TREATMENT OF THE BRASS SMELTER FURNACE FLUE DUST

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Abstract
The objective of this work is to examine method for treatment of flue dust generated by brass smelting. The process such as brass smelting generate metal rich flue dust. As a result of increasingly stringent government regulation of waste disposal it has become important to utilize flue dusts as sources of metals and other chemicals. For the production of industrial zinc oxide, low grade flue dust was mixed with coal and heated to the point where zinc vapor was formed. The vapor was burned immediately with air above the charge, and the finely divided zinc fume was carried with the off gases and was collected in bag filter. The zinc oxide product was very finely divided. Because of sufficiently high purity (79.5 % Zn) it may be used as a pigment.

1. INTRODUCTION
In a typical recycling facility, the smelting process begins with the melting of copper zinc alloy in an induction furnace. Metal slag, consisting mainly of zinc, copper and impurities, floats to the top, and is then separated. Part of zinc and copper are vaporized and form fine particles of oxide dust, which are filtered out as flue dust in a baghouse. Zinc oxide represents the most valuable component of the dust. There are many methods of treating the flue dusts, which include pyrometallurgical [1] and hydrometallurgical [2-4] processes

2. THEORY OF ZINC OXIDE REDUCTION

2.1. Thermodynamic of reduction
Like every metallurgical reaction the reduction with carbon and carbon monoxide is governed by the prevailing chemical equilibria and by reaction kinetics. From thermodynamic data the standard Gibs energy change and the equilibrium constant may be calculated for the various reactions of the type:

\[ \text{MeO} + \text{CO} \rightarrow \text{Me} + \text{CO}_2 \]  \hspace{1cm} (1)

The corresponding gas ratio \( \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \) is shown in Fig. 1 for a number of metals of industrial importance. As long as the metal and the oxide coexist at condensed phases, i.e., with their activity equal to or close to unity, this gas ratio has a definite value and is a function only of temperature. It is seen that the ratio varies between about \( 10^5 \) for the reduction of \( \text{Cu}_2\text{O} \) to \( \text{Cu} \) and \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \), to values of the order of \( 10^3 \) or less for the reduction of \( \text{MnO} \) and \( \text{SiO}_2 \) to the corresponding metals. Even lower gas ratios would be found for the reduction of \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \). The reduction of \( \text{ZnO} \) represents an exceptional case. At low temperatures \( \text{ZnO} \) is reduced to form liquid \( \text{Zn} \), and the gas ratio is a function of temperature only. At higher temperatures zinc vapor is formed:

\[ \text{ZnO} + \text{CO} \rightarrow \text{Zn} \text{(g)} + \text{CO}_2 \]  \hspace{1cm} (2)
Figure 1. Equilibrium gas ratio \( p_{\text{CO}_2}/p_{\text{CO}} \) as a function of inverse temperature for the reduction of various oxides.

In this case the gas ratio is given by \( p_{\text{CO}_2}/p_{\text{CO}} = K/p_{\text{Zn}} \) where \( K \) is the equilibrium constant and \( p_{\text{Zn}} \) the partial pressure of zinc vapor. Of these, the equilibrium constant is a function of temperature only, whereas \( p_{\text{Zn}} \) may have any value. In Fig. 1 the gas ratio \( p_{\text{CO}_2}/p_{\text{CO}} \) is plotted for \( p_{\text{Zn}} = 1 \) atm. This curve intersects the curve for liquid zinc at the boiling point of zinc, \( 907 \) °C, that is liquid and gaseous zinc are in equilibrium with the same atmosphere, and consequently in equilibrium with each other. For a partial zinc pressure of \( 0.1 \) atm. the gas ratio is displaced upward by one logarithmic unit, and the intersection with the curve for liquid zinc will be at about \( 740 \) °C, which is the dew point of zinc vapor at \( 0.1 \) atm. For a zinc pressure of \( 10 \) atm. the curve is displaced downward by one logarithmic unit, and so on. In greater detail Fig. 2 gives the gas ratio \( p_{\text{CO}_2}/p_{\text{CO}} \) for the reaction 2.

Figure 2. Equilibrium gas ratio \( p_{\text{CO}_2}/p_{\text{CO}} \) as a function of inverse temperature for the reduction of zinc oxide.
In order for carbon to reduce ZnO continuously, both of the equilibria 2 and Boudouard reaction:

\[ \text{CO}_2 + \text{C} = 2\text{CO} \]  

must be satisfied, i.e., the reduction will take place at the intersection of the above two sets of curves. Furthermore, for the reduction of pure ZnO with carbon the numbers of zinc and oxygen atoms are equal. This makes the pressures of Zn, CO and CO$_2$ interrelated by the stoichiometric relation $p_{\text{Zn}} = p_{\text{CO}} + 2p_{\text{CO}_2}$. Therefore, the system of ZnO-C is consisted of three components Zn, O and C and one restriction ($n_{\text{Zn}} = n_{\text{O}}$). With three phases (ZnO, C and gas) one degree of freedom exist, i.e., the system is fixed at given temperature or given pressure. Under the conditions of reduction $p_{\text{CO}_2}$ is small compared to $p_{\text{CO}}$, and then is $p_{\text{Zn}} \cong p_{\text{CO}} \cong 1/2p_{\text{tot}}$. Thus for a total reaction pressures of 1 atm the curves for the $p_{\text{Zn}}$ and $p_{\text{CO}}=0.5$ atm apply. These curves intersect at about 920°C (point A). This, therefore, is the lowest temperature at which solid carbon can reduce zinc oxide at 1 atm total pressure.

