



## Hydrometallurgical recovery of zinc and lead from electric arc furnace dust using mononitriilotriacetate anion and hexahydrated ferric chloride

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### Abstract

The purpose of this work was to study the feasibility at laboratory-scale of a new hydrometallurgical process for treating electric arc furnace dusts (EAFD). The proposed process is intended to extract zinc and lead from EAFD without destroying the iron oxides matrix. So, this material can be recycled by the steel industry. Independently of the origin of the samples, major mineralogical forms present in these wastes are  $\text{Fe}_3\text{O}_4$ ,  $\text{ZnO}$ ,  $\text{ZnFe}_2\text{O}_4$  and  $\text{PbOHCl}$ . The proposed process consists of a hydrometallurgical treatment of wastes based on selective leaching of zinc and lead. Initially, a leaching is carried out utilizing a chelating agent, nitrilotriacetate anion ( $\text{NTA}^{3-}$ ), as the protonated form  $\text{HNTA}^{2-}$ . Treatment of five EAFD samples for an hour at room temperature with a molar solution of reagent results in total leaching of the  $\text{ZnO}$ . In all cases the solubilized iron does not exceed 3 wt.%. The recovery of zinc and lead is performed by precipitation of metallic sulfides with a solution of  $\text{Na}_2\text{S}_4$  sodium tetrasulfide 2 M. These metallic sulfides can be used as metallurgical raw materials and the chelating reagent can be reused in the process after pH adjustment. The results of the normalized leaching test AFNOR X31-210 conducted on the leaching residues, shows that all the samples meet acceptance thresholds for hazardous wastes landfill. However, the residues contain a considerable amount of zinc as  $\text{ZnFe}_2\text{O}_4$ . The extraction of the zinc element requires the destruction of the ferrite structure. In this process,  $\text{ZnFe}_2\text{O}_4$  is treated by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The reaction consists in a particle  $\text{O}^{2-}/\text{Cl}^-$  exchange allowing the recovery of zinc as  $\text{ZnCl}_2$  and iron as hematite  $\text{Fe}_2\text{O}_3$ . The separation of these products is accomplished by simple aqueous leaching. All of the zinc is extracted in a 8 h treatment at  $150^\circ\text{C}$  with a molar ratio  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{ZnFe}_2\text{O}_4$  equal to 10. Ultimate solid residues, which have been concentrated in iron, can be oriented towards the steel industry. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrometallurgical recovery; EAFD; Selective leaching; Zinc; Lead

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## 1. Introduction

Production of steel in the electric arc furnace generates a dust by-product mainly composed of iron oxides and non-ferrous metals. The average iron concentration in the dust is approximately 30 wt.% [1]. Among the non-ferrous metals present in the dust, zinc is the most important. The zinc content is, on the average, 20 wt.% [2] as ZnO and ZnFe<sub>2</sub>O<sub>4</sub>. In spite of high level of iron oxides, direct recycling in blast furnace or in EAF is impractical because of possible operating problems [3]. Due to the presence of significant amounts of leachable compounds of lead, cadmium, chromium or nickel, electric arc furnace dust (EAFD) are classified as hazardous wastes. There are two possibilities to manage these by-products. The most commonly method used is disposal in hazardous wastes landfills after a solidification/stabilization [1,4] treatment using hydraulic binders. The cost of the treatment is approximately 180 €/t. The other method of treatment is beneficiation by hydrometallurgy [5–9] or pyrometallurgy [10–13]. The treatment objective is to extract non-ferrous metals like zinc or lead to allow the recycling of matrix and to avoid the disposal of it.

World production of crude steel by electric way was about 286 million t in 2000 [14]. The weight of dust collected in a typical EAF is about 15–20 kg/t of steel produced leading to a global dust quantity ranged between 4.3 and 5.7 million t each year around the world. With an average zinc content of 20 wt.%, EAFD represent a possible recovery of zinc from 0.86 to 1.14 million t per year. Thus, the beneficiation of rich zinc-bearing wastes like EAFD is becoming necessary as minerals are being exhausted.

At present time, in France, the only alternative to landfilling is treatment utilizing the Waelz process [10]. This pyrometallurgical process does not allow direct recycling of dust. Indeed, the product of the process consists in a mixture of lead, zinc and iron oxides which have to undergo an additional treatment in order to be recycled. Moreover, the economics of the Waelz process requires zinc concentrations higher than 16 wt.%. This is the reason why this pyrometallurgical process cannot be utilize to treat all of the dust.

