Problems and Prospects of Halogen Element Contained Dust Treatment in Recycling

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For processing the halogen element contained dust (for example, Electric Arc Furnace Dust and Auto Shredder Residue) generated at the time of recovery of valuable metals by the smelting furnace, the problem of EAF dust processing, such as comparisons of the present technology in pyro-metallurgy and hydro-metallurgy, behavior of the zinc volatilization in pyro-metallurgy, mechanism of the impurities accumulation in hydro-metallurgy, and de-halogen processing were described using computer simulation.

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1. Introduction

Although steel material is a metal which is comparatively easy to recycle, zinc plating is given to a used automobile steel plate and used steel materials for construction, and it follows that volatilization of zinc on them in recovery of the iron in an electric furnace.

As a result, EAF dust occurs.

Although on-site processing of EAF dust is also progressing, for the improvement in the recovery rate of a valuable metal, the repetition in a system results in a fall tendency as a rate of volatilization of zinc.

And new problems, such as accumulation of the impurities in a system, are also realized.

Furthermore, it points also to performing processing of the shredder dust of a car (or Auto Shredder Dust), and processing of waste plastic by an electric furnace, and importance will be further attached to these problems from now on.

For the EAF dust processing, the problems, such as comparisons of the present technology for the pyro-metallurgy and hydro-metallurgy, behavior of zinc volatilization in pyro-metallurgy, mechanism of impurities accumulation in hydro-metallurgy, de-halogen processing, and the prospects of EAF dust processing will be described based on the analysis using computer simulation.

2. Present Technology

In recovery of valuable metals from EAF dust, zinc and lead are mainly collected.

At present, the pyro-metallurgical reduction process (volatilization of zinc and lead is promoted) is used.

In equipment, a rotary kiln, a moving bed furnace, and a top blowing furnace etc. are employed.

However, the room of improvement, such as zinc content in the crude zinc oxide as a product or a reduction pellet (it is hereafter indicated as RP), halogen content, and exhaust gas processing, is left behind.

In the pyro-metallurgical method, zinc, lead and halogen content of RP, or concentration of exhaust gas is mainly controlled by temperature, atmosphere, and retention time.

From an equipment side, chemical engineering and chemical reaction engineering factors do influence further.

The notional performance of each process is shown in Fig. 1.

From the view point of thermodynamics and kinetics, the relative relations about EAF dust processing, such as a rotary kiln, a moving hearth furnace, and a top blowing furnace, are shown.

Qualitatively, if EAF dust is held under a strong reducing atmosphere at high temperature for a longer time, RP of low zinc and halogen content will be generated.

For example, a rotary kiln is used at the temperature of about 1373 K, and converter technology at high temperature of 1773 K or more and a moving furnace near 1573 K.

Since zinc and lead are contained as valuable metals in generated EAF dust and halogen is contained simultaneously, de-halogen processing may also be required.

If shredder dust will be processed from now on, it is expected that the halogen content in EAF dust will increase.
3. Thermodynamic Approach

3.1 Pyro-metallurgy

3.1.1 Zinc volatilization

In the reduction smelting of zinc, the coexistence domains of various species, such as zinc vapor Zn (g), zinc oxide ZnO, hematite Fe$_2$O$_3$, magnetite Fe$_3$O$_4$, wüstite FeO, and metal iron (Fe$^{2+}$) can be described by using a potential diagram of the Zn-Fe-O-C system.

Figure 2 shows the relationship between temperature and atmosphere ($P_{CO}/P_{CO_2}$) of Zn-Fe-O-C system. In the reduction smelting of zinc, since the configuration of coexisted iron changes with atmosphere drastically, the volatilization reaction and operation conditions of zinc smelting are influenced greatly.

At the temperature of 1273 K or more, the vapor pressure of zinc is set to 1 atmosphere or more and by ten or more as $P_{CO}/P_{CO_2}$ ratio which maintains the reduction atmosphere with which metallic iron (Fe$^{2+}$) can coexist. The hematite which Fe$_2$O$_3$ (s) is simultaneously reduced step by step to magnetite Fe$_3$O$_4$ (s) and wustite FeO (s), finally reduced to metallic iron Fe (s).

