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Ammonium Chloride Solution Leaching of Crude Zinc Oxide Recovered from Reduction of EAF's Dust

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EAF's dust has been treated mainly by pyrometallurgical reduction process in rotary kiln furnace to recover valuable metal elements such as Zn and to avoid the disposal of hazardous materials to waste. Recently, hydrometallurgical eletrowinning of zinc from a zinc-amino chloride solution obtained by the leaching of EAF's dust was developed to recover high grade zinc metal from EAF's dust. But there are some disadvantages in each process such as difficulty of operation condition control and sticking problem in kiln process and low extractability and recovery of zinc owing to insoluble zinc-ferrite in electrowinning process. We propose a new combined process of pyrometallurgical one and hydrometallurgical one to treat EAF's dust efficiently and economically. In this study, ammonium chloride solution leaching of crude zinc oxide recovered from reduction of EAF's dust was carried out to find out the efficiency of zinc extraction from it and the possibility for performance of eletrowinning in the proposed process. Effects of various leaching variables such as leaching temperature, concentration of leaching solution and leaching time were investigated. And the leaching results of the crude zinc oxide were compared with those of EAF's dust. The extraction percents of zinc in ammonium chloride solution leaching of the crude zinc oxide recovered from reduction of EAF's dust were above 80% after 60 minutes of leaching under the leaching condition of 4M NH_4Cl concentration and above leaching temperature of 70℃. And the concentrations of zinc in the leached solution were obtained above 50g/ℓ. The activation energy calculated for zinc extraction in NH_4Cl leaching was 58.1KJ/mol for EAF's dust and 15.8KJ/mol for the crude zinc oxide recovered from reduction of EAF's dust.
Keywords : ammonium choride, leaching, crude zinc oxide, EAF's dust

Introduction

EAF's dust classified as a hazardous waste in many countries contains heavy metals and other elements that can contaminate air and water posing risks to human health.[1] But these metals are also valuable sources that can be extracted from the dust for reuse.[2][3] EAF's dust is produced nearly 300,000 tons a year in Korea. Recently steelmakers have been facing the problem of dust disposal occurred by legal and regulatory maneuvering.[4] EAF's dust has been treated in foreign countries mainly through the reduction process at high temperature in rotary kiln furnace to recover precious metal elements contained in the dust and to dump it without any environmental risks. The crude zinc oxide recovered through this pyrometallurgical process, generally, contains a lot of chlorine and goes to ISP plant to obtain zinc metal from it. In fact, the countries as like Korea, where the ISP plant had not been already existed, can not adopt this one as an EAF's dust treatment process because it needs a large investment to build the ISP plant which has the economical capacity of 150,000 ~ 200,000T/Y. Besides that, this process has also some disadvantages such as the difficulty of operation condition control and the sticking problem occurred on inner wall of kiln furnace. Recently, hydrometallurgical electrowinning process, EZINEX process,[5] has been developed and commercialized to recover high purity zinc metal from EAF's dust. In this process, however extractability and recovery of zinc from EAF's dust are low because the dust is leached directly in ammonium chloride solution and zinc-ferrite can not be leached easily. And also this process has a problem that the leaching residues should be returned to EAF, but steelmakers are not satisfied with it. In order to develop an efficient process for EAF's dust treatment, it seems like that two aspects should be taken into consideration. One is to control the operation condition of process more easily, and the other is to recover the precious metal elements economically without the possibility of environmental pollution risks.

Now we propose a new combined process of pyrometallurgical one and hydrometallurgical one to treat EAF's dust efficiently and economically, as shown in Fig.1. In the first stage of this process, as shown in the proposed flowsheet, EAF's dust is reduced in rotary hearth furnace (RHF) where the operation condition is controlled more easily than in rotary kiln furnace without sticking problem. The crude zinc oxide can be recovered through this reduction process and there is a possibility for reuse the reduction residues as iron sources, if the EAF's dust is reduced with mixing of other iron oxide such as millscale. Recently, RHF reduction process, FASTMET process,[6] has been demonstrated and commercialized by Kobe steel, LTD. in Japan to produce direct reduced iron (DRI) from steel dusts.[7] And also we had already confirmed the possibility for reuse the reduction residues of EAF's dust mixed with millscale as iron sources in laboratory scale of RHF,[8][9] and so the residues need not be disposed. In the second stage, high purity zinc metal from the crude zinc oxide recovered by the reduction in RHF can be obtained by electrowinning as same as in EZINEX process. But the demonstration of this electrowinning process has not been reported yet.