The inventory of different existing processes for EAFD treatment shows that pyrometallurgical and hydrometallurgical processes have both advantages and disadvantages. Pyrometallurgical processes are more expensive than hydrometallurgical processes and do not allow total beneficiation of the dusts in spite of a very high yield of non-ferrous metals extraction. Hydrometallurgical processes are cheaper but do not allow lead extraction or ZnFe<sub>2</sub>O<sub>4</sub> leaching.

In this paper, a new hydrometallurgical treatment is proposed. It consists of the following steps:

- direct atmospheric leaching of dust using solutions of sodium hydrogenonitritotriacetate allowing the selective dissolution of easy leachable compounds such as ZnO and PbOHCl;
- recovery of zinc and lead in the leachate by sulfide precipitation;
- treatment of the solid residue with FeCl<sub>3</sub>·6H<sub>2</sub>O in order to destroy zinc ferrite.

The results discussed in this paper have been obtained with five different samples of EAFD.

## 2. Experimental

### 2.1. Characterization of samples

The different dust samples used in this investigation came from carbon steelmaking except sample E which came from stainless steelmaking.

#### 2.1.1. Chemical analysis

A sample of 10 g of dust was digested in 100 ml of concentrated hydrochloric acid. The suspension was boiled for 20 min. After filtering, dissolved metals were analyzed by atomic absorption spectrometry (AAS).

#### 2.1.2. XRD analysis

X-ray powder diffraction was performed on each sample (INEL CPS 120 diffractometer with a curved position sensitive detector using Co K $\alpha$  radiation). The diffraction patterns were analyzed with WINDIF Software allowing to perform a search by matching experimental file and database.

#### 2.1.3. Normalized leaching test AFNOR X31-210

The AFNOR X31-210 leaching test [15] was conducted with the five dust samples. A 100 g dust sample was placed in a 21 bottle with 1 l of deionized water and shaken for 24 h with a constant rotational motion rate in a leaching bench (Heidolph Reax 20). The mixture was then filtered using a 0.45  $\mu\text{m}$  cellulose filter. Analysis consisted of pH measurement and Cr, Pb, Zn and Ni concentration determinations using AAS. The soluble fraction was determined by evaporation of 100 ml of leachate. If  $m_1$  is the initial weight of the sample utilized and  $m_2$  the weight after evaporation, soluble fraction is given by  $(m_2/m_1) \times 100$ .

### 2.2. Selective leaching

Reagent of selective leaching utilized is nitrilotriacetate ion  $\text{N}(\text{CH}_2\text{CO}_2)_3^{3-}$  as the protonated form  $\text{N}(\text{CH}_2\text{COOH})(\text{CH}_2\text{CO}_2)_2^{2-}$ . The concentration of the solution was equal to 1 M for a pH value of 8.

#### 2.2.1. Effect of the temperature

The effect of the temperature was investigated using a temperature controlled bath. Leaching was performed on samples at 20, 50, 80 and 110 °C for 1 h. In each case, a sample of 10 g of dust was immersed in 100 ml of molar  $\text{HNTA}^{2-}$  solution corresponding to a solid/liquid ratio of 100 g/l.

#### 2.2.2. Effect of $\text{HNTA}^{2-}/\text{ZnO}$ ratio

For the study of the above parameter, experiments were performed at 20 °C. The  $\text{HNTA}^{2-}/\text{ZnO}$  molar ratio were varied in the range from 4 to 16.

#### 2.2.3. Recovery of leached metals by sulfide precipitation

The precipitation reagent used was a sodium polysulfide solution ( $\text{Na}_2\text{S}_4$ ), which was prepared by disproportionation of elemental sulfur in sodium hydroxide solution [16,17].

#### 2.2.4. Analysis of leaching solid residue

After each leaching experiment, the solid residue was characterized by chemical and XRD analysis and was subjected to the AFNOR X31-210 leaching test, previously applied over the original samples of dust.

#### 2.3. Destruction of zinc ferrite $ZnFe_2O_4$

After the first leaching step, the solid residue, which contains zinc in ferrite form ( $ZnFe_2O_4$ ), was treated using  $FeCl_3 \cdot 6H_2O$  at  $150^\circ C$  for 8 h. The treatment was performed in a 250 ml Pyrex flask including a cooler tube and heating was ensured by a thermostated oil bath. From  $36.5^\circ C$ ,  $FeCl_3 \cdot 6H_2O$  melts in its crystallization water leading to a molten medium. A molar ratio  $FeCl_3 \cdot 6H_2O/ZnFe_2O_4$  equal to 10 was utilized [18].

