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Basic Consideration on EAF Dust Treatment Using Hydrometallurgical Processes

By T. Nakamura*1, E. Shibata*1, T. Takasu*2, H. Itou*2

Electric Arc Furnace (EAF) dust, defined as special industrial waste in Japan, is treated through pyrometallurgical processes in which crude ZnO powder is recovered. An on-site type process, however, is desired to reduce treatment cost and cost of transportation of the dust. A hydrometallurgical process is considered to be suitable for such an on-site treatment. Although many EAF dust treatment processes by hydrometallurgical method have been proposed, most of them have not been commercialized in Japan. A short review of hydrometallurgical processes foe EAF dust was done and a new hydrometallurgical process for EAF dust was proposed in this study. Nitric acid solution is used for the extraction of ZnO from the dust. Some characteristics of the process are as follows:

1. Recovery of Zn from zinc ferrite in EAF dust is the target, while the dissolution of Fe is limited by controlling the pH of the solution.
2. Zn is recovered as metallic Zn by electrowinning from the solution and nitric acid is regenerated in the anode.

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Keywords: *EAF dust, Zn recovery, Hydrometallurgical Process*

1 Introduction

Steel production from electric arc furnaces (EAF) has increased and this trend continues in future. As a result, growing quantities of EAF flue dust with higher zinc contents will be treated and more recycled zinc will become available. Schematic material flow for zinc-coated steel scrap is shown in Fig.1. When steel is being produced from scrap, the zinc remaining on the feedstock is volatilized and captured in the flue dust which is filtered out from the furnace gases. Substantial quantities of these dusts are upgraded and then used as feedstock for the production of primary zinc. Where this treatment is not economic, then most of EAF dusts were landfilled in old days. However the dust is currently listed as a hazardous waste and put in regulated dumps, awaiting technical developments. Industry is aware of the potential for further recovery of zinc and is increasing the amount of these materials that are treated to recover the zinc content.

EAF dust treatment processes developed nowadays are summarized in Figure 2. Both commercial operation processes and pilot plant operation processes are listed in this figure but laboratory scale and under developing processes were not listed.

A few hydrometallurgical processes have been developed and only one commercial process is operated that is EZINEX process [1]. Of course, many theoretical proposal have done in the hydrometallurgical processes [2] but still commercial process is limited. Some hydrometallurgical processes proposed are summarized in Table 1.

There are considered several reasons for a very few commercial hydrometallurgical process. Main reasons are follows:

1. low ability for impurity problem in the dust. especially halogens and silica
2. secondary treatment for leaching residues is necessary and its high cost in advanced countries due to lack of landfill sites.

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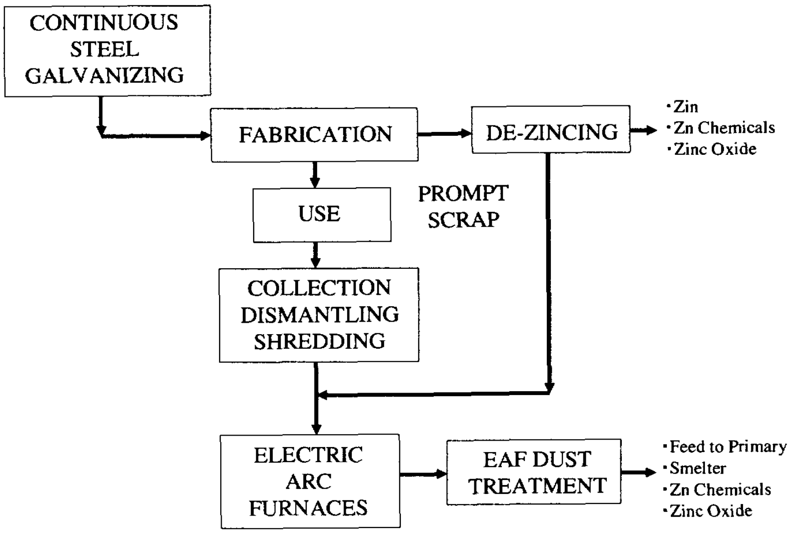

