

Recycling of an electric arc furnace flue dust to obtain high grade ZnO

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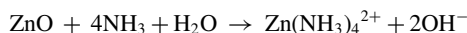
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Abstract

The production of steel in electric arc furnace (EAF) generates a by-product called EAF dusts. These steelmaking flue dusts are classified in most industrialized countries as hazardous residues because the heavy metals contained in them, tend to leach under slightly acidic rainfall conditions. However, and at the same time they contain zinc species which can be used as a source to obtain valuable by-products. The present investigation shows results on the processing of an EAF flue dust using ammonium carbonate solutions. Once zinc is dissolved:



with other impurities (i.e. cadmium and copper), these are eliminated from the zinc solution via cementation with metallic zinc. The purified zinc solution was evaporated (distilled) until precipitation of a zinc carbonate species, which then was calcined to yield a zinc oxide of a high grade. For the unattacked dust residue from the leaching operation, mainly composed of zinc ferrite, several options can be considered: back-recycling to the furnace, further treatment by sodium hydroxide processing or a more safely dumping due to its relatively inertness.

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1. Introduction

Steelmaking by means of electric arc furnace (EAF) procedure in the steel output is increasing. However, major pollution, that is released into the atmosphere during the steelmaking process, includes, among other contaminants, the EAF dusts.

Due to its physical and chemical (content of heavy metals) properties, these EAF dusts were categorized as hazardous wastes according to the US EPA classification, dated-back in 1980. Being considered as hazardous wastes in most of the industrialized countries, these residues must be stored in specialised landfills. On the other hand, these dusts, and due to their content in, i.e. zinc, can be used as secondary raw material in the production of this metal or other products.

These considerations had led to the treatment of these dusts and thus reducing their environmental impact. There are two possibilities to manage these EAF dusts: hydrometallurgical and pyrometallurgical processes. They consisted in the extraction of

nonferrous metals, i.e. zinc, in order to recycle the residue in the steelmaking industry; however, the hydrometallurgical processes are regarded as more eco-friendly for treating materials having a relatively low zinc content [1]. A third option that can be considered for these dusts is their inactivation, i.e. their stabilization prior to permanent disposal.

Considering the hydrometallurgical processing for the dusts, several hydrometallurgical treatments for the recovery of zinc and other metals from these zinc-bearing wastes have been proposed [1–9]. In a number of these procedures normally the basic sequence leaching-solvent extraction-electrowinning has been applied to the recovery of zinc, though it can be also considered other type of treatment which renders other saleable product such as zinc oxide thus opening markets for the same initial material.

In the present work, a high grade zinc oxide is obtained after leaching of the EAF dust with ammonium carbonate solutions and the subsequent treatment steps of cementation, evaporation (distillation) and calcination.

2. Experimental

The flue dust used in the present work came from a steel-making facility located near Madrid (Spain). Its composition,

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Table 1
Composition of the flue dust

Zn	29%
Cu	0.3%
Pb	4%
Cd	0.07%
Fe	25%
Cl	4%
MnO	3%
SiO ₂	3%

shown in Table 1, falls well within into the typically one described for these dusts [1,2,10]. Normally all these elements are present in the material as oxides; in the case of zinc, this element is present as zinc oxide (ZnO, zincite) and also as zinc ferrite (ZnFe₂O₄, franklinite) with a proportion of near 50% in the zinc ferrite form [11].

Leaching and cementation experiments were carried out in a glass reactor provided of mechanical shaking and at 20 °C for the time required.

X-ray powder diffraction was carried out with a Siemens D5000 diffractometer, whereas the thermal decomposition investigation described in Section 3.5 was studied using a Shimadzu D50 equipment.

Analysis of the different elements in the different steps has been carried out by atomic absorption spectrometry using a Perkin-Elmer 1100B spectrophotometer.

3. Results and discussion

3.1. Leaching with water

The elimination of the chloride content of the dust is achieved by leaching the flue dust with water; this preliminary pre-treatment is necessary in order to avoid the contamination of the final product by chloride ions. This elimination can be carried out in one step at a pulp density of 30% and 1 h of reaction at 20 °C. At the same time, not any appreciable quantity of metals, except calcium, is leached.

3.2. Leaching with ammonium carbonate solutions

Ammonium carbonate was chosen as leaching agent for the flue dust for two reasons, first because it can be complexed to zinc and second because it can be regenerated reasonably well and thus further recycled.

Preliminary results showed that the variation of the ammonium carbonate concentration in the range 60–200 g/l has little influence on the leaching of zinc (average recoveries of 45%) from the dust.

Different pulp densities were experimented and also different contact times, the aqueous solution contained 100 g/l ammonium carbonate at pH 10.5, the results of these experiments are shown in Table 2.

From these results, it can be deduced that the pulp density has a relative influence in the percentage of zinc leached from the dust, though the difference is more evident when the higher pulp density is used. Regarding the leaching of other base metals,

Table 2
Leaching of EAF dust with ammonium carbonate solutions

Pulp density (%)	Time	Zn (%)	Pb (%)	Cd (%)	Cu (%)
2.4	30 min	40	14	99	70
	2 h	42	20	99	76
4.8	30 min	43	15	77	68
	2 h	49	16	86	72
9.1	30 min	30	12	35	49
	2 h	33	12	33	48

it can be concluded that as the pulp density is decreased the percentage of leaching of these elements is increased. As can be expected, no chloride was found in the leached solution.

The change of the contact time has not a great influence in the leaching of the metals contained in the flue dust.

As can be seen from Table 2, zinc can be recovered in this step at an approximate 45%, evidently this is due to the presence of the zinc ferrite species in the flue dust which remained unattacked.