### 3. Results and discussion

#### 3.1. Characterization of samples

##### 3.1.1. Chemical analysis

The results of chemical analysis are shown in Table 1. The major element present in the dusts is iron in a content varying from 16 to 44 wt.%. Zinc was the most prevalent non-ferrous metal with a content in the range from 7 to 28 wt.%. Lead content did not exceed 2 wt.% except for sample A. Sample E, resulting from stainless steelmaking contained important amounts of nickel and chromium. Speciation of zinc evidences that this element exists under two main mineralogical forms: zincite  $ZnO$  and zinc ferrite  $ZnFe_2O_4$ . The respective proportions of both compounds are a function of the molar ratio  $Zn/Fe$  [19]. Ferrite form is predominant for low ratios whereas  $ZnO$  is the major compound when the molar ratio  $Zn/Fe$  reaches high values. The amount of zinc present in the zincite can vary from 30 to 70%.

##### 3.1.2. XRD analysis

The results of XRD analysis are shown in Table 2. According to the peaks detected and their respective intensities, we concluded that the majority compounds of the dust are zincite, zinc ferrite and/or magnetite  $Fe_3O_4$ . In samples with high content in lead, laurionite

Table 1  
Chemical composition of the five electric arc furnace dust samples studied

Chemical composition (wt.%)	A	B	C	D	E
Fe	22	44	27	26	16
Zn	28	7.4	15.5	22.8	16.4
Zn rate under $ZnO$ form	60	30	52	55	70
Pb	7.8	0.2	2.4	1.4	1.5
Cr	0.3	0.5	0.4	0.9	7.2
Ni	0.02	0.07	0.04	0.04	2.2
Ca	4.4	0	6.1	4.4	5.3
Mn	1.7	4.4	2.6	3.8	2.6

Table 2  
XRD analysis of the dusts studied

Sample	Mineralogical revealed forms
A	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , ZnO, PbOHCl, CaSiO <sub>3</sub>
B	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , ZnO
C	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , ZnO, PbOHCl, CaSiO <sub>3</sub>
D	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> /Mn <sub>3</sub> O <sub>4</sub> , ZnO
E	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , FeCr <sub>2</sub> O <sub>4</sub> , ZnO

PbOHCl was found. No other mineralogical form of lead was detected in the different analysis. Due to the presence of nickel and chromium, the analysis of sample E reveals chromite FeCr<sub>2</sub>O<sub>4</sub> and nickel chromite NiCr<sub>2</sub>O<sub>4</sub> forms. The XRD analysis performed on the residues obtained after hydrochloric acid leaching of all the samples evidences the presence of minor compounds such as Zn<sub>2</sub>SiO<sub>4</sub> (Willemite), CaSiO<sub>3</sub> and SiO<sub>2</sub>.

### 3.1.3. Normalized leaching test AFNOR X31-210

The leaching test AFNOR X31-210 was conducted on all dust samples. The results are presented in Table 3 where they are compared with acceptance thresholds in hazardous wastes landfill. Samples A, C and E do not meet the acceptance criteria. In these conditions, these waste will be stabilized before landfilling. In addition, samples B, C and E which contained less than 16 wt.% zinc, cannot be treated by the Waelz process.

### 3.2. Selective leaching

The different leaching parameters were initially studied on a reference sample: EAFD A. This dust was selected because of its high lead content allowing us to study zinc and lead leaching simultaneously.

A protonated form of nitrilotriacetic acid was chosen for its ability to dissolve significative amounts of ZnO and PbO without solubilizing iron oxides. The maximum solubilities reached, determined in a previous work [20], are 39.1, 17.8 and 0.7 g/l, respectively. In the case of ZnO and PbOHCl, the leaching reactions can be written as follows:

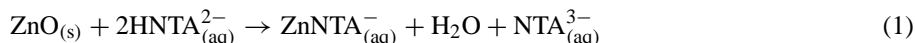


Table 3  
Results of leaching test AFNOR X31-210 utilized with the five dust samples

Parameters	Acceptance thresholds since the 1 April 1998 [3]	A	B	C	D	E
pH	4 < pH < 13	8.2	10.4	11	9.3	11.4
Soluble fraction (%)	7	0.97	0.13	0.3	0.4	1.1
Total Cr (mg/kg)	35	13.7	ND <sup>a</sup>	ND	ND	1750
Pb (mg/kg)	35	64.3	ND	42	<5	<5
Zn (mg/kg)	175	0.48	12.3	3	<1	<1
Ni (mg/kg)	35	<1	<1	<1	<1	<1

<sup>a</sup> ND: not detected.

