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Hydrometallurgical Treatment of EAF Dust by Direct Sulphuric Acid Leaching at Atmospheric Pressure

V. Montenegro[1] · S. Agatzini-Leonardou[1] · P. Oustadakis[1] · P. Tsakiridis[1]

Abstract The present paper presents a part of the research efforts of the laboratory of Metallurgy, National Technical University of Athens, Greece, aiming at developing a purely hydrometallurgical method, able to treat the zincferous dust, generated during the production of steel from scraps in Electric Arc Furnace (EAF), efficiently and economically and especially so for annual capacities lower than 50,000 tonnes of dust, for which the currently applied industrial methods are not economical. The proposed method is based on direct sulphuric acid leaching of the EAF dust and it succeeds to recover the valuable metals contained in it, such as zinc, lead and cadmium, converting the initially hazardous waste into a residue suitable to be fed to cement industry. The EAF dust sample, provided by a Greek steel plant, was initially leached with water, at certain conditions, to remove as much of the contained calcium as possible without co-dissolution of other metals. The washed dust was further subjected to three–stage leaching at atmospheric pressure, using sulphuric acid concentrations of 2N and 3N and temperatures 25 °C, at the first stage, and 95 °C, at the second and third stages. Total percent extraction values achieved were 97 % for zinc and 97 % for cadmium. Almost all lead, 99.7 %, remained undissolved as lead sulphate in the leach residues. It was shown experimentally that lead can be recovered as saleable lead sulphide while zinc can be recovered from the pregnant solution by solvent extraction with D2EHPA. Finally, based on the results, a conceptual flowsheet of the proposed integrated hydrometallurgical method for the treatment of EAF dust was established and is given.

Keywords EAFD · Water washing · Leaching · Sulphuric acid · EAF dust

Introduction

Crude steel production takes place by two major routes: the Basic Oxygen Furnace (BOF), which processes primary sources, such as iron oxide ores, and the Electric Arc Furnace (EAF), which treats secondary sources, such as iron scraps. Both technologies have certain environmental impacts.

Almost 30 % of the crude steel produced worldwide and 100 % of the crude steel produced in Greece use the EAF technology. In this case, a considerable amount of dust, around 15–20 kg per tonne of steel, containing zinc (Zn), lead (Pb) and cadmium (Cd) together with iron (Fe), is generated and is classified, according to the European Waste Catalogue and Hazardous Waste List, as a hazardous waste [1].

In Greece, the steel is produced by three companies, in five plants. These are the SIDENOR Group, with the Thessaloniki plant (600,000 t/y) and the Almyros plant (900,000 t/y) [2], the HELLENIC HALYVOURGIA, with the Aspropyrgos Plant (400,000 t/y) and the Velestino Plant (700,000 t/y) [3] and the HALYVOURGIKI Inc., with the Elefsina Plant (500,000 t/y) [4]. At full capacity, all Greek steel plants produce around 40,000 tonnes (t) of dust annually (Bourithis El., Melt shop manager, Halyvourgiki, Athens, Greece, July 2012. Personal communication).

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Table 1 Bibliographic data relating to the hydrometallurgical treatment of EAF dust

Leaching agent	Temperature (°C)	Time (h)	Pulp density (%)	Metal recovery (%)					Reference
				Zn	Cu	Fe	Pb	Cd	
H_2SO_4 0.4M	80	1	5	67		10			[15]
H_2SO_4 0.5M	80	1	8	75		10			[14]
H_2SO_4 1M	25	3	10	88		75		95	[13]
H_2SO_4 5M	25	2	10	71	67	15		89	[16]
H_2SO_4 5M	25	2	5	79	71	16		96	[16]
HCl 0.3M	260	1.7	2	99		22	100	100	[17]
HCl 5M	25	2	10	75	81	42	42	96	[16]
HCl 5M	25	2	5	95	95	32	100	100	[16]
1 Step H_2SO_4 1.5M–2 Step 5M NaCl (plus 10 % HCl)	95	2–0.17	1 step 20 2 step 5	72		6.3	99		[20]
1 Step H_2SO_4 2M–2 Step 5M NaCl	80	1	20	69		10	89		[21]
HNO_3 5M	25	2	10	71	69	15	100	94	[16]
HNO_3 5M	25	2	5	71	76	11	100	96	[16]
HNO_3 0.26M	30	1	1	58		6			[10]
NaOH 2.5M	60	4	0.2	77					[9]
NaOH 5M	25	42	16.6	35			64		[18]
NaOH 5M	25	4	5	59	1	0.05	46	16	[16]
NaOH 6M	90	4	10	74		0.3			[11]
NaOH 6.5M	80	2	10	80					[19]
NaOH 10M	25	3	14	32	12	0.01	27		[12]
NaOH 10M	95	3	14	85	18	0.012	90	16	[12]
$(NH_4)_2CO_3$ 1M	20	2	4.8	49	72		16	86	[22]
$(NH_4)_2CO_3$ 2M	25	4	20	49	44	0.5	29	49	[18]