Zinc ferrite (ZnO-Fe$_2$O$_3$ (s)), which is relatively stable at low temperature, decomposes above 1073 K. Above 1273 K, it is shown that volatilization of zinc is possible also under coexistence of metallic iron (Fe$^{2+}$).

3.1.2 Behavior of halogen element

In EAF dust processing, since there are many kinds of halogen compounds, the quantitative consideration are difficult in the present time.

Each halogen element, such as chlorine (Cl), fluorine (F), or bromine (Br) could be converted to hydrochloric acid (HCl), hydrofluoric acid (HF), hydrobromic acid (HBr), etc. under coexistence of water (H$_2$O).

When taking the halogen compounds of zinc and lead into consideration, reactions with these gas ingredients are also important.

As a much more practical system, the influence of reduction atmosphere and halogen is grasped by the Zn-Fe-O-C-Cl system.

Moreover, in order to grasp the influence of water vapor (H$_2$O), complex systems need to be examined further like a Zn-Fe-O-C-Cl-H system.

Figure 3 shows the chemical potential diagram of Zn-Fe-O-C-Cl system at 1473 K. The horizontal axis is made into activity of carbon, $a_c$, the vertical axis is made into oxygen potential log $P_{O_2}$, and it is the case of log $P_{Cl_2}$ = 0.001 MPa by chlorine. When oxygen potential log $P_{O_2}$ is high, zinc chloride vapor ZnCl$_2$ (g) coexists with iron chloride FeCl$_3$ (g), if it coexists with hematite Fe$_2$O$_3$ and oxygen potential log $P_{O_2}$ becomes low.

Figure 4 shows the chemical potential diagram of Zn-Pb-O-C-Cl-H system at 1473 K. In order to consider the influence of water (H$_2$O), the horizontal axis was made to vapor pressure of water $P_{H_2O}$, and the vertical axis was made into oxygen potential log $P_{O_2}$.

The domain where the thermal hydrolysis under existence of water (H$_2$O) becomes predominant can be considered. To accomplish the thermal hydrolysis of zinc chloride ZnCl$_2$ (g), the hydrolysis reaction of lead chloride PbCl$_2$ (g) is shown below.
\[ \text{ZnCl}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{ZnO}(s) + 2\text{HCl}(g) \]  
\[ \text{PbCl}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{PbO}(s) + 2\text{HCl}(g) \]

Figure 5 shows the chemical potential diagram of Zn-Pb-Fe-O-C-Cl-H system at 1000 K.

In order to consider the volatilization reaction of lead chloride PbCl\(_2\), calculation temperature was fixed at 1000 K as the middle temperature, that is the boiling point of which is between 774 K and 1223 K.

Lead chloride PbCl\(_2\) becomes significant under the weak oxidizing conditions that zinc oxide ZnO may exist.

However, if liquid lead metal Pb(l) will be produced under reduction condition, it is hard to volatilize.

### 3.2 Hydro-metallurgy

The crude zinc oxide produced by pyro-metallurgical processing by the rotary kiln of EAF dust contains chloride and fluoride as halogen compound. Halogen elements can be removed by washing by using some compound which can be easily dissolved.

However, the compound which is hard to decompose also exists in the halogen compound which has passed through pyro-metallurgical processing. Decomposition by addition of sodium carbonate (Na\(_2\)CO\(_3\)) or sodium hydrate (NaOH) is also used together. The main de-halogen reactions are shown below.

\[ \text{PbCl}_2(l) + \text{Na}_2\text{CO}_3(l) \rightarrow \text{PbCO}_3(s) + 2\text{NaCl}(l) \]  
\[ \text{PbFCl}(s) + \text{Na}_2\text{CO}_3(l) \rightarrow \text{PbCO}_3(s) + \text{NaCl}(l) + \text{NaF}(l) \]

Table 1 shows the solubility of the main halogen compounds.