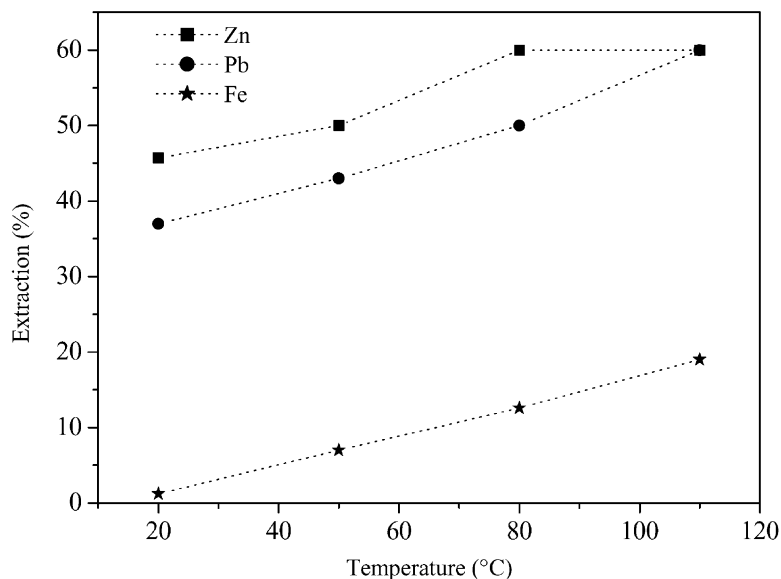
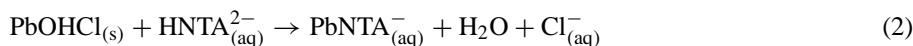


Fig. 1. Effect of temperature on the zinc, lead and iron leaching (sample A).



### 3.2.1. Effect of temperature

The results of temperature investigations are plotted in Fig. 1. The increase of temperature from 20 to 110 °C produced an increase in zinc and lead leaching. Unfortunately, at these conditions, the selectivity of leaching is not ensured and important amounts of iron are found in the leachate. For all other experiments, selective leaching using  $\text{HNTA}^{2-}$  was performed at room temperature.

### 3.2.2. Effect of $\text{HNTA}^{2-}/\text{ZnO}$ ratio

Fig. 2 shows that total extraction of zinc present in the sample A as  $\text{ZnO}$  form needs a  $\text{HNTA}^{2-}/\text{ZnO}$  molar ratio of 8. The yield of lead leaching follows the same evolution as shown in Fig. 3. Leaching yield of zinc and lead reached its maximum for a residence time of 1 h. The treatment of this dust required a  $\text{HNTA}^{2-}/\text{ZnO}$  ratio higher than the stoichiometry indicated by the reaction (1) for several reasons.  $\text{ZnO}$  was not the only leachable compound present in the sample.  $\text{PbOHCl}$  was also leached. Moreover, EAFD are wastes containing basic compounds able to react with  $\text{HNTA}^{2-}$  to give deprotonated species  $\text{NTA}^{3-}$ . Under this form, the leaching power of the reagent decreases. A ratio  $\text{HNTA}^{2-}/\text{ZnO}$  equal to 8 made possible the treatment of any EAFD whatever its leachable metals content and whatever its basicity.

### 3.2.3. Recovery of leached metals by sulfides precipitation

After  $\text{HNTA}^{2-}$  leaching, zinc and lead contained in the leachate ( $8 < \text{pH} < 9$ ) were precipitated as sulfides utilizing tetrasulfide solutions at 2 mol/l according to the following

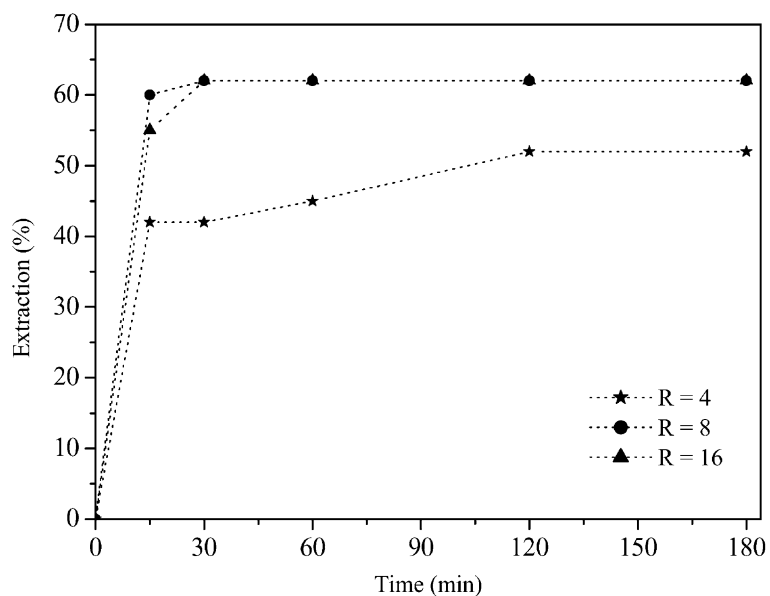


Fig. 2. Effect of HNTA<sup>2-</sup>/ZnO molar ratio on the zinc leaching (sample A).

