Hydrometallurgically Recovering Zinc from Electric Arc Furnace Dusts

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The increasing use of zinc-containing scrap for steel production has lead to a high zinc content in the electric arc furnace and converter flue dusts. The cost of disposing of this residue is high due to environmental restrictions. Various recycling processes have been developed for these dusts, but most never reached the pilot plant stage and many investigations were stopped because of metallurgical and economical inefficiencies. While pyrometallurgical methods have to deal with high energy consumption, low zinc yield, and valueless residues, hydrometallurgical processes could offer an economical recycling alternative. This paper describes hydrometallurgical methods for recovering zinc from steel industry dust. These methods can be integrated in the primary zinc-winning process or in galvanization. Investigations of sulfuric-acid leaching show high zinc solubility but also a high iron content in the final liquor. As a result, steps for purification are required that cannot be conducted economically. Alternatively, a NaOH leaching gives a satisfying zinc yield and a very low solubility for the iron that remains in the residue.

INTRODUCTION

The worldwide annual zinc production is about 8.1 million tonnes. Two-thirds of this amount are produced from ores. About 2.9 million tonnes could be recovered by recycling zinc products and wastes.[1] Nowadays, the main application of zinc is for galvanizing steel. The amount of zinc used for this purpose has grown from 1.5 million tonnes in 1975 to almost 3.4 million tonnes in 2000. At the end of their life cycle, most of the different zinc-coated steel products return to the steel mill as scrap. The zinc in electric arc furnace (EAF) dusts or converter flue dusts is generated from fuming and oxidation of the zinc present in the charged scrap. The collected dust is classified as hazardous waste. Because more and more zinc is being consumed for galvanizing car bodies, the zinc content in steel mill dusts will increase steadily.[1] The EAF dusts may have zinc contents up to 35%, while converter dusts only contain two to five percent. These poor wastes are recirculated to the converter until they reach a zinc content up to 20%. Both dusts contain zinc values between ore grade and concentrate grade and can be seen as a potential zinc resource.

Although 4.9 million tonnes of this by-product, with a zinc content of 1.4 million tonnes, were produced worldwide in 1997, only 200,000 tonnes of zinc were recycled from EAF dust.[2] This low recycling rate can be attributed to several factors. To treat EAF dust in electrolytic zinc plants, which cover 82% of the primary zinc production, the chlorine and fluorine content in the resulting electrolyte must be very low to avoid severe cathode and anode corrosion and cathode sticking problems.[2] In addition, many countries do not have tight restrictions for the disposal of EAF and converter dusts, and disposal is more economical than recycling. Nevertheless, the main reason for the low recycling rate of steel mill bag filter dust is the lack of a suitable process for this purpose. In the last ten years, enormous efforts have been made to find an economical method for recovering zinc from steel mill dusts.

Electric arc furnace dust currently is recycled by pyrometallurgical techniques to produce an upgraded zinc oxide. The predominant technology for this purpose is the so-called Waelz rotary kiln process. The zinc oxide in the EAF dust is reduced at temperatures up to 1,250°C in a CO-CO_2 atmosphere. The reduced zinc evaporates because of its low boiling point and re-oxidizes in the upper part of the kiln. The resulting oxide dust with up to 60% zinc is collected by different filter systems. However, similar to most pyrometallurgical processes treating these wastes, the energy consumption is too high. Further problems, such as an insufficient zinc yield and numerous impurities in the final product, are reasons why the search for an alternative process is still important.[3] Several different technologies have been developed in recent years. Because pyrometallurgical methods such as the plasma process, Contop, the AllMet process, and Ausmelt technology often failed to reach the pilot plant stage,[4,5] interest in hydrometallurgical methods has increased. Treating EAF dust directly in the primary hydrometallurgical zinc production has the advantage of low energy consumption, which has led to various investigations and process developments.[6] Different solvents have been examined, from sulfuric acid, hydrochloric acid, and caustic liquors to acetic acid. Many pilot plants were built to test hydrometallurgical technologies such as the MRT, EZINEX, and Modified Zincex process or the Cardiff process. Most of those plants, however, had to stop production after only a few years because of various problems.[6,7]

The Department of Non-ferrous Metallurgy of the University of Leoben tried to develop a hydrometallurgical technology in which converter flue dusts are leached so that the resulting liquor can be directly used in electrolytic galvanizing. Concentrated converter dusts were used because, until now, only a few efforts have been made to recover the zinc content of these dusts.

EXPERIMENTS

The experiments were carried out in laboratory scale. The analyses were done by atom absorption spectrometry (AAS) or titration. A typical analysis of the used converter dust is shown in Table I.