Fig.1 The Materials Flow for Zinc-coated Steel Scrap

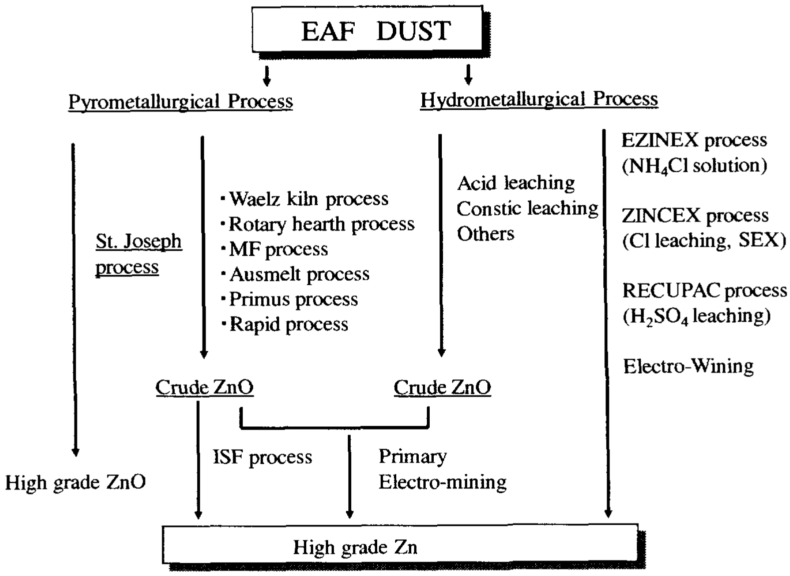

Fig.2 Schematic presentation of EAF Dust Treatment

Processes are roughly divided into two groups in terms of leaching agents. Both of acidic and alkaline solutions are used as leaching agents. H_2SO_4 and HCl solutions are used as an acidic solvent and NH_4OH and NaOH solutions are taken as an alkaline solvent [3]. Acidic solutions are very familiar to use and cheep but there is a trouble to treat iron ions in the solutions if $ZnFe_2O_4$ dissolves into the leaching agents. Traditional electrowinning process is applicable to obtain metallic Zn from the H_2SO_4 solution. The electrowining process of Zn from a HCl solution has been proposed but not operated in commercial scale [4]. On the other hand, no trouble of iron ions is expected in alkaline solutions after leaching [5] but cost of agents is higher than that of acids and some technical problems lie to get metallic Zn in the electrowinning.

A hydrometallurgical process was chosen in our project to develop an EAF dust treatment process because it is more compact than a pyrometallurgical process and easy to make a closed

Table 1 Comparison of hydrometallurgical processes for EAF dust treatment.

Type of Solvent		Reaction	Final Product	Process	Pb
Acid	H_2SO_4	$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$	Zn	electrowinning	remain in residue
	HCl	$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$	Zn	electrowinning	dissolve to solution
Alkaline	NaOH	$ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O$	Zn (powder)	electrowinning	dissolve to solution
	NH_3	$ZnO + 2NH_4^+ + 2NH_3 \rightarrow Zn(NH_3)_4^{2+} + H_2O$	ZnO	thermal decomposition	dissolve to solution

system. However, there is an important point to be decided before development. Recovery ratios of Zn in hydrometallurgical processes are normally lower than those of pyrometallurgical processes. Of course, if strong leaching conditions, for example, high concentration of solvents and high temperature, were applied, high leaching ratios of Zn would be obtained. However such operations will become difficult and both capital and running costs will be high. Then, compact and soft leaching process is desired. Following basic concept for the process was established.