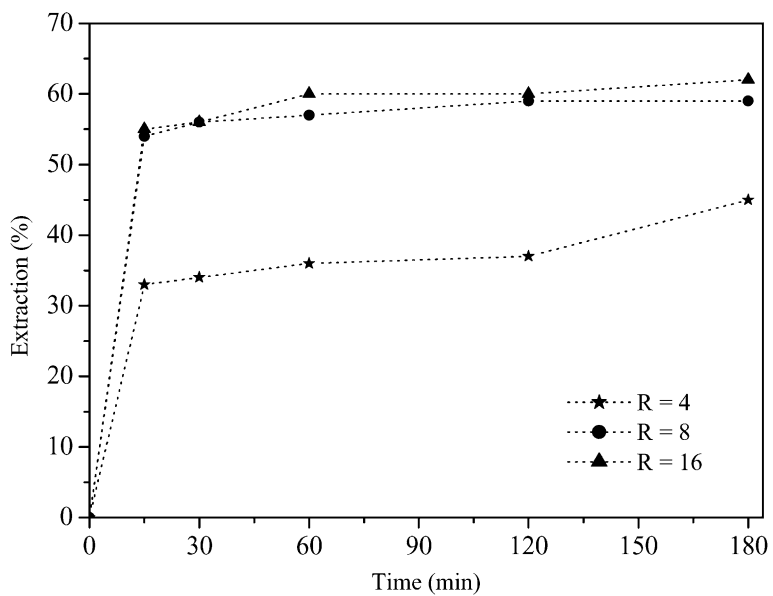


Fig. 3. Effect of HNTA<sup>2-</sup>/ZnO molar ratio on the lead leaching (sample A).

Table 4  
Concentrations of metals in HNTA<sup>2-</sup> leachate of sample A

Concentration (g/l)	Initial leachate	Leachate after precipitation of metal sulfides
Fe	0.27	0.25
Zn	8.33	0.12
Pb	2	<10 <sup>-3</sup>

Table 5  
Chemical analysis of initial sample A and its HNTA<sup>2-</sup> leaching solid residue

Chemical composition (wt.%)	Raw dust A	Leaching solid residue
Fe	22	30
Zn	28	16
Pb	7.8	4.2

reactions:

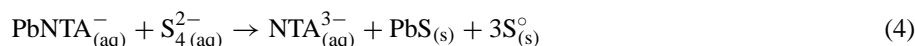
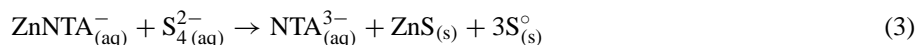


Table 4 gives the composition of the leachate resulting from the treatment of sample A before and after metallic sulfide precipitation. According to the low concentrations of metals found in the solution after precipitation, the reagent can be recycled for a new leaching step after pH adjustment [20]. The metallic sulfide cake contains 29.5 wt.% of zinc, 7.7 wt.% of lead and 62.8 wt.% of sulfur.

#### 3.2.4. Analysis of leaching solid residue

Table 5 reports iron, zinc and lead levels of the leaching solid residue compared to the raw dust. The mass of this residue was approximately 70% of the initial waste. The iron content increased by 35% whereas zinc and lead contents decreased approximately by one-half. Mineralogical analysis (Table 6) confirmed the total leaching of ZnO and PbOHCl.

The results of leaching test AFNOR X31-210, presented in Table 7, demonstrated that the treated dust meets acceptance criteria in hazardous wastes landfills contrary to the raw dust for which lead exceeds the acceptance value. To envisage a beneficiation of this solid residue in steel industry, the extraction of zinc as ZnFe<sub>2</sub>O<sub>4</sub> is necessary.

Table 6  
XRD analysis of initial sample A and its HNTA<sup>2-</sup> leaching solid residue

Raw dust A	Leaching solid residue
ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , ZnO, PbOHCl, CaSiO <sub>3</sub>	ZnFe <sub>2</sub> O <sub>4</sub> /Fe <sub>3</sub> O <sub>4</sub> , CaSiO <sub>3</sub>

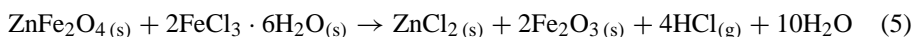


Table 7  
Results of AFNOR X31-210 leaching test of initial sample A and its HNTA<sup>2-</sup> leaching solid residue

	Raw dust A	Leaching solid residue
Pb (mg/kg)	64.3	<1
Zn (mg/kg)	0.48	ND
pH	8.23	6.8
Soluble fraction (%)	0.97	<10 <sup>-4</sup>