Investigations with Sulfuric Acid

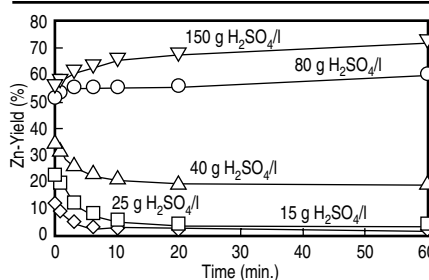A solid-liquid ratio had to be determined first. Investigations at values be-

Table I. Chemical Analyses of Used Converter Dust

Elements	Mass (%)
Al	0,11
Ca	7,00
Cu	0,16
Fe	45,00
K	1,41
Mg	0,42
Mn	0,39
Na	0,30
Pb	2,23
Si	0,42
Zn	18,54
Cl	0,66
O	23,36

Figure 1. The effect of the acid concentration on the zinc yield with increasing leaching time at 84°C.
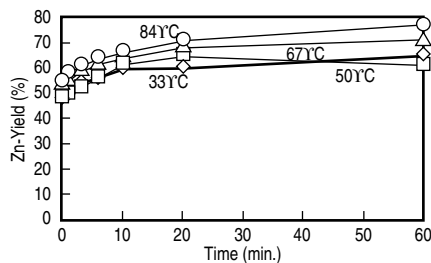
Figure 2. The effect of temperature on the zinc yield at different leaching times and an acid content of 150 g H_2SO_4/l.
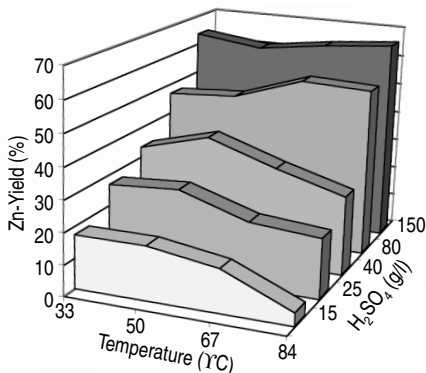

Figure 3. The effects of temperature and acid concentration on the zinc yield at a leaching time of 20 minutes.

tween 50 g/l and 200 g/l did not show any impact of the solid-liquid ratio on the zinc yield. Very low values and those higher than 200 g/l were not successful and led to different problems with the handling of the resulting liquor. Thus, a solid-liquid ratio of 100 g/l was chosen for the entire program. To guarantee an effective mixing of dust and liquor, 300 rpm was determined to be the optimum speed for the stirring device. Variations of leaching time, acid concentration, and temperature as investigated parameters led to the following results.

Figure 1 shows the zinc yield for leaching times up to 60 minutes subject to acid concentrations between 15 g H_2SO_4/l and 150 g H_2SO_4/l. The temperature was at a constant level of 84 °C for the curves in Figure 1. It can be seen that acid concentrations below 40 g H_2SO_4/l lead to a very low zinc yield, which even decreased after only a few minutes leaching time.

Investigations with an acid concentration below 40 g H_2SO_4/l were also performed at 33°C, 50°C, and 67°C. The results indicate similar trends, but the descent of zinc yield starts earlier at lower temperatures. The decreasing zinc yield at low acid concentrations can be interpreted as follows: The low amount of sulfuric acid in the liquor is spent dissolving zinc, iron, etc. and forming their sulfates within the first minutes. During this time, the pH-value of the leach solution increases from nearly zero to four. When the pH value reaches a level of five, a digestion of zinc-hydroxide occurs. Consequently, this decreases the zinc yield, as shown in the diagram.

In Figure 2, the temperature effect is illustrated for a high acid concentration. The zinc yield differs only in a range of at least ten percent.

Figures 1 and 2 indicate that the maximum of the different curves is reached after a leaching time of 15–20 minutes. Figure 3 reflects test results obtained at a constant leaching time of 20 minutes.

The behavior of iron and its compounds in the solution is also of great interest. Figure 4 shows the iron yield in the liquor as a function of the leaching time and various sulfuric acid concentrations.

Similar to the results for zinc, the data in Figure 4 indicate a very fast increase of the iron content in the solution, obtaining a maximum concentration after 20 minutes. Also comparable to zinc, the slight decrease of the yield at low H_2SO_4 concentrations can be attributed to the digestion of iron hydroxide at pH levels above five. Experiments with different temperatures suggest that the iron yield is influenced by the temperature in the same way as the zinc yield. A lower temperature (e.g., 50°C) causes only a small decrease in iron yield of about 5–10%. For acid concentrations lower than 80 g H_2SO_4/l, the yield is not affected by the temperature.

Figure 5 indicates the dependence of the iron yield on acid concentration and temperature for a leaching time of 20 minutes.

