MnO$_2$ form less than 500°C. The partial pressure of chloride gas will become a maximum around 400°C, when there is no moisture.

KEY WORDS: dust; thermodynamic analysis; injection of dust; EAF; chlorides; fluorides; zinc recovery.
2. Facility of Dust Filtering System and Measurement of Temperature and Gas Concentration during Operation

Figure 1 shows the dust filtering system equipped with No. 3 EAF in Aichi Steel Co. The steel pipe with 200 cm in diameter is connected from EAF to the bug filter, in which the combustion tower and the cooling tower are equipped for oxidizing and cooling the generated dust, respectively. The blower having impeller is used for the suction of air including the dust, which flowrate was about 5 600 m$^3$/min (at 250°C).

Measurements of the temperature and the gas composition of O$_2$, CO and CO$_2$ were carried out during operation. Three positions, (a), (b) and (c) were selected for the measurements as shown in Fig. 1. An air is just mixed at the combustion tower for oxidizing the generated dust, because the gas temperature including the dust is high, the oxidation of the dust will proceed easily. The dust temperature gradually decreased from the cooling tower until the blower. The temperature at the position (c) in Fig. 1 was around 200°C (variation was from 100 to 400°C). At the position (a), the temperature was around 500°C and the variation of temperature during the operation accompanied with the dust injection is shown in Fig. 2. The variation of O$_2$ and CO$_2$ concentration are also shown in Fig. 2. The variation of CO gas was also measured together with O$_2$ and CO$_2$. Since the concentration range of CO gas was ppm order and the way of changing was the same as CO$_2$, CO was neglected from the Fig. 2. Four operations were carried out within 5 h and two scrap charges were performed in each operation. The combination of the dust injection and the slag injection were selected and performed in the respective operation on the basis of the experimental design theory.

The temperature at the outlet of the combustion tower decreased from 500 to 100°C, when the scrap was charged. According to this action, O$_2$ concentration increased from 15 to 21 % and CO$_2$ decreased from 8 to almost 0 %. When the arc was applied, the temperature increased until 500°C rapidly, and the variation of O$_2$ and CO$_2$ showed opposite behavior. These behaviors would be resulted from the combustion reaction of carbon and the oxidation reaction of metallic elements evaporated from EAF. The cycle of these variations of temperature and the gas concentrations was almost the same and repeated according to the arc melting operation.

Figure 3 shows the relationship between the concentration of oxygen and the temperature at the position (a). These results will be caused by the following reactions.

$$\text{C} + \frac{m}{2} \text{O}_2(g) = \text{CO}_2(g) \quad \text{(1)}$$

$$n\text{Me} + \frac{m}{2} \text{O}_2(g) = \text{Me}_n\text{O}_m \quad \text{(Me: metallic element)} \quad \text{(2)}$$

The CO$_2$ increase showed in Fig. 2 would be caused by the reaction (1). If there were no halogen elements (chlorine and fluorine), it is considered that most of compounds in the dust will be an oxide. However, the content of chlorine and fluorine is increasing with the dust recycle operation. Figure 4 shows the variation of zinc, chlorine and fluorine in the dust during the dust injection operation, in which total dust injection was about 150 tons for the first 10 d. The content of zinc in the dust increased from 24 to 35 % and the chlorine increased from 3.8 to 5.3 %. During 5 d recess, the zinc and chlorine contents decreased in this period. The behavior of fluorine content was not so clear to the dust injection, however, overall behavior of the fluorine content followed the dust injection.
3. Dust Composition and Distribution of the Elements in the Dust Layer Adhered on the Impeller

Figure 5 shows the result of XRF (X-ray fluorescent) analysis of the dust deposited on the impeller of blower. The main components were zinc and iron, and lead, chrome and manganese were also contained in the dust. Distribution of these elements in the deposited dust layer was measured using \( \mu \)-XRF (beam size: 100 \( \mu \)m) and showed in Fig. 6. The thickness of the layer was about 1 mm. The distribution of each elements consisted of a layer which was roughly parallel to the macroscopic layer. The locations of zinc and iron were almost the same and lead was concentrated in the area where the iron content was low.