### 3.3. Destruction of zinc ferrite ZnFe<sub>2</sub>O<sub>4</sub>

Zinc ferrite presents a very stable crystallographic structure of spinel type. Leaching by HNTA<sup>2-</sup> solutions does not affect this compound even if the temperature is increased. Recovery of zinc requires the destruction of the crystal lattice. The work of Humbert [21], found that the behavior of free iron oxides and zinc ferrites in O<sup>2-</sup>/Cl<sup>-</sup> exchange reactions, allowed one to utilize hexahydrated ferric chloride, FeCl<sub>3</sub>·6H<sub>2</sub>O. This compound reacts with ZnFe<sub>2</sub>O<sub>4</sub> from 100 °C according to the following reaction:



The solid residue resulting from HNTA<sup>2-</sup> leaching of sample A was treated for 8 h at 150 °C utilizing a molar ratio FeCl<sub>3</sub>·6H<sub>2</sub>O/ZnFe<sub>2</sub>O<sub>4</sub> equal to 10. Aqueous leaching yields a ZnCl<sub>2</sub>/FeCl<sub>3</sub> solution from which zinc can be recovered by different ways: Riveros and Dutrizac proposed to separate both metals by hematite precipitation leaving zinc in solution [22] and Humbert performed the separation Fe<sup>3+</sup>/Zn<sup>2+</sup> by means of ion exchange [21]. The evolution of the composition of solid residues arising from each step of the process is given in Fig. 4. The final product contains only zinc traces. Its iron content is 42 wt.% corresponding to 60% as α-Fe<sub>2</sub>O<sub>3</sub> form. The other forms detected by XRD are mainly silicates. Chemical analysis shown that the solid residue contained again 7 wt.% of lead but neither XRD nor scanning electronic microscopy (SEM) allowed to evidence mineralogical forms of this element.

### 3.4. Global treatment of various EAFD samples

Fig. 5 shows the flow sheet proposed for the treatment of the five samples.

#### 3.4.1. Zinc leaching yield

Samples A, C, D, E were treated in two steps of the process whereas sample B was directly treated with FeCl<sub>3</sub>·6H<sub>2</sub>O because zinc is mainly present as ZnFe<sub>2</sub>O<sub>4</sub>. Fig. 6 shows zinc extraction yields obtained after HNTA<sup>2-</sup> leaching and FeCl<sub>3</sub>·6H<sub>2</sub>O treatment, for each sample studied. For samples A, C, D and E, the yield of zinc extraction exceeds 90%. In the case of sample B, the yield is lower (80%). XRD analysis revealed the presence in the residue of Zn<sub>2</sub>SiO<sub>4</sub>, compound on which HNTA<sup>2-</sup> leaching and FeCl<sub>3</sub>·6H<sub>2</sub>O treatment have no effect. For sample A, this two-step process leads to the recovery of 99.9% of zinc.

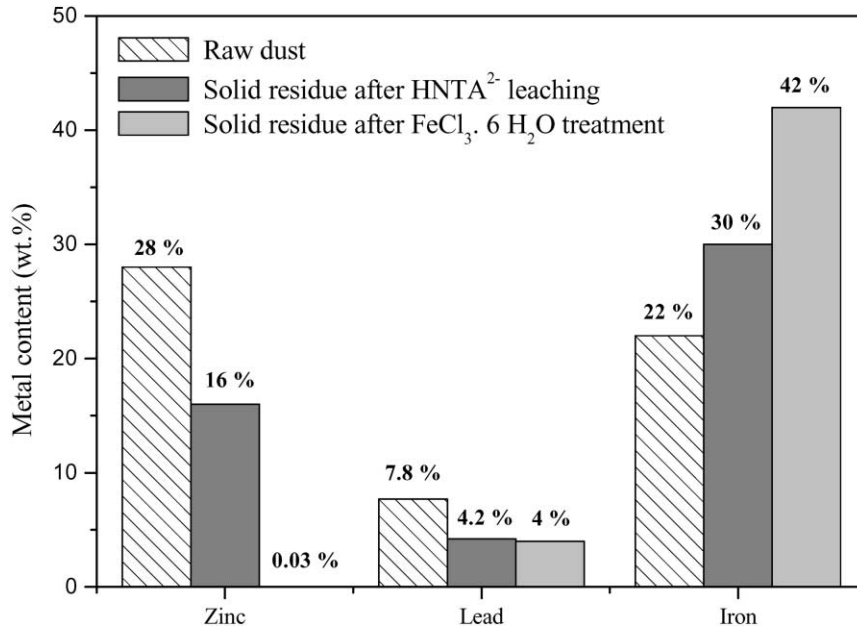


Fig. 4. Evolution of zinc, lead and iron content during the treatment of sample A.