Unfortunately, in Greece there are no disposal facilities for industrial hazardous wastes yet, and the EAF dust, suitably covered, is stored temporarily in the open air. Currently, the only available option is the dust transportation abroad and its pyrometallurgical treatment either by the WAELZ Process [5] or by other very similar processes, such as the AUSMELT, the PRIMUS, the ZINCOX, the OXYCUP, the CONTOP and the Electric Smelting Reduction Furnace (ESRF) [6], for the recovery of zinc, lead and cadmium. However, the cost for its transportation and pyrometallurgical treatment, around 120–140€ per tonne of dust, would be prohibitive for the Greek steel plants. Its pyrometallurgical treatment in place by any pyrometallurgical process, including the mixed pyro–hydro Tecnicas Reunidas Modified ZINCEX Process [7, 8], is also considered uneconomical as the annual production of EAF dust in Greece, mentioned above, is much lower than the limit of 100,000–120,000 tonnes of dust per year for the economic viability of those methods (Dr. Gustavo Diaz Nogueira, Division Director, Proprietary Technology Development, Tecnicas Reunidas, Personal communication, 20th February 2014). Consequently, the Greek steel companies urgently need a solution to their dust management problem.

It is generally well established that hydrometallurgical processes provide much lower capital and operating costs compared with pyrometallurgical ones. So far, however, there hasn't been any industrial, purely hydrometallurgical method to leach the EAF dust directly, despite the vast amount of laboratory-scale work [6] that has been carried out on leaching of dust with several leaching agents. The data from the literature survey, as indicatively is shown in Table 1 [9–22], show a great variability of conditions and, therefore, the results cannot be directly compared. Additionally, conditions which ensure high metals recoveries are out of plant practice.

For these reasons, the Laboratory of Metallurgy of N.T.U.A. has started to investigate the possibility of developing an integrated hydrometallurgical method able to treat the EAF dust efficiently and economically and especially so for dust annual capacities lower than 50,000 tonnes per year.

The present paper describes part of this research. More specifically, the paper presents primarily a leaching study,

Table 2 Chemical composition of EAF dust used

Element	Zn	Fe	Pb	Ca	Cd	Si	Cl	Mn	Mg	Na	K
wt%	22.7	14.4	4.2	13.3	0.09	1.5	4.8	1.0	0.7	1.3	1.6
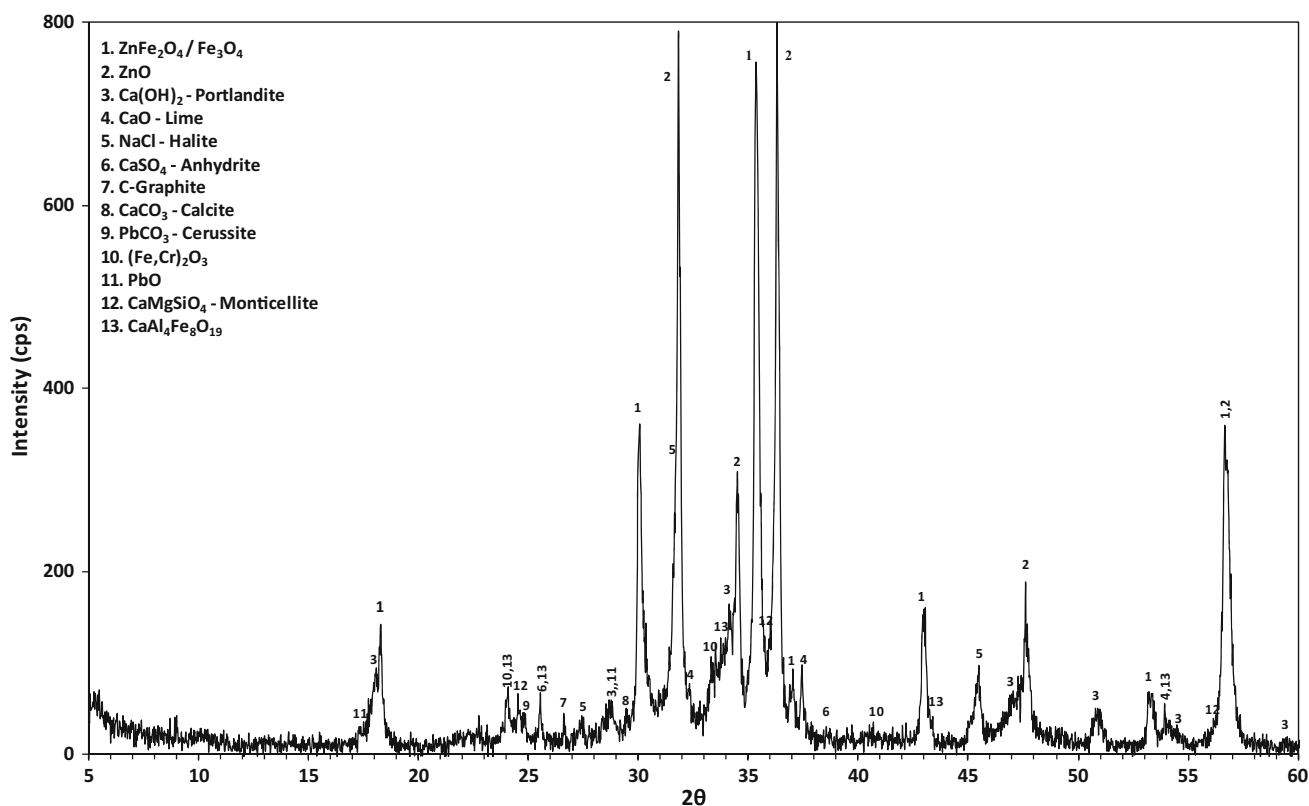
Fig. 1 XRD pattern of the EAF dust processed