This dust layer was crushed and the powder was served to the XRD (X-ray diffraction) analysis for determining the kind of compounds. Figure 7 shows the result of XRD analysis (the number beside the compound means the one in the ASTM card). It was found that quite complicated compounds existed in the dust. However, almost 100% peaks could be explained. The iron compounds were \( \text{ZnFe}_2\text{O}_4 \), \( \text{Fe}_2\text{O}_3 \) and \( \text{FeF}_3 \), the zinc compounds were \( \text{ZnO} \), \( \text{ZnF}_2 \) and \( \text{ZnCl}_2 \), lead ones were \( \text{PbCl}_2 \), \( \text{PbF}_2 \) and manganese one was \( \text{MnO}_2 \). The chromium compound was very small and difficult to detect by XRD.

4. Thermodynamic Analysis of Dust Generation: Zn–Fe–Pb–Mn–Cr–O–Cl–F System

The precise thermodynamic analysis will be difficult for the Zn–Fe–Pb–Mn–Cr–O–Cl–F system. However, as the basic system is Zn–Fe–O–Cl–F system, the preliminary analysis was carried out for Zn–O–Cl–F and Fe–O–Cl–F systems, respectively.

Figure 8 shows the predominance diagrams on the Zn–O–Cl, Zn–O–F and Zn–Cl–F systems. The result of XRD showed the existence of \( \text{ZnO} \), \( \text{ZnF}_2 \) and \( \text{ZnCl}_2 \) (Fig. 7). The possible partial pressure range for the existence of those compounds was examined. As it was considered that the temperature range of the dust deposition would be less than 500°C, the range from 500 to 100°C would be enough temperature range to analyze. In Zn–Cl–F system, both of \( \text{ZnF}_2 \) and \( \text{ZnCl}_2 \) can be formed in the following range of \( P_{\text{Cl}_2} \) (Fig. 8(b)).

\[-15<\log P_{\text{Cl}_2}<0 \quad \ldots \quad (3)\]
\[
\log P_{\text{F}_2}=-40 \quad \ldots \quad (4)
\]

Although the chlorine partial pressure is as high as 1 atm around 150°C, \( \text{ZnF}_2 \) can be formed, when the partial pressure of \( \text{F}_2 \) is as low as \( 1 \times 10^{-40} \text{ atm} \). From Figs. 8(c) and
It can be assumed that the partial pressure of chlorine $P_{\text{Cl}_2}$ was from 0.001 to 0.0001 atm ($P_{\text{O}_2}/H_2O=0.2$ atm at 500°C), because the $P_{\text{Cl}_2}$ should be larger than $10^{-4}$ atm for the coexisting of ZnO and ZnCl$_2$. From these considerations, it was found that the ZnF$_2$ would be always dominant when there was small quantity of fluorine existing in the system. And the partial pressure of chlorine should be larger than $10^{-3}$ atm for the ZnCl$_2$ formation when the oxygen partial pressure was 0.2 atm.

Figure 8 shows the predominance diagrams on the Fe–F–Cl and Fe–Cl–O systems. From Fig. 8(a), FeF$_3$ is dominant in a relatively high $P_{\text{Cl}_2}$ ($=0.1$). When the partial pressure of fluorine is around $10^{-4}$ atm at 200°C, $P_{\text{Cl}_2}$ should be high and around $10^4$ atm for the formation of FeCl$_3$, that is, it is almost impossible to form (Fig. 8(c)). These results indicate that Fe$_2$O$_3$ and FeF$_3$ will be dominant in Fe–Cl–F system with a relatively high Cl$_2$ pressure.

4.1. Equilibrium Composition in Zn–Fe–Pb–Mn–Cr–O–Cl–F System

To understand the deposited dust composition, thermodynamic calculation from 1800°C to ambient temperature was performed. Based on the chemical composition of dust, the rate of vaporization of metallic elements were determined as shown in Table 1. Chlorine and fluorine were treated as gas phase at the beginning of the calculation, al-
though those elements originated from solid phase (dust).

Table 2 shows the kinds of compounds which are possible to form from the elements, Zn, Fe, Pb, Mn, Cr, O, Cl and F. In the preliminary calculation, 41 compounds in gas phase and 39 compounds in solid phase were taken into account. An assumed amount of input was shown in Table 1. The SOLGASMIX equilibrium routine which is integrated in the HSC Chemistry package was used to calculate the equilibrium composition. From the result of the preliminary calculation, low concentration compounds less than 0.1 mol%, which were marked by asterisk (*; Table 2), were neglected for the final calculation. 14 compounds in gas phase and 20 compounds in solid phase were taken into account for the final calculation.