In this study, leaching tests of the crude zinc oxide recovered from reduction of EAF's dust in ammonium chloride solution carried out to find out the efficiency of zinc extraction from it and the possibility for performance of electrowinning in the proposed process. And the leaching results obtained were compared with those of EAF's dust.

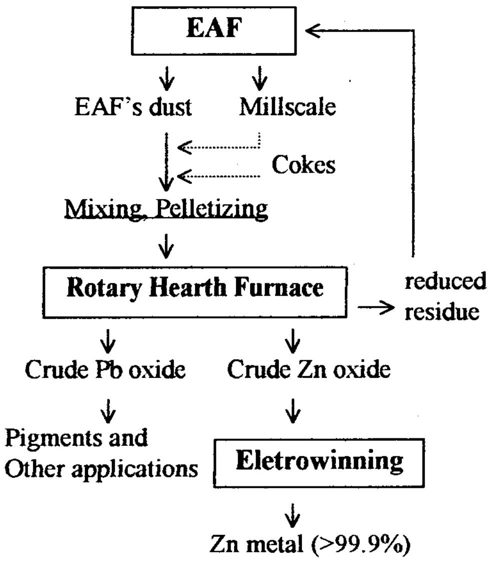

Fig. 1. Flowsheet of the proposed process for the treatment of EAF's dust.

Experimental materials and methods

EAF's dust and crude zinc oxide sample used in this investigation were donated by Inchon Iron and Steel Co., LTD. in Korea and Mitsui Mining and Smelting Co., LTD. in Japan, respectively. The crude zinc oxide was a product recovered by volatilization from reduction of EAF's dust in rotary kiln furnace.

The chemical analysis of two kinds of samples used in this study is shown in Table 1.

Table 1. Chemical analysis of samples.

(wt %)

Samples / Elements	EAF's dust	Crude zinc oxide
Fe	33.15	2.32
Zn	12.71	58.88
Pb	1.57	5.74
Cd (ppm)	147	1585
Cu	0.14	0.15
Na	0.61	2.14
K	0.66	0.94

The results obtained in the X-ray diffraction pattern of these samples are shown in Fig.2. The mineralogy of EAF's dust is varied and complex. Although some particles are homogeneous and consist of a single mineral, most particles are polymineralic and belong to the spinel group including magnetite (Fe_3O_4), franklinite ($ZnFe_2O_4$) and jacobsite ($MnFe_2O_4$).[10] The peaks of the crude zinc oxide sample are characteristic of ZnO.

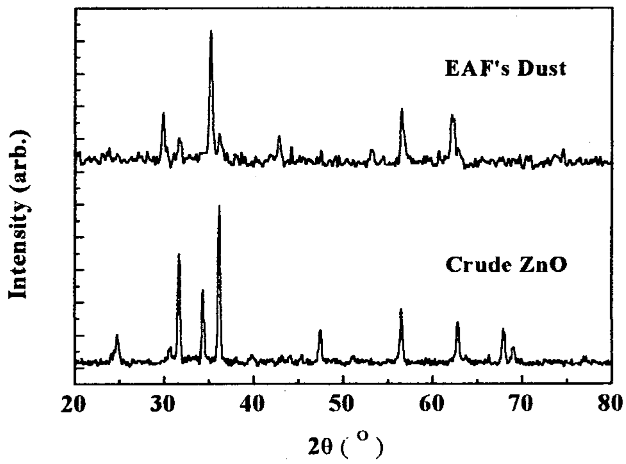

Fig. 2. Results of X-ray diffraction analysis for EAF's dust and the crude zinc oxide.

Fig.3 shows the results of particle size distribution analysis for the samples. As shown in the figure, particle sizes of EAF's dust and the crude zinc oxide range from less than 1 μ m to more than 50 μ m. The majority of the particles of both samples are 5~10 μ m in diameter.

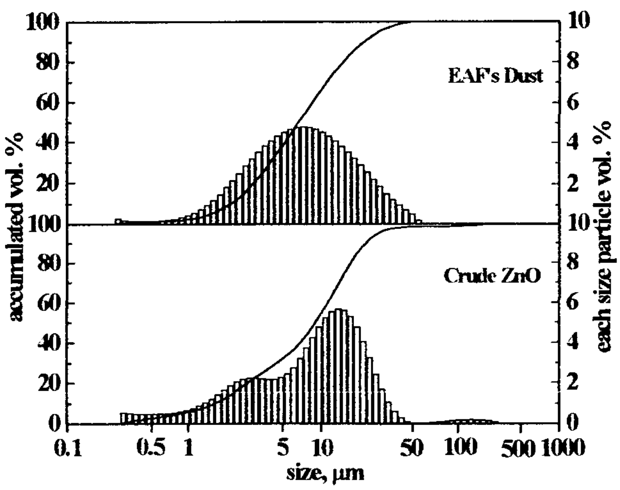

Fig.3. Results of particle size distribution analysis for EAF's dust and the crude zinc oxide

The leaching experiments for these samples were carried out in a 1-L pyrex glass reactor using the leaching solution of different NH_4Cl concentrations at various leaching temperatures and times. The concentrations of zinc in leached solutions were analyzed by ICP at Korea Basic Science Institute.

