

## 論文の内容の要旨

論文題目 Recycling process of electric arc furnace dust by selective chlorination and evaporation method

(選択塩化揮発法を用いた電気炉ダストのリサイクルプロセス)

氏 名 孫 国棟

EAF dust is a special industrial waste produced in steelmaking process and needs extra treatment before recycling or landfill. The high content of Zn and Pb also makes it valuable resources if treated properly. There are two difficulties in the treatment of EAF dust. One is the presence of  $\text{ZnFe}_2\text{O}_4$ . It is a comparatively stable component and decrease the extracting efficiency especially in hydrometallurgical process. The other one is the efficient separation of Zn and Fe to make them valuable resources. The present EAF treating processes including pyrometallurgical process and hydrometallurgical process could not solve these two problems well. Chlorination metallurgy has been widely used in the extraction of metals from lean and complex ores. It has the advantages of high reactivity and good discrimination among different metals, which could meet the requirement to solve these two difficulties. However, the utilization of chlorination process in the treatment of EAF dust is not sufficient. So in present research, the feasibility of selective chlorination of Zn and Pb from EAF dust using chlorination agents  $\text{Cl}_2$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  was confirmed. The influence of various experimental parameters on the chlorination and evaporation reactions was investigated. The reaction mechanism was analyzed based on the attained results. The efficiency using different chlorination agents was also compared.

With the great consumption of natural resources, massive wastes are produced. The treatment of

industrial wastes becomes important for the targets of environmental protection and economic benefit. The ironmaking and steelmaking process is one of the biggest raw material and energy consumer in modern society, producing huge amount of byproduct. Electric arc furnace (EAF) dust was one of the major byproduct, featuring by high content of Zn, Pb and Fe because of the use of steel scraps as raw material. The present EAF treating processes mainly focus on the recycling of Zn. Waelz kiln process, Mitsui Furnace (MF) process and Electrothermal Distillation Furnace process are the primary treating processes in industry. The application of chlorination in the treatment of solid waste is wide, but as for treating the EAF dust, the research is not sufficient, especially using solid chlorination agents. Theoretically, the chlorination of Zn by chlorination agents is possible and the chlorination experiments focused on the chlorination agents  $\text{Cl}_2$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ .

The chlorination experiment and experimental results using  $\text{Cl}_2$  as chlorination agent were conducted. The influences of experimental temperature, reaction time on the chlorination and evaporation reactions were investigated. The feasibility of selective chlorination and evaporation of Zn and Pb from EAF dust was confirmed with the presence of abundant  $\text{O}_2$ . Temperature was the most important influencing factor on the chlorination efficiency. The removal fraction of Zn and Pb continuously increased with time. But as the zinc content in dust decreased, the chlorination and evaporation reaction rates became smaller. When the reaction temperature was higher than 1023 K, the removal of Zn and Pb could be accomplished in 30 min. The removal fractions of Zn and Pb could reach 98% and 99%, respectively. When temperature was lower than 1023 K, much longer reaction time was needed to reach a high removal fraction of Zn and Pb. It was confirmed that small portion of Fe was chlorinated in the experimental temperature range. Zinc oxide was chlorinated and vanished from the residue prior to zinc ferrite.

In the chlorination experiment using  $\text{MgCl}_2$  as chlorination agent, the feasibility of chlorination treatment with  $\text{MgCl}_2$  was confirmed. The influence of various experimental parameters carrier gas flow rate, reaction temperature, reaction time, atmosphere and  $\text{MgCl}_2$  amount on the chlorination reaction and

evaporation was investigated. In order to get a high removal fraction of Zn and Pb, 1023 K was necessary and temperature higher than 1023 K made no obvious influence.  $\text{MgCl}_2$  was an effective chloride agent to recover Zn and Pb from EAF dust and 10 min was enough to accomplish the process. Even though the presence of  $\text{O}_2$  could obviously decrease the Fe loss fraction, there was still at least about 20% Fe loss. In the atmosphere of Ar, in order to maintain high Zn removal fraction and decrease the Fe loss, it was important to control the reaction time and  $\text{MgCl}_2$  amount. 0.8 to 1.0 g  $\text{MgCl}_2$  and about 10 min was obligated for the treatment of 1 g dust.

The chlorination experimental results using  $\text{CaCl}_2$  as chlorination agent are analyzed. The influences of various experimental parameters such as carrier gas flow rate, reaction temperature, reaction time and atmosphere were investigated. The feasibility of chlorination treatment using  $\text{CaCl}_2$  was confirmed, even though the reaction time needed was much longer than that using  $\text{Cl}_2$  and  $\text{MgCl}_2$ . In present reaction condition, 300 min was necessary to remove 97.84% Zn and 100% Pb at 1273 K. Different from the other chlorination agents, the presence of  $\text{O}_2$  could obviously decrease the iron loss while had no obvious effect on the removal fraction of Zn.

The possible reaction mechanisms of chlorination reaction was illustrated. In the similar reaction condition, the chlorination reaction rate constants of  $\text{Cl}_2$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  in the initial stage of the reaction were calculated. It shows that at the same temperature, the chlorination reaction rate constants of  $\text{Cl}_2$  and  $\text{MgCl}_2$  were very close and one order larger than that of  $\text{CaCl}_2$ . This was in accordance with the experimental result that the removal of Zn from EAF dust was extremely slow. The apparent activation energy was also calculated based on the experimental results. The apparent activation energy of the chlorination reaction with  $\text{Cl}_2$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  was calculated 85 kJ/mol, 490 kJ/mol and 566 kJ/mol, respectively. The apparent activation energy of  $\text{CaCl}_2$  was the highest, which could explain the requirement for high reaction temperature and gas flow rate to reach a high removal fraction of Zn.

The utilization efficiency of each experimental group was calculated. For  $\text{Cl}_2$ , reaction temperature

had great influence on the utilization efficiency of chlorination agent. It increased from 5.6% to 27.4% when the reaction temperature increased from 923 to 1073 K. In order to remove Zn efficiently from EAF dust, high flow rate of  $\text{Cl}_2$  was required. In the design of industrial process, the recycling of  $\text{Cl}_2$  is necessary. The utilization efficiency of  $\text{MgCl}_2$  and  $\text{CaCl}_2$  was 54.2% and 55.4%, respectively when the reaction condition was efficient and economic. The waste of solid chlorination agent was caused by the evaporation and the chlorination of Fe.

EAF dust consists of particles with different sizes. The chlorination of EAF dust was analyzed with the aid of the unreacted core model. In the chlorination reaction of EAF dust,  $\text{Cl}_2$  passed through the boundary layer and produced porous  $\text{Fe}_2\text{O}_3$  layer reacting with the unreacted  $\text{ZnO}$  and  $\text{ZnFe}_2\text{O}_4$ . The produced gaseous  $\text{ZnCl}_2$  passed through the  $\text{Fe}_2\text{O}_3$  layer and boundary layer. In the chlorination reaction using  $\text{Cl}_2$ , dust particles were exposed in the  $\text{Cl}_2$  and  $\text{O}_2$  atmosphere while in that of  $\text{MgCl}_2$  and  $\text{CaCl}_2$ , the dust particles were immersed in  $\text{MgCl}_2$  solution and  $\text{CaO-CaCl}_2$  solution, respectively. The rate determining step was considered to be the chlorination reaction.