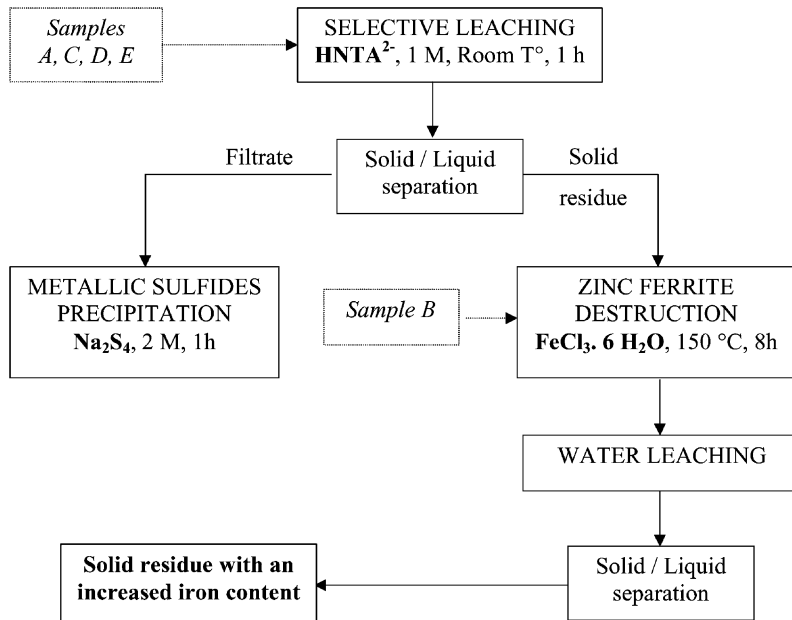


Fig. 5. Flowsheet proposed for EAFD treatment.

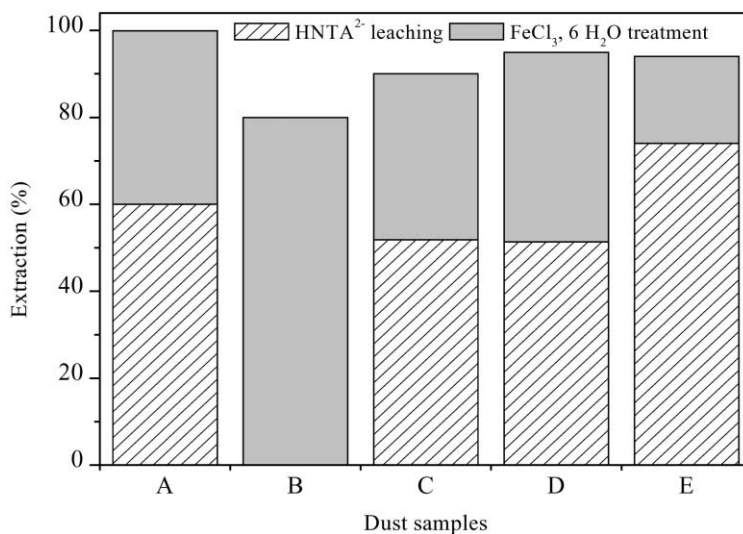


Fig. 6. Extraction of zinc by HNTA<sup>2-</sup> and FeCl<sub>3</sub>·6H<sub>2</sub>O from the five dust samples.

### 3.4.2. Composition of metallic sulfide cakes

Composition of metallic sulfide cakes obtained after HNTA<sup>2-</sup> leaching step is presented on Fig. 7. All sulfide cakes contained approximately 30 wt.% of zinc. Lead contents are very small being about 0.8 wt.%, except for sample A. The average composition of metallic sulfide cakes arising from our process can be compared with zinc ore concentrates obtained

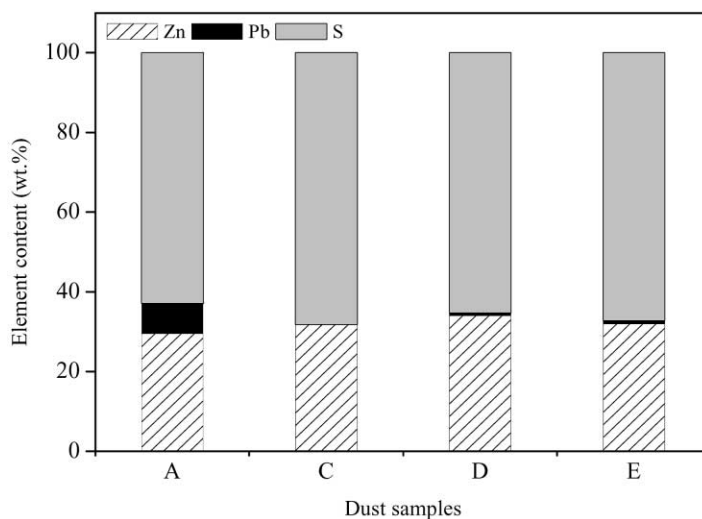


Fig. 7. Composition of metallic sulfide cakes.