(a) onsite treatment in EAF work
(b) soft leaching by an acid solution
(c) recovery of high purity Zn
(d) closed system

2 Characteristics of EAF Dusts

It is well known that the main Zn compounds in EAF dusts are ZnO, $ZnFe_2O_4$ and solid solutions of them. The ratio of these depends on the type of furnaces and operations, especially the dust collection systems. Typical EAF dusts were analyzed chemically and characterized by XRD and EPMA. Chemical composition of EAF dusts used in the experiments and content of free ZnO are shown in Table 2, while XRD patterns of these samples are shown in Fig. 3. The content of free ZnO was estimated from the amount of Zn dissolved into a 30 vol% CH_3COONH_4 solution. The content of free ZnO was not so high but almost one third of the total Zn.

Table 2 Examples of chemical composition and free ZnO in EAF dusts

Sample	Composition(mass%)							
	T. Zn	F. ZnO	Fe_2O_3	SiO_2	Al_2O_3	CaO	Pb	C
A	8.5	3.2	41.5	8.1	3.0	6.6	0.5	13.4
B	21.4	7.8	40.2	3.0	1.1	2.4	2.0	4.2

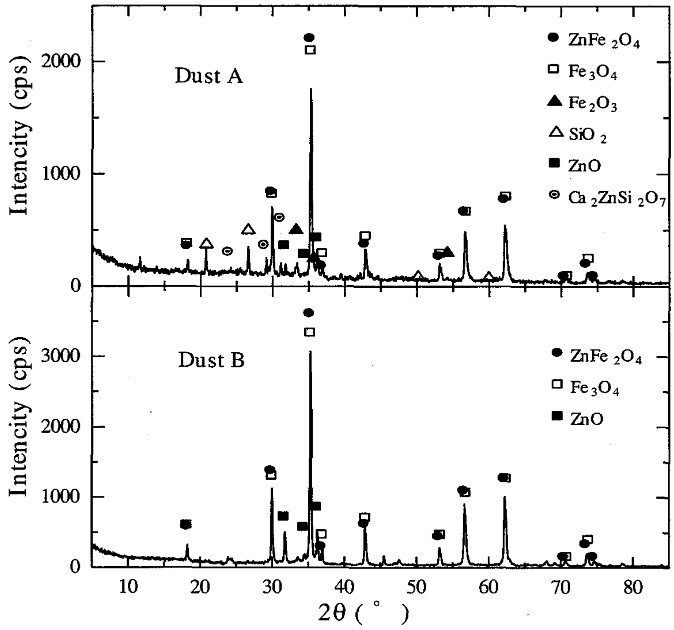

Fig.3 X-ray diffraction patterns of EAF dusts used in the present study.

3 A Hydrometallurgical Process for EAF Dust Treatment

Let us see the conditions for mild leaching of EAF dust in a normal acid solution. Potential-pH diagram of the Zn-Fe-O-H system at 298K is shown in Fig. 4. Zn^{2+} and iron hydroxide co-exist at the area of hatched line. Therefore, if pH of the acid solution is controlled to around 4 with proper oxidation potential, only ZnO is dissolved into the solution and iron oxides remain in the residue. This means that a rough separation of Zn from Fe in the leaching stage can be achieved. Since an acid solution of pH=4 is not strong, treatment of such solution will be easy.

What kind of acid is suitable for the process? Commercial Zn electrowinning is operated with H_2SO_4 solution but it is also well known that the operation is not easy to get high current efficiency. Impurity control in the H_2SO_4 solution is a key process element. The electrowinning of Zn in a HCl solution is not easy since Cl_2 gas generates in the anode. Therefore, nitric acid leaching and electrowinning was chosen. Although there is almost no difference between a nitric acid solution and other acid solutions in the leaching behavior, the electrowinning of Zn in a nitric acid solution is quite different from that in other acid solutions. Normally a smooth metal deposition