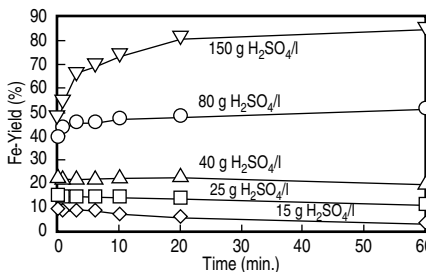Other metals of interest, such as cop-

Figure 4. The effect of leaching time and sulfuric acid content on the iron yield at 84°C.
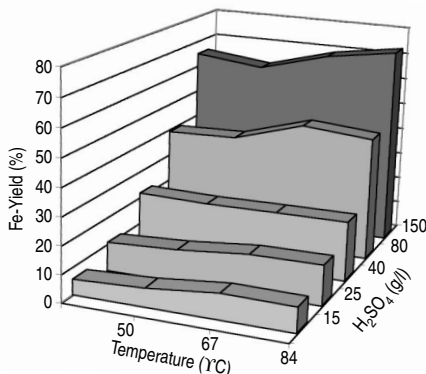

Figure 5. The effects of temperature and acid concentration on the iron yield at a leaching time of 20 minutes.
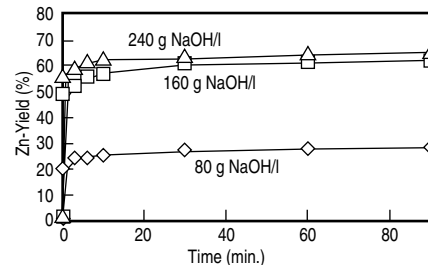

Figure 6. The effect of leaching time and caustic soda content on the zinc yield at 80°C.

per, cobalt, and nickel, were not detectable with the applied analytical system. Lead oxide is transferred to lead sulfate, which remains in the residue because it is virtually insoluble in sulfuric acid. Lime is dissolved and the calcium is digested as gypsum, which is one of the reasons for the high acid consumption.

The investigations into sulfuric acid leaching of converter dusts can be interpreted as follows. The missing zinc-iron selectivity in the leaching process, combined with a high iron content in the dust, makes it necessary to reduce the iron in the resulting liquor. Such purification methods as the goethite or jarosite process do not make sense because of the huge amounts of residue produced with these techniques. Alternatives such as solvent extraction have disadvantages, including low efficiencies and high operating costs because of many required process steps. An additional problem in using sulfuric acid is the poor solubility of zinc ferrite.[8] Even with high amounts of acid, the entire amount of zinc cannot be recovered from the dusts. Also, the fluorine and chlorine content of the resulting liquor are far too high for use in zinc electrolyses. To reduce fluorides and chlorides and to destroy insoluble ferrites, a thermal treatment of the dust prior to the leaching process would be necessary.

Investigations with Caustic Soda

Alternatively, experiments with caustic soda were carried out. One advantage of sodium hydroxide is the good selectivity between iron and zinc because of the insolubility of iron compounds. The results are shown in the following diagrams.

Figure 6 describes the zinc solubility subject to leaching time and caustic soda concentration. Each of the different graphs shows a very fast increase of the zinc yield within the first two or three minutes, with a maximum yield of 65% reached after about ten to 20 minutes. While the curves of the higher NaOH concentrations have nearly the same trend, the one with only 80 g NaOH/l shows a lower yield. Comparatively high amounts of NaOH are necessary to obtain sufficient zinc solubility. Only a small part (about 20%) is used to form Na_2ZnO_2; the rest remains as free caustic soda in

the leach. The maximum yield of 65% is caused by the insolubility of zinc ferrites. The influence of temperature on the zinc solubility at a high sodium-hydroxide content is quite low, as demonstrated in Figure 7.

Liquors with low NaOH concentrations show a little increase in the zinc yield with increasing temperature. In Figure 8, the effects of temperature and sodium hydroxide content on the yield are shown for a leaching time of ten minutes.

The amount of copper, iron, cobalt, and nickel is very low in the resulting liquor (<0,01 g/l) and, therefore, not detectable by the employed AAS. Lead oxide is partly dissolved and makes an additional lead purification step necessary (e.g., by means of digestion). Approximately 20% of the fluorine components in the dust remain in the residue while chlorine is dissolved completely in the liquor.

Compared with the sulfuric acid leaching method, the use of caustic soda shows nearly the same zinc yield, with the advantage of a satisfying zinc-iron selectivity. As mentioned previously, purification is necessary to eliminate lead from the liquor. Zinc can be extracted from the sodium hydroxide liquor by digestion as zinc carbonate or hydroxide or by electrolyses. Lime is used to recover caustic soda.

Similar to the sulfuric acid leaching, a pyrometallurgical treatment prior to the leaching process is necessary to destroy the zinc ferrite obtaining higher zinc yield[9] and to reach lower fluorine and chlorine concentrations.