Dissolution of zinc can be represented in a simplified form as



reaction that in general terms also represents the dissolution of copper and cadmium. In this equation, n may show values ranging from 1 to 4, though due to the experimental conditions used in this work, the latter is the most probable coordination number for ammonia ligands.

On the other hand, and since the composition (chemical and mineralogical) of these residues is a characteristic of each dust, the experimental conditions for the leaching of these hazardous materials needed to be studied individually.

3.3. Cementation step

The zinc-bearing solution obtained from the leaching of the flue dust with ammonium carbonate solution at a pulp density of 4.8%, was then passed to the cementation step.

Zinc was selected as cementing agent for the reason that it can cement almost all the metals present into the leaching and also because it will not contaminate the solution with another strange element.

Table 3 shows the results obtained from this step, in which other experimental conditions were: 20 °C, 10 min of reaction time and 5 g of zinc dust added per liter of solution. It can be seen that the solution became almost purified for copper, cadmium and lead. It can be also noted that though zinc dust has been used as cementing agent, large chunks of zinc could be also

Table 3
Cementation with zinc dust of the leached solution

	Zn	Pb	Cd	Cu
Feed leach solution (g/l)	7.2	0.34	0.03	0.07
Solution after cementation (g/l)	8.1	0.01	0.0008	0.002
% Cementation	–	97.1	97.3	97.1

Table 4
Analysis of obtained zinc oxide

% Weight lost	29.8
Zn (%)	80
Cu (%)	0.01
Pb (mg/g)	0.06
Cd (mg/g)	0.05
Mn (mg/g)	0.02

used but this would lengthen the time needed for satisfactory cementation.

The treatment of the cement can be considered if the concentration of the metals contained in it makes feasible and economically acceptable this situation.

3.4. Precipitation of zinc carbonate

The filtrate obtained in the above step is further treated by distillation; this step can be done as steam distillation or vacuum distillation operations; in either case, it is necessary to increase the temperature of the solution to near 80–90 °C. At this point, ammonia and carbon dioxide drive off of the solution and can be recovered and recycle to make-up the leaching reagent.

In the present investigation, when the evaporation of the solution has been stopped, the solution contained approximately 0.2 g/l zinc, solution that could be also recycled to the leaching step.

Analysis of the solid obtained from this step showed that the zinc content is 57.6% compared with 59.5% (calculated from hydrozincite); as can be seen from this result, a pure zinc carbonate is obtained; a X-ray diffraction study of the solid obtained showed that the precipitated zinc species responds to a $Zn_5(CO_3)_2(OH)_6$ (hydrozincite) stoichiometry.

3.5. Calcination to zinc oxide

To have an idea of the temperature required to transform the zinc carbonate species to zinc oxide, a number of experiments were conducted at temperatures ranging from 300 to 1100 °C and 2 h. Results from these experiments indicate that to obtain a better break down of the zinc carbonate structure temperatures above 500 °C are necessary (i.e. 28.0% of weight lost at 300 °C against >29% above 500 °C, with zinc content in the solid of 77% at 300 °C and 80% at 500 °C and above). The investigations of the calcinations process showed, that in general terms, the reaction time, 2 or 4 h, is not as important as the temperature.

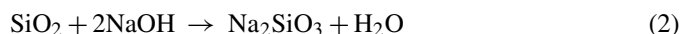
Typical analysis of the product obtained from this step, i.e. at 900 °C and 2 h, is shown in Table 4, the product matches very well the specifications of a very pure zinc oxide (80.34% Zn). It can be seen that a high grade (>99.5%) zinc oxide can be obtained from the flue dust.

3.6. Treatment of the residue obtained from the ammonium carbonate leaching

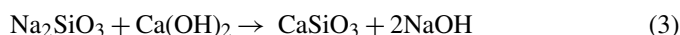
It has been shown before (Table 2), that the recovery of zinc and lead is not complete using this ammonium carbonate leach-

ing step, however, further recovery of these two metals can be accomplished with sodium hydroxide solutions, i.e. 5–8 M and temperatures in the 75–90 °C range, by this process zinc and lead compounds are dissolved forming MO_2^{2-} , where M stands either for zinc or lead and with yields around 30–35% for zinc with respect to the original zinc content of the EAF dust. Under this conditions, a part of the zinc remained in the residue, due to the presence of the still-unreacted zinc ferrite. Though the next possibility has not proven in the present investigation, a more complete zinc recovery can be obtained if the material is fused with solid NaOH and dissolved in sodium hydroxide solutions [4,5].

On the other hand, it is expected that silicate formed during leaching:

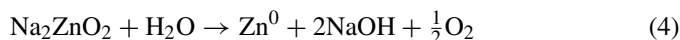


could be eliminated by the addition of calcium hydroxide:



In the above sequence of reactions, iron remained as a solid phase (probably as hematite) avoiding problems associated to its presence in the solution, i.e. promotion of anode corrosion and increase the iron uptake in the zinc cathode in the electrowinning step.

From the alkaline solution, lead is recovered as a by-product by cementation with zinc or even precipitated using a suitable sulphide salt (i.e. sodium sulphide), whereas zinc is finally recovered by electrowinning in alkaline media:



4. Conclusions

The results presented in this work show that this type of alkaline treatment renders a saleable zinc-product, and at the same time a less harmful residue is obtained, mainly constituted by highly unreactive iron species, and since most of the heavy metals, i.e. cadmium and lead, are leached. However, the real possibilities of such treatment may be proven at a higher scale and always when a market for such a type of product (high grade zinc oxide) exists.

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