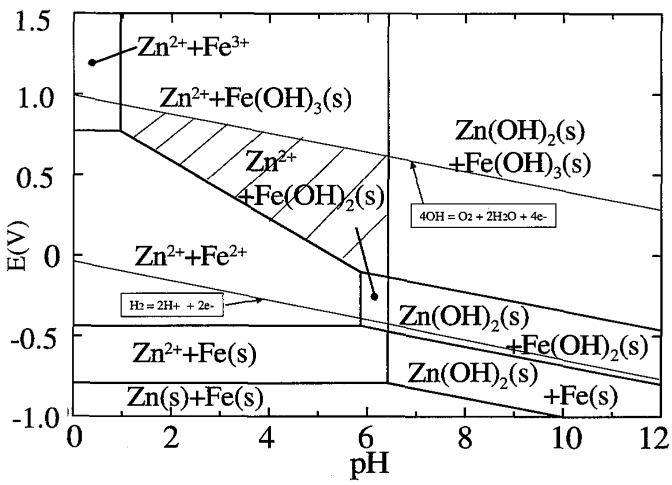

Fig.4 Potential-pH diagram in a Zn-Fe-O-H system at 298K.

is hardly done in a nitric acid solution. This means that powdery/dendritic Zn or ZnO will be obtained from a nitric acid solution, which is a disadvantage in a normal electrowinning operation. It will, however, be beneficial in this case because ZnO powder is obtained from electrowinning in a nitric acid solution and there is a possibility of establishing a continuous deposition and recovery system in the cathode.

4 Results

A schematic flow sheet of the new EAF dust treatment process is shown in Fig. 5. EAF dust is firstly leached by water to remove chlorine from the dust. After that, the dust is leached by a dilute nitric acid solution to recover Zn. After filtration the residue is returned to EAF as an iron source. The filtrate is purified by addition of Zn powder and metallic impurities precipitate and then they are filtered. Finally electrowinning is performed in the solution. Zn/orZnO are deposited at the cathode and O_2 is generated at the anode, where nitric acid is regenerated. Regenerated nitric acid is returned to the leaching stage. Therefore, a perfectly closed system is achieved Beaker scale tests were carried out to confirm the new process. 1g of dust was leached by 100 ml of nitric acid solution (2 vol%) at 303K with 200 rpm of stirring speed. The result is shown in Fig. 6, which was shown before [6]. Zn in both dusts A and B rapidly dissolved into the nitric acid solution and Zn content in the solution reached saturation after 20 minutes. 50 mg of Zn (about 60% of total Zn) in dust A and 110 mg of Zn (about 50% of total Zn) in dust B dissolved at these conditions. Final pH was about 0.6 in both experiments. The results of the tests suggest that part of $ZnFe_2O_4$ was dissolved in these conditions. However, Fe is also dissolved at the same time. The Fe amount dissolved from dust A was higher than that from dust B. Although dissolution reactions of Zn and Fe are not simple, it is clear that about half of Zn is dissolved from the EAF dust even into a dilute nitric acid solution when pH is less than 1.