Figures 10 and 11 show the calculation results of equilibrium composition in the dust. Figure 10 shows the variation of compounds in gas phase and Fig. 11 shows the one in solid phase.

In higher temperature than 1 400°C, main constituent in gas phase is Zn(g) (except O₂). From 1 400 to 500°C, largest one is ZnCl₂(g), and the second ones are ZnF₂(g), FeF₃(g), PbCl₂(g), PbCl₃(g) which are stable in different temperature range (Fig. 10). The maximum chlorine partial pressure exists around 400°C, which means that the injection of humid air for the cooling will increase the HCl content in the gas. This result would be very important to understand the actual dust behavior that the dust sticking occurred inside the filtering system. If all the dust particles were dried, there would be no sticking. The reason of sticking could be explained by the wetting and/or the active surface near the melting point. In these consideration, it might be important the existence of HCl (or Cl₂) and ZnCl₂. If the content of HCl gas in the dust increased, the sticking of dust particle would be promoted and the adhesion of dust
inside the blower would increase. How to eliminate the Cl₂ gas evolution and the formation of HCl gas in this temperature range will be the important factor to prevent the dust adhesion in the filtering system. Moreover, as the melting point of ZnCl₂ is 287°C, the property of ZnCl₂ less than 287°C will be adhesive and it could be a cause of dust adhesion also.

In solid phase (Fig. 11), the main constituents are ZnFe₂O₄ and Fe₂O₃. In the temperature range less than 1000°C, the constituents are ZnO, MnF₂, MnO₂, ZnCl₂, ZnF₂ and PbCl₂. And the chlorides ZCl₂, PbCl₂ and oxides MnO₂ will form less than 500°C. These compounds are in quite good agreement with the result of XRD (Fig. 7). Only MnF₂ and FeF₃ were different between the thermodynamic calculation and the actual dust composition. However, if the fluorides deposited around 1000°C from gas phase (ref. Fig. 10), the fluorides were FeF₃, PbF₂ and ZnF₂, which were the same compounds in the actual dust. These behaviors of dust deposition were just discussed from the macroscopic point of view by thermodynamic analysis. The microscopic mechanism of dust deposition such as the site of deposition will be very important knowledge. In future, another approach for the dust deposition will be necessary to clarify the microscopic mechanism.

In present study, the existence of oxychloride such as (ZnOCl, FeOCl, etc.) did not taking into account.

The behavior of oxychloride will be important for a detailed analysis. Recently, S. H. Son, et al. have published the data on the vapor pressure of zinc oxychloride. The formation of gaseous ZnOCl should be considered in high oxygen pressure.

\[ \text{ZnCl}_2(g) + 1/2 \text{O}_2(g) = \text{ZnOCl}(g) + 1/2 \text{Cl}_2(g) \]  
\[ \Delta G^\circ = -14.3 + 0.069T \text{ (kJ/mol)} \]  

Using Eq. (6), the vapor pressure of ZnOCl is relatively large and almost the same level (\( P_{\text{ZnOCl}} = 0.022 \)) as Cl₂ gas at 500°C. However, data for other oxychlorides could not be established sufficiently until now. And the ZnOCl gas will deposit as ZnCl₂, so that the discussion on the dust deposition will need further experimental data.

5. Conclusions

The dust sampled from the impeller of blower in the dust filtering system of EAF during the dust injection operation was examined by XRD and XRF. Quite complicated compounds formed in Zn–Fe–Pb–Cr–Mn–O–Cl–F system were found in the dust. Thermodynamic analysis from 1800°C to ambient temperature was performed and the equilibrium composition around ambient temperature obtained from the calculation was in excellent agreement with the actual composition in the dust.

Obtained results are as follows.

1 Main constituents in the dust are ZnFe₂O₄ and Fe₂O₃. Relatively dominant compounds are as follows: Fluorides are FeF₃, ZnF₂ and PbF₂, chlorides are ZnCl₂ and PbCl₂, and oxides are ZnO and MnO₂.

2 From the thermodynamic calculation, it was found that the fluorides deposited around 1000°C from gas phase. And the chlorides ZCl₂, PbCl₂ and oxides MnO₂ will form less than 500°C.

3 The partial pressure of chloride gas becomes a maximum around 400°C, which will form HCl produced by the reaction with moisture in the air. Moreover, deposited ZnCl₂ less than the melting point (287°C) will be adhesive. These results will cause to the adhesion of the dust in the filtering system.

REFERENCES