Results and discussion

1. Effect of stirring speed

Extractability of zinc in leaching solution can be dependent upon stirring speed. The first series of leaching tests was carried out on EAF's dust to check the effect of stirring speed and to find out optimum stirring speed for zinc extraction. In these tests, EAF's dust was leached at different stirring speeds under the leaching condition of NH_4Cl concentration of 4M, leaching temperature of 70℃, leaching time of 30 minutes and pulp density of 100g/ ℓ. The results of the leaching tests are presented in Fig.4. The rate of zinc extraction becomes higher as increasing stirring speed of 150 r.p.m.. Owing to high viscosity of leaching solution of about over 10% pulp density, sticking of lots of EAF's dust particles on the inner wall of reactor upside of leaching solution surface was observed during the leaching at high stirring speed. The extraction rate may be seemed to be slow at higher than stirring speed of 150 r.p.m. owing to this sticking phenomena. All of other leaching tests had been carried out at the stirring speed of 150 r.p.m..

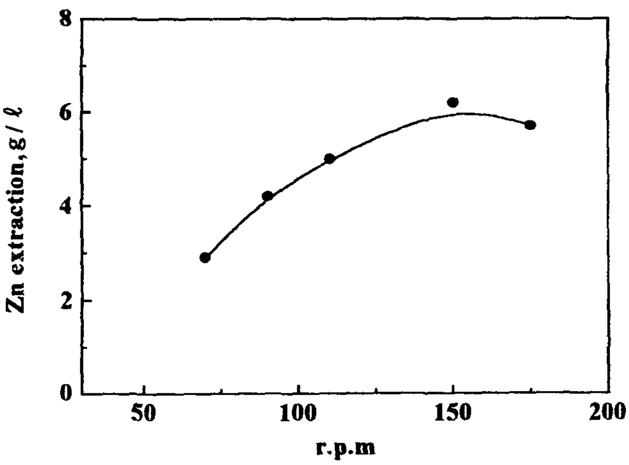

Fig. 4. Effect of stirring speed on zinc extraction from EAF's dust.
(Leaching conditions : 4M NH_4Cl, temperature 70℃, time 30 minutes, pulp density 100g/ ℓ)

2. Effect of NH_4Cl concentration

Leaching rates for EAF's dust and crude zinc oxide volatilized by reduction of EAF's dust were measured at different NH_4Cl concentrations under constant leaching condition of leaching temperature of 70℃ and pulp density of 100g/ ℓ. The results obtained are plotted in Fig.5 and Fig.6, respectively. As shown in Fig.5, although the rate of zinc extraction from EAF's dust becomes higher as increasing NH_4Cl concentration, the concentrations of zinc extracted in leached solution are only about 5.3g/ ℓ, 5.6g/ ℓ and 6.5g/ ℓ for 2M, 3M and 4M NH_4Cl, respectively, even after 60 minutes of leaching. For the crude zinc oxide, as shown in Fig.6, the rate of zinc extraction is far higher than that of EAF's dust and is also accelerated by increasing NH_4Cl concentration. The concentrations of zinc extracted after 60 minutes of leaching are about 23g/ ℓ, 38g/ ℓ and 50g/ ℓ for 2M, 3M and 4M NH_4Cl, respectively.

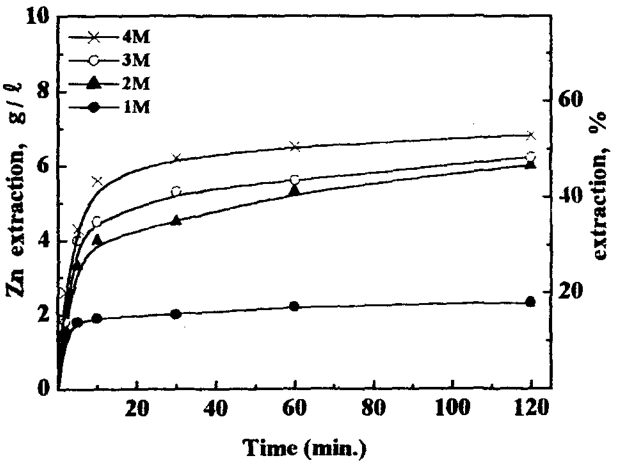

Fig. 5. Effect of concentration of NH_4Cl on zinc extraction from EAF's dust.
(Leaching conditions : temperature 70℃, pulp density 100g/ ℓ, strring speed 150 r.p.m.)