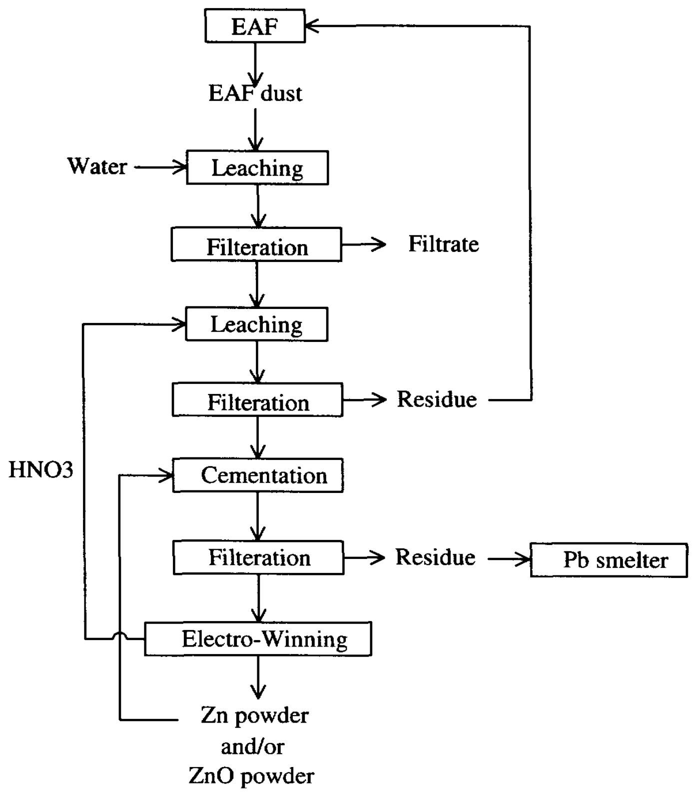

Fig.5 A schematic flow sheet of the new EAF dust treatment process.

The effect of solid/liquid ratio on the dissolution behaviors of Zn and Fe are shown in Fig.7 for dust A. An increase of solid/liquid ratio results in a decreased final leaching extraction of Zn and Fe in both samples and increased the final pH in the solutions. These results confirm theoretical considerations and suggest that 0.1 solid/liquid ratio during leaching is suitable for the leaching of ZnO from the dust, while iron oxide remains in the residue at around pH = 4.0.

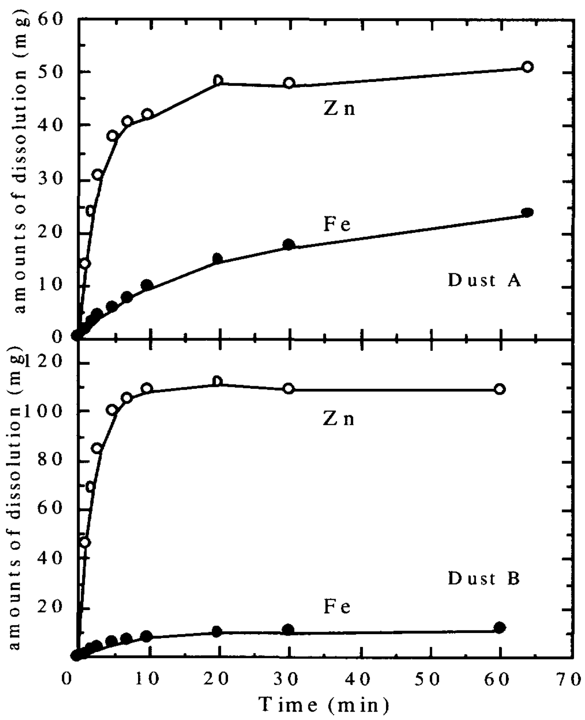

Fig.6 Dissolution rates of Zn and Fe from EAF dusts into a dilute nitric acid solution [6].