PYROMETALLURGICAL TREATMENT OF ZINC FERRITES

Expanded investigations in this field were done by R.L. Nyirenda. The results show that it is complicated to destroy the zinc ferrite effectively by pyrometallurgical treatment. Experiments with synthetic zinc ferrite result in a very low reduction rate combined with the formation of solid mixtures of ZnO, Fe_3O_4, and FeO. At about 750°C the formation of $Fe_{0.85-x}Zn_xO$ is possible, while the formation of ZnO in FeO and Fe_3O_4 takes place at even lower temperatures. This causes a lower zinc yield in the subsequent leaching process, which can be attributed to the poor solubility of iron compounds.[4,8,10]

The authors' investigations and thermodynamical calculations were performed by using the analysis provided in Table I. Figure 9 illustrates the behavior of the different compounds and elements in a reducing atmosphere (e.g., hydrogen) with increasing temperature. The graph for $ZnFe_2O_4$ in the lower right corner of the diagram shows that a destruction of zinc ferrite at temperatures above 450°C should be possible with hydrogen as a reduction gas. Calculations with carbon monoxide as reduction gas results in a similar trend. However, a complete destruction of zinc ferrite can only be achieved above 550°C.

Experiments with carbon monoxide and carbon monoxide-nitrogen mixtures were not successful. Reactions took a very long time and a complete destruction was not possible in any case. Leaching after the thermal treatment shows only a slight increase in zinc yield. In a few cases the opposite took place and the zinc yield in the liquor decreased. This can be explained by the fact that solid mixtures of ZnO and FeO may be formed, as described by Nyirenda.[10]

Experiments with hydrogen-nitrogen mixtures led to satisfying results. After the reduction treatment, zinc yields up to 100% were reached when the resulting pre-treated dust was leached with caustic soda. Figure 10 illustrates the effect of nitrogen-hydrogen mixtures as a reducing gas on the zinc yield during a subsequent caustic soda leaching. The diagram shows that the maximum zinc yield of 100% was possible when using nitrogen-hydrogen mixtures with more than 50% hydrogen.

The reduction time for a 500 g sample was 30 minutes and the temperature was 550°C. Variation of time suggests that a lower reduction time of 20 minutes is also possible to reach the maximum yield.

Figure 10. The zinc yield after leaching with NaOH of dust reduced with different hydrogen-nitrogen mixtures.
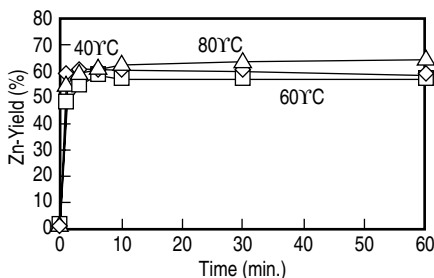
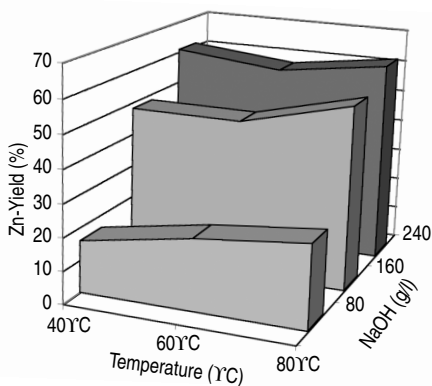Figure 7. The effect of leaching time and temperature at a caustic soda content of 240 g NaOH/l.

Figure 8. The effects of temperature and NaOH concentration on the zinc yield at a leaching time of ten minutes.
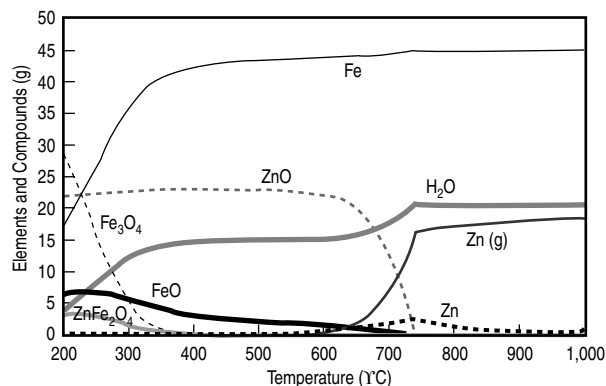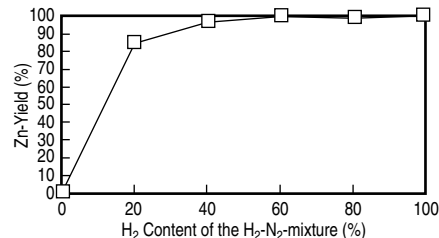
Figure 9. The behavior of different elements with increasing temperature in a hydrogen atmosphere (initial amount = 100 g).

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