2.2. Kinetic of reduction

The reduction of ZnO with carbon consists of:

a) Reduction with CO on the ZnO surface (reaction 2)

b) The Budoard reaction on the carbon surface (reaction 3)

c) Diffusion of the gases between the two surfaces

These three steps are coupled in series, and the slowest step will be rate controlling. Measurements of the overall reaction indicate that this is slower than both the intrinsic reaction on the ZnO surface and on the carbon surface [5]. This should mean that diffusion between the two surfaces is rate controlling. In principle it should therefore be possible to increase the reaction rate by increasing the surface area, and decrease the distance between the two surfaces. This is obtained by intimate mixing of zinc flue dust and coke.

2.3. Heats of reaction and condensation

The reduction of zinc oxide with carbon is a strongly endothermic process. Thus for $\text{ZnO} + \text{C} = \text{Zn} + \text{CO}$, $\Delta H = 238$ kJ. To this must be added the heat content of the reaction products at 1000°C, including the heat of vaporization of zinc, a total of 138 kJ, giving a total heat requirement of 376 kJ/mol or about 5750 kJ/kg of zinc.

At the equilibrium temperature for the reduction the driving force and consequently the reaction rate are zero. Overheating to 1300°C is necessary to get an acceptable reduction rate. At such a temperature the gas composition on the ZnO surface will approach equilibrium with ZnO, and the gas composition on the carbon surface will approach equilibrium with carbon. The evolving gas will have a CO$_2$/CO ratio between those which apply for the two surfaces, and closest to the one which has the highest reaction rate. The intrinsic reaction rate per unit area is larger for the ZnO reduction than for the Boudouard reaction. By using an excess of coke, however, the total area of the coke surface may be many times larger than that of the ZnO surface, and the resulting gas mixture may have a CO$_2$/CO ratio close to the value for equilibrium with carbon. In practice a low CO$_2$ content in the gas is desired, and this is accomplished by using 2 to 3 times the stoichiometric amount of carbon and the highest possible temperature, i.e., high driving rate.

3. EXPERIMENTAL

3.1. Dust characterization

A single bulk composite sample, consisting of brass smelter furnace flue dust, was used for the laboratory scale study. The composition of the flue dust is given in Table 1.
Table 1. Chemical analysis of composite dust

<table>
<thead>
<tr>
<th>Element</th>
<th>Assay, dust, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>63.5</td>
</tr>
<tr>
<td>Cu</td>
<td>1.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.6</td>
</tr>
<tr>
<td>Cl</td>
<td>1.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Zinc, copper and lead account for about 65 wt % of the dust. They are in the form of oxides. Zinc oxide represents the most valuable component of the dust. Other potential recourses include copper oxide and lead oxide.

3.2. Reduction of zinc oxide
Thermal process have been operated on a laboratory equipment scale. A simplified flowsheet for process is shown by figure 2.

Fig. 2. Flow sheet for treatment of flue dust

Flue dust was fed into the electric furnace and mixed with coal and heat was introduced by conduction through the ceramic walls and into the charge. Ceramic retort was used, because contact with hot oxidizing combustion gases would be harmful for the charge. Overheating to 1300 °C, reduces and volatilizes the metals in the dust, and zinc vapor was formed. The non volatile components form slag which settled at the bottom of the furnace.

3.3. Reoxidation of zinc vapor
Zinc vapor was formed and oxidized with additional air in the space above the charge, and was carried of with the furnace gases. Other metals in the charge was tapped from the heart either as metall (lead) or as matte (iron and copper), whereas the stable oxides form a slag. Some lead was also evaporated as PbS, which oxidizes to give PbSO₄ which mixes with the zinc fume. Owning to the heat which radiates back from the combustion of the vapor, the heat requirement for zinc fuming is much less than for the reduction to metal. Going from the essentially zinc oxide raw material to essentially zinc oxide product the chemical enthalpy change is small, and the major part of the applied fuel energy is found as physical heat in the furnace gases, which may have a temperature of more than 1300 °C. This heat was recovered in cooler, whereby the gas is cooled to 100 to 200 °C before was passed on to the bag filter. Thus the zinc fuming process only "borrow" the fuel.
4. CONCLUSIONS
Based on previous work in the literature and the experimental results of this study, a pyrometallurgical process for treating of brass smelting flue dust is proposed. Initially, the flue dust is mixed with coal and fed into the electric furnace and heat is introduced into the charge. Ceramic retort is used, because contact with hot oxidizing combustion gases would be harmful for the charge. Overheating is reduced and volatilized the zinc in the flue dust, and zinc vapor is formed and oxidized to zinc oxide product. Because is very finely divided and sufficiently high purity (79.5 % Zn) it may be used as a pigment.

LITERATURE