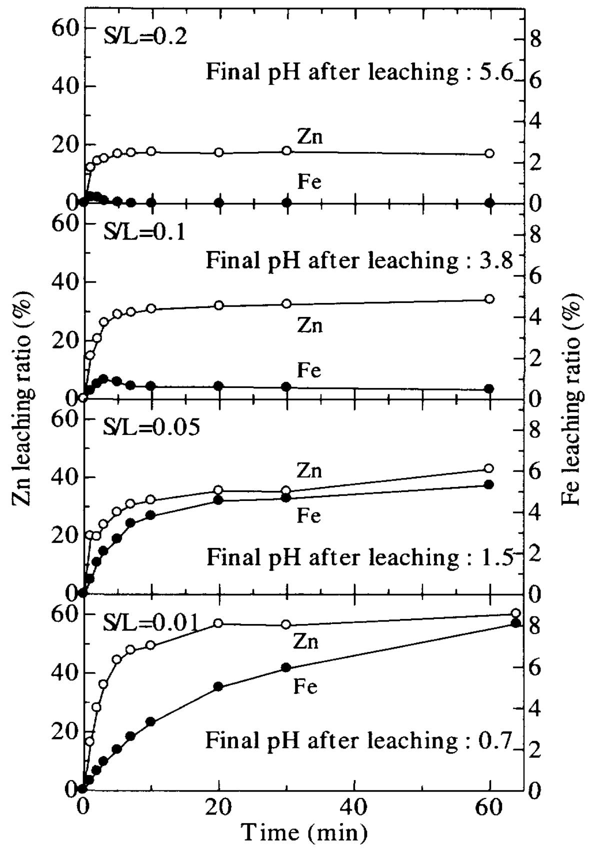

Fig.7 Effect of solid/liquid ratio on leaching behaviors of Zn and Fe in dust A. (HNO_3:0.26mol/L, at 303K, stirring speed: 200rpm)

The electrowinning experiments were conducted for 1 hour with constant-current method using Al cathode and Fe anode (10×10mm square) in a nitric acid solution, which contains 10g/l of Zn and is controlled at pH=3. The solutions were prepared by using high grade reagent ZnO. Partial results are shown in Table 3. Current efficiencies were measured by Zn analysis in the deposits. Over 100% of apparent current efficiencies were obtained with the current densities from 1 to 3 kA/m^2. Dendritic Zn and ZnO were found in the deposition. Since dendritic type Zn deposits are easily oxidized, there is a possibility to be oxidized during washing. Another mechanism to get ZnO deposition is through Zn^{2+} ion deposition as a hydroxide due to a shift to high pH on the cathode. Although the mechanism of ZnO formation on the cathode is not completely clear, the high current efficiency supports the new process.

The future of EAF dust processing is heading in two directions. One is a large-scale pyrometallurgical process that has a good performance for saving energy but gives only crude zinc oxide. The other is an on-site hydrometallurgical process in which soft acid is used to leach only zinc oxide. The residue which contains a certain amount of zinc is returned to the electrical arc furnace as a source of iron. Then, a securing landfill place that is one of biggest difficulties in the hydrometallurgical process is solved. In this case high quality crude zinc oxide which can be used directly in the existing electrowinning process was produced.

Table 3 Electrowinning results from nitric solution containing Zn.
anode: Pt, cathode: Al, electrolysis time: 1 hr.

Current Density (A/dm^2)	Amount of Coulomb (C)	Zn Amount on Electrode Surface (mg)	Zn Amount in Electrolyte (mg)	Apparent Current Efficiency (%)
1.0	36.373	13.85	0.00	112.42
2.0	71.798	27.67	0.00	113.80
3.0	110.654	42.06	0.00	112.22
4.0	144.452	44.25	0.31	91.08

The execution of the RoHs directive became real, the restriction of lead and cadmium becomes severer from the current state. In the ISF process, it is necessary to rectify lead and cadmium to obtain the purity that equals electric zinc. In the tough going and the stop of the ISF process are economically successive by the price hike of the coke in recent years. The destination disappears by stopping the ISF process though a considerable, rough zinc oxide has been reproduced by metallic zinc in the ISF process so far. Therefore, the process development to reproduce a rough zinc oxide by smelting electrolysis is needed. The management of impurities is an important still problem to make a rough zinc oxide the raw material of the electrolysis zinc smelting the past. Especially, the removal of the halogen elements such as chlorine and fluorine is needed. A rough zinc oxide is washed with water and a thin sodium carbonate solution usually. The example of the application on an actual smelting site still is not reported though this principle is known from of old.

5 Conclusions

A new hydrometallurgical process for EAF dust treatment is proposed in this study. Nitric acid solution is used for the extraction of ZnO from the dust. The results of beaker scale tests confirmed initially the new dust treatment process. Some characteristics of the process are as follows:

1. Dilute nitric acid solution was used as a leaching agent.
2. Zn recovery from zinc ferrite is not achieved but the dissolution of Fe is limited by controlling pH.
3. Zn is recovered as metallic Zn or ZnO by electrowinning and nitric acid is regenerated at the anode.

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