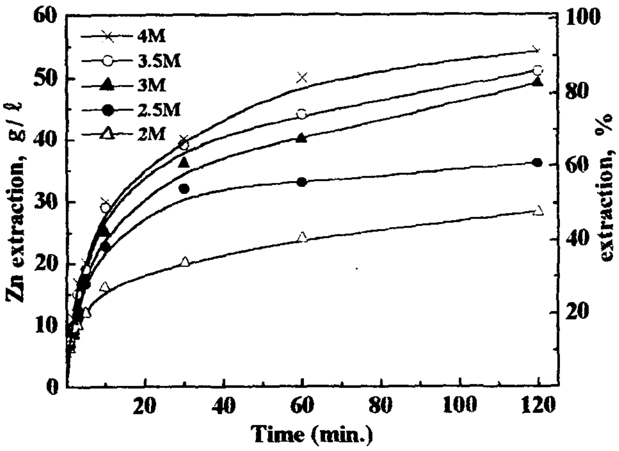

Fig. 6. Effect of concentration of NH_4Cl on zinc extraction from the crude zinc oxide.
(Leaching conditions : temperature 70℃, pulp density 100g/ ℓ, stirring speed 150 r.p.m.)

The resulting leaching rate data for the crude zinc oxide were assigned to a simplified rate equation of the form,

$$r = k'[NH_4Cl]^n$$

where r is the leaching rate of zinc, $[NH_4Cl]$ is the mean NH_4Cl concentration, n is the reaction order, and k' is a function of rate constant, pulp density and fraction of leached zinc. Fig.7 shows how the initial leaching rate of the crude zinc oxide varies with NH_4Cl concentration, on a log-log scale. The slope is an expression of reaction order, n, and has a value of 0.33. But to obtain more accurate value of n, a short-time experimental tests that the variation of k' can be negligible should be done.

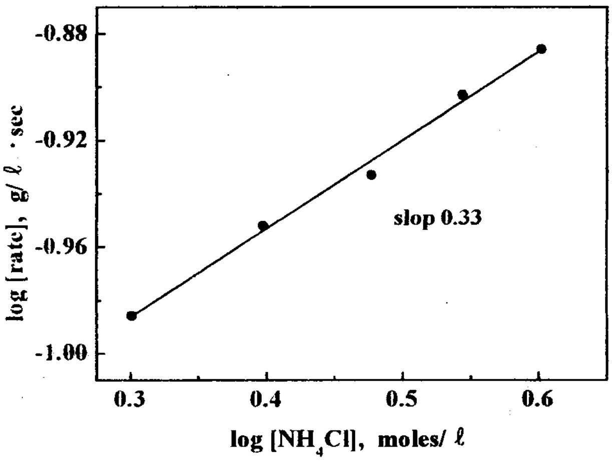

Fig. 7. Dependence of initial leaching rate on NH_4Cl concentration for the crude zinc oxide.

3. Effect of leaching temperature

The effects of leaching temperature on zinc extraction from EAF's dust and the crude zinc oxide were studied at different temperatures in 4M NH_4Cl solution. The results obtained are presented in Fig.8 and Fig.9, respectively. Increasing the temperature distinctly accelerates the leaching rate. The concentrations of zinc in leached solution after 60 minutes of leaching at 70°C, 80°C and 90°C in 4M NH_4Cl solution are observed about 6g/ ℓ, 7g/ ℓ and 8g/ ℓ for EAF's dust, and 48g/ ℓ, 50g/ ℓ and 54g/ ℓ for the crude zinc oxide, respectively. These values correspond to the extraction percents of zinc of about 47%, 55% and 63% for EAF's dust and about 81%, 85% and 92% for the crude zinc oxide, respectively. The proportions of zinc present as oxide and ferrite have a significant effect on leaching treatment and recovery options because the former is soluble to a varying degree in most leachants whereas ferrites tend to be insoluble. The range in the amount of soluble to insoluble zinc compounds has been stated to vary from 50 to 80% soluble with the condition under which EAF's dust is formed.[11)]