using dilute sulphuric acid solution, which includes the following successive steps:

1st step: water-washing (leaching with water) of the EAF dust in order to remove the chloride ions and also as much of the calcium contained as possible in order to avoid overconsumption of sulphuric acid.

2nd step: leaching of the washed dust with sulphuric acid at 25 °C, in order to leach the easily dissolved free zinc oxide.

3rd and 4th step: hot leaching of the 2nd step residue, in two stages, in order to dissolve the difficult zinc ferrite.

Also, the recovery of lead as lead sulphide, the purification of zincferous leach solutions and the recovery of zinc and cadmium from the purified solutions were briefly studied.

Finally, a conceptual flowsheet of the proposed integrated hydrometallurgical method for the treatment of EAF dust was established and is given.

Experimental

Material

The electric arc furnace dust (EAFD) sample used was received from the dust collecting system of the HALYVOURGIKI steel plant, at Elefsina, Attica, Greece. The sample was homogenized and submitted to chemical analysis by atomic absorption spectrometry (AAS), using a Perkin Elmer 4100 instrument. The mineralogical phases of the dust and the leach residues were identified by X-ray powder diffraction (XRD), using a Bruker D8-Focus diffractometer with nickel-filtered CuKα radiation ($\lambda = 1.5405$ Å) and the generator operating at 40 kV and 40 mA. The morphology of