Table 8  
Compared composition of the obtained sulfide cakes and zinc ore concentrates

Chemical composition (wt.%)	Sulfide cakes produced	Zinc ore concentrates
Zn	33	50
Fe	ND	11
Pb	≈1	1
S	65	31

in mining industry [23] after differential flotation of zinc ores (Table 8). Even if sulfide cakes are poorer in zinc than mining concentrates, they have the advantage of not containing iron. Therefore, during the roasting of this raw material, there will not be formation of ferrite  $ZnFe_2O_4$ , making the extraction of zinc by the acid leaching of roasted metallic sulfides easier.

#### 3.4.3. Evolution of metals content of solid residues

Table 9 shows firstly the evolution of metals concentration in the solids yielded by each step of the process and secondly the evolution of the weight of these solids. The solid residues resulting from  $HNTA^{2-}$  leaching present a weight loss ranged between 15 and 30%. The zinc and lead contents are important but the results of leaching test AFNOR X31-210 demonstrated that the solid are inert from a chemical point of view.

In the solids obtained at the end of the process, it can be observed that there was a doubling of the iron content in most of the samples studied, due to the use of a reagent containing iron.

Table 9  
Evolution of metal content in raw dusts and leaching solid residues for the five samples

	Sample A	Sample B	Sample C	Sample D	Sample E
<i>Raw dust</i>					
Sample weight (g)	10	10	10	10	10
Metal content (wt.%)					
Zinc	22	7.4	16	23	16
Lead	7.8	ND	2.3	1.4	1.5
Iron	28	38.6	16	26	16
<i>Solid residue after <math>HNTA^{2-}</math> leaching</i>					
Residue weight (g)	7	Not performed	8.2	8.5	6.7
Metal content (wt.%)					
Zinc	16	Not performed	9	12	6.4
Lead	4.2	Not performed	2.2	1.2	1
Iron	30	Not performed	18.5	30	23
<i>Solid residue after <math>FeCl_3 \cdot 6H_2O</math> treatment</i>					
Residue weight (g)	5	7.3	4.4	6.1	5.7
Metal content (wt.%)					
Zinc	0.03	2	3.6	2	2
Lead	4	ND	4	1.7	1.2
Iron	42	52.3	43	57	40

The final solids contained more than 40 wt.% of iron, for a zinc average content of 2 wt.% and represented between 44 and 73% of the weight of the raw dusts. After the two leaching steps, the lead content of all samples was approximately equal to the initial value because of the weight loss of the wastes. The mineralogical form of unleached lead compounds could not be detected neither by XRD analysis nor by SEM. Like in the EZINEX process [12], we can predict that this residue can be recycled to the electric arc furnace. Indeed, although the EZINEX process does not allow the extraction of  $ZnFe_2O_4$ , the residue of leaching which contains important amounts of zinc is nevertheless recycled at an amount of 1 wt.% of the furnace load. In the case of a total extraction of zinc and lead, recycling of solid residue at blast furnace level can be envisaged.

With regard to nickel and chrome in the sample E (stainless steel dust), the two-step process had no effect on their mineralogical forms.

#### 4. Conclusion

This work showed the feasibility at laboratory-scale of a new hydrometallurgical two-step process for EAFD. The first step consists of a preferential leaching of ZnO and PbOHCl, leading to an inert solid residue suitable for disposal. Precipitation of metallic sulfides with  $Na_2S_4$  solutions allows the recovery of leached metals and the recycling of leaching reagent. Metallic sulfide cakes produced in the treatment are usable in zinc smelting industry as raw material. The second step allows the total extraction of zinc destroying  $ZnFe_2O_4$  by means of  $FeCl_3 \cdot 6H_2O$ . Final residue is concentrated in iron and contains small amounts of non-ferrous metals such zinc or lead. It can be recycled either in an electric arc furnace or a blast furnace.

This process may be applicable to other zinc- or lead-bearing solids (roasted sulfides, Waelz oxides, metallurgical scraps, etc.) and can be adaptable to the composition of the matrix. For example, if in a given sample, zinc is majoritary under ZnO form, only the first step will be practiced. On the other hand, if zinc ferrite is the predominant mineralogical form, the solid will be directly treated by  $FeCl_3 \cdot 6H_2O$ . Some experiments carried out with samples of roasted sulfides and Waelz oxides showed that the zinc extraction yield could reach 99.5%.

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