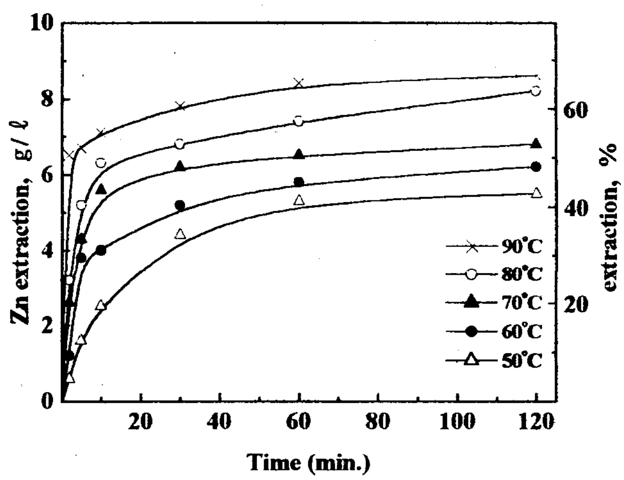

Fig. 8. Effect of leaching temperature on zinc extraction from EAF's dust.
(Leaching conditions : 4M NH_4Cl, pulp density 100g/ ℓ, stirring speed 150 r.p.m.)

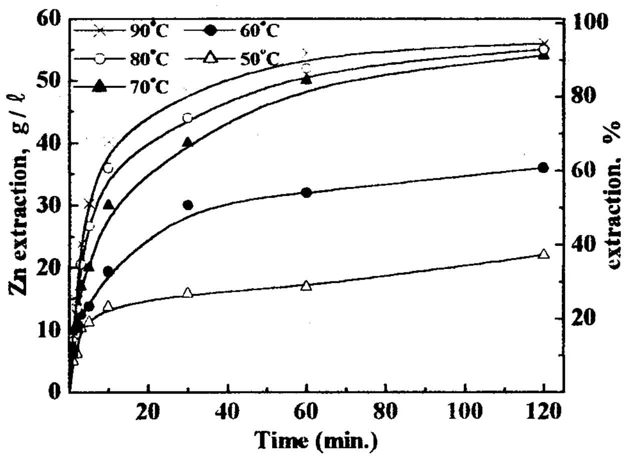

Fig. 9. Effect of leaching temperature on zinc extraction from the crude zinc oxide.
(Leaching conditions : 4M NH_4Cl, pulp density 100g/ ℓ, stirring speed 150 r.p.m.)

Arrhenius plots for EAF's dust and the crude zinc oxide leached with 4M NH_4Cl are shown in Fig.10. The activation energy calculated with the initial leaching rates is 58.1KJ/mol for EAF's dust and 15.8KJ/mol for the crude zinc oxide. The activation energy for the reaction of zinc extraction from EAF's dust is higher than that of the crude zinc oxide. This is not surprising since solvent ions should be diffused into EAF's dust particles

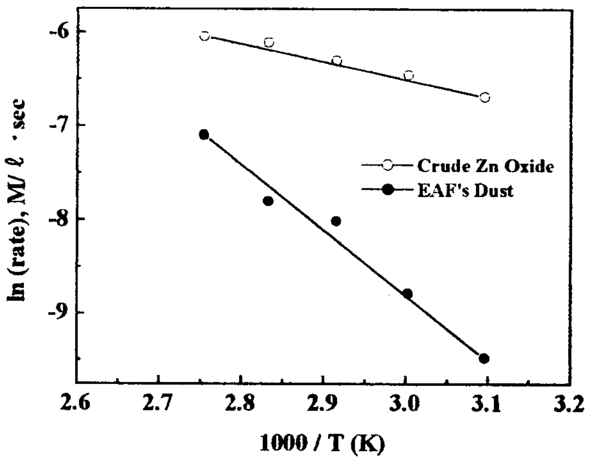

Fig. 10. Arrhenius plots for EAF's dust and the crude zinc oxide leached with NH_4Cl.

Conclusion

The results obtained from this study were summarized as follows ;

1. The extraction percents of zinc in ammonium chloride solution leaching of the crude zinc oxide recovered from reduction of EAF's dust were above 80% after 60minutes of leaching under the leaching condition of 4M NH_4Cl concentration and above 70℃. And the concentrations of zinc in the leached solution were obtained above 50g/ ℓ .

2. Reaction order, n, for the leaching reaction of the crude zinc oxide was obtained a value of 0.33 from the initial experimental leaching rate data for different concentrations of NH_4Cl.

3. The activation energy calculated for zinc extraction in NH_4Cl leaching was 58.1KJ/mol for EAF's dust and 15.8KJ/mol for the crude zinc oxide recovered from reduction of EAF's dust.

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