In the de-halogen processing by hydrometallurgical process, washing method is mainly performed, because solubility of the chloride of zinc or lead is relatively large.

However, the solubility of the fluoride, the sulfate, or the carbonate of lead is small, respectively.

### Potential-pH diagram of Pb-Cl-CO\(_3\) system and potential-pH diagram of Pb-Cl-SO\(_4\) system at 298 K

In an actual de-halogen process, there are zinc (Zn), lead (Pb), chlorine (Cl), fluorine (F) and sulfate ion (SO\(_4\)) in the solution.

Since the solubility of lead sulfate (PbSO\(_4\)) is very small, existence of sulfate ion (SO\(_4\)) as anion cannot be disregarded.

Main precipitation reactions are shown below.

\[ \text{PbCl}_2(l) + 2\text{H}^+(l) + \text{SO}_4^{2-}(l) \rightarrow \text{PbSO}_4(s) + 2\text{HCl}(l) \]  
\[ \text{PbCl}_2(l) + 2\text{H}^+(l) + \text{CO}_3^{2-}(l) \rightarrow \text{PbCO}_3(s) + 2\text{HCl}(l) \]

Table 1 Solubility of main halogen compounds.  

<table>
<thead>
<tr>
<th>Species</th>
<th>Solubility</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{ZnCl}_2</td>
<td>77.0</td>
<td>w</td>
</tr>
<tr>
<td>\text{PbCl}_2</td>
<td>1.07</td>
<td>w</td>
</tr>
<tr>
<td>\text{PbFCl}</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>\text{NaCl}</td>
<td>26.43</td>
<td>w</td>
</tr>
<tr>
<td>\text{Na}_2\text{CO}_3</td>
<td>22.7</td>
<td>w</td>
</tr>
<tr>
<td>\text{PbSO}_4</td>
<td>4.52</td>
<td>S/10^{-2}</td>
</tr>
<tr>
<td>\text{ZnSO}_4</td>
<td>36.49</td>
<td>w</td>
</tr>
<tr>
<td>\text{NaF}</td>
<td>3.98</td>
<td>w</td>
</tr>
</tbody>
</table>

w: Anhydrite mass/g contained in saturated solution 100 g  
s: Anhydrite mass/g contained in saturated solution 1 dm\(^3\)
Although an example of a thermodynamic calculation result was shown, for simplicity, activity of each species was fundamentally set to be 1.

In practice, there are many interactions between metals, oxides, or salt, respectively.

4. Future Deployment

4.1 Chemical engineering approach

A certain amount of quantification of the reaction in a furnace based on mass transfer and heat transfer is attained.

For example, the feature of a rotary kiln is that mass transfer in a bed layer, a gas layer, and from a gas layer to wall heat transfer and bed layer and mass transfer movement accompanied by a reaction in a bed layer can take place simultaneously, and these move in the direction of axis.

A much more efficient operation criteria will be shown by the technical development in this direction.

4.2 Mineral engineering approach

Although calculated in consideration of existence of various species in thermodynamic examination, mineral engineering approach is also effective in further detailed examination of an actual materials and an actual product.

Table 2 shows the main minerals encountered in reduction smelting of zinc.

The oxide of zinc, the oxides of iron, and the compounds consisting of these exist, and the form and size are also complicated. By using the configuration analysis by both the optical microscope and the electron microscope, the validity of the thermodynamic approach could increase further.

4.3 Behavior of exhaust gas

Although the exhaust gas in reduction smelting of zinc contains oxygen gas \( \text{O}_2 \) (g), carbon dioxide \( \text{CO}_2 \) (g), carbon monoxide \( \text{CO} \) (g), and zinc vapor \( \text{Zn} \) (g), if halogen elements coexist, it could serve as complex composition.

It is necessary to recognize these reactions correctly and to consider exhaust gas processing.

About the behavior of an organic chlorine compound, computer simulation is possible.\(^5\)

5. Direction of New Technical Development

The process proposed for the processing of EAF dust is shown in Table 3.

In each process, although the improvement is made continuously, about the mechanism of volatilization of zinc or lead, there are also many unknown areas.

The unified view established about the reaction of halogen is not necessarily.

Thermodynamically, although the tendency can be considered by using a potential diagram, the side point of chemical engineering cannot be ignored. Since an equipment factor also contributes significantly, the subject in this direction needs a systematic approach.

Complete compilation of knowledge mine or database is also progressing quickly and simulation based on suitable modeling is also reaching a practical use level.

Thus, the direction of new technical development will promote as a more effective use of RP by the advanced processing by metallurgical plant aided by computer.

6. Conclusion

I want to also aim at recovery of lead and zinc as a valuable metal, or solution of an environmental problem with saving resources by effective use of steel materials of RP by the advanced processing in the non-ferrous metal industry of about 5 million-ton of EAF dust produced by the steel industry.

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Table 2 Main minerals encountered in zinc reduction smelting.\(^3\)

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical equation</th>
<th>Type of crystal</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zincite</td>
<td>( \text{ZnO} ) (s)</td>
<td>Hexagonal</td>
<td>White</td>
</tr>
<tr>
<td>Zinc ferrite</td>
<td>( \text{ZnO} \cdot \text{Fe}_2\text{O}_3 ) (s)</td>
<td>—</td>
<td>Grey</td>
</tr>
<tr>
<td>Hematite</td>
<td>( \text{Fe}_2\text{O}_3 ) (s)</td>
<td>Trigonal, Cubic</td>
<td>Red</td>
</tr>
<tr>
<td>Magnetite</td>
<td>( \text{Fe}_3\text{O}_4 ) (s)</td>
<td>Cubic</td>
<td>Black</td>
</tr>
<tr>
<td>Fayalite</td>
<td>( \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 ) (s)</td>
<td>—</td>
<td>Black</td>
</tr>
<tr>
<td>Wustite</td>
<td>( \text{FeO}_x ) (s)</td>
<td>Cubic</td>
<td>Black</td>
</tr>
<tr>
<td>Litharge</td>
<td>( \text{PbO} ) (s)</td>
<td>Tetragonal</td>
<td>Red</td>
</tr>
<tr>
<td>Lead silicate</td>
<td>( \text{PbO} \cdot \text{SiO}_2 )</td>
<td>Monoclinic</td>
<td>Grey</td>
</tr>
<tr>
<td>Silica</td>
<td>( \text{SiO}_2 )</td>
<td>Hexagonal, rhombic</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 3 Process proposed for processing of steel dust.\(^4\)

<table>
<thead>
<tr>
<th>Area</th>
<th>Processing method</th>
<th>Type</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asia</td>
<td>Conventional method</td>
<td>Pyro</td>
<td>Crude ZnO</td>
</tr>
<tr>
<td>Japan</td>
<td>Rotary Kiln process</td>
<td>Pyro</td>
<td>Crude ZnO</td>
</tr>
<tr>
<td>USA</td>
<td>Conventional method</td>
<td>Pyro</td>
<td>Crude ZnO</td>
</tr>
<tr>
<td>CANADA</td>
<td>Rotary Kiln process</td>
<td>Pyro</td>
<td>Crude ZnO</td>
</tr>
<tr>
<td>EU</td>
<td>Conventional method</td>
<td>Pyro</td>
<td>Crude ZnO</td>
</tr>
</tbody>
</table>

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Fig. 7 Potential-pH diagram of Pb-Cl-SO\(_4\) system at 298 K.
I want to promote both the technical development by computer aided analysis continued to be in the future and the check of an effect according the on-site test based on systematic analysis to enforcement in development of the advanced processing method.

In addition, it is expected that both the development of industry and environmental preservation could also be attained by the effective use of EAF dust produced by an advanced processing.

REFERENCES

5) GTT: Thermodynamics calculation software “FACTSAGE”.