the solid particles was examined by scanning electron microscopy (SEM), using a Jeol 6380LV Scanning Electron Microscope, at 20 kV accelerating voltage. Chemical composition of the samples particles was determined by an Oxford INCA Energy
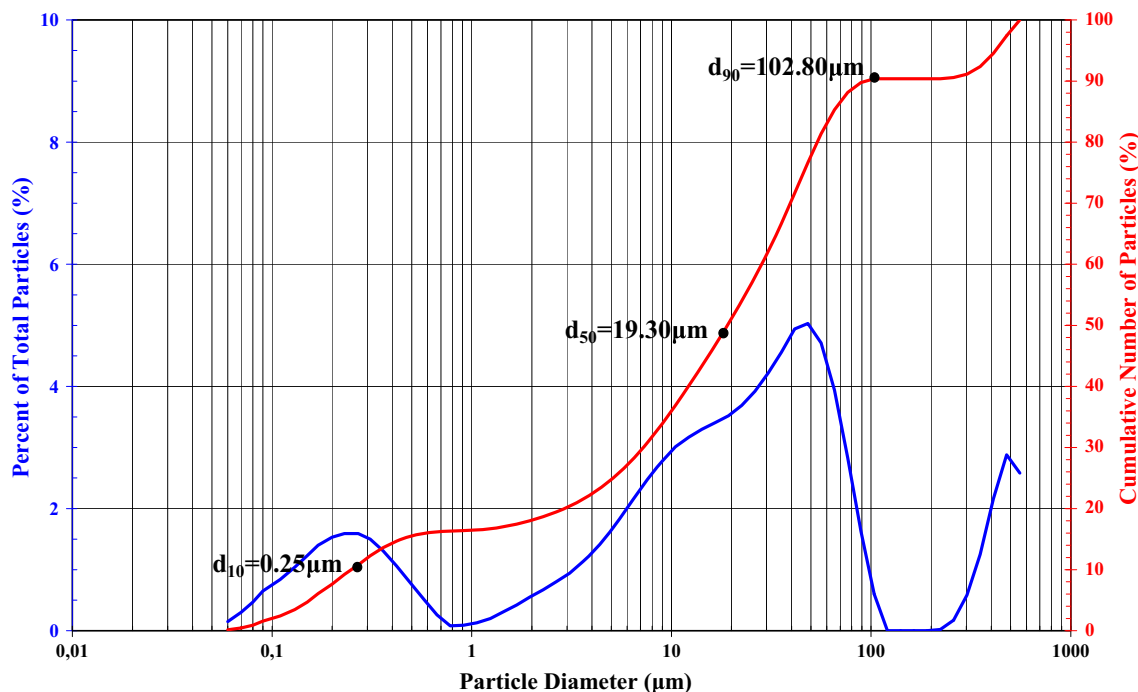
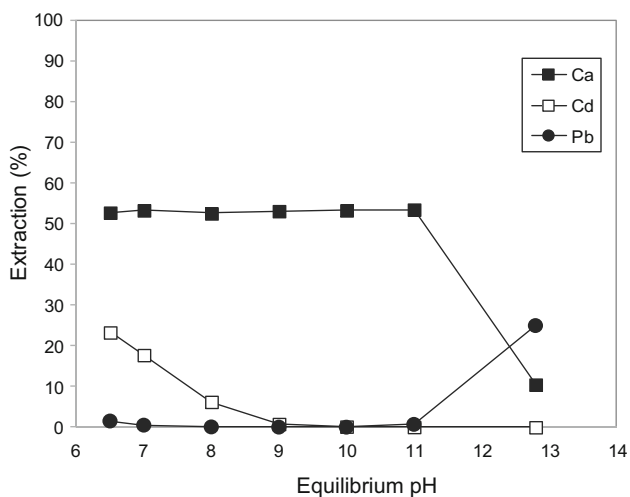**Fig. 2** Particle size distribution of the EAF dust processed

Fig. 3 Water-washing of the EAF dust. Extraction (%) of metals versus equilibrium pH (25 °C, 20 % pulp density, 60 min)
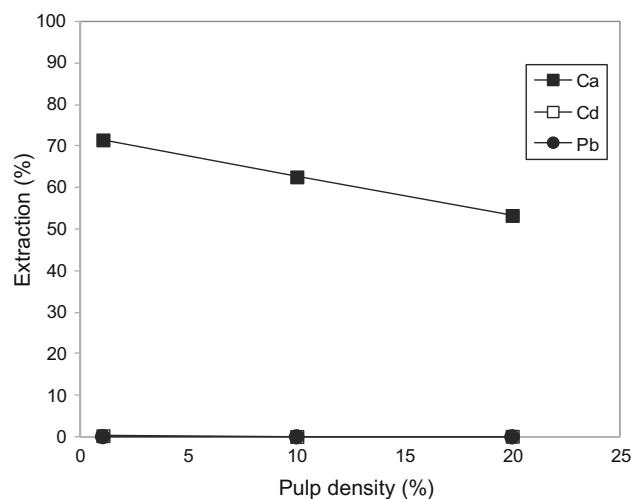

Fig. 4 Water-washing of the EAF dust. Extraction (%) of metals versus pulp density (25 °C, equilibrium pH 10, 60 min)

Dispersive Spectrometer (EDS), connected to the microscope.

Experimental Procedure

Leaching experiments were carried out in a 500 ml five necked, glass split reactor, open to the atmosphere. The central neck was occupied by a glass stirrer, passing through a stirrer guide to prevent lateral motion of the stirrer. The stirrer was connected to a variable speed motor.

Two of the remained necks contained a vapour condenser and a thermocouple, while the fourth was used for the dust addition and the fifth remained closed throughout the experiment and was opened only for pulp sampling. The flask was heated using a heating mantle with a transformer to regulate the heat input and the temperature of the slurry was controlled to the specific temperature value ±1 °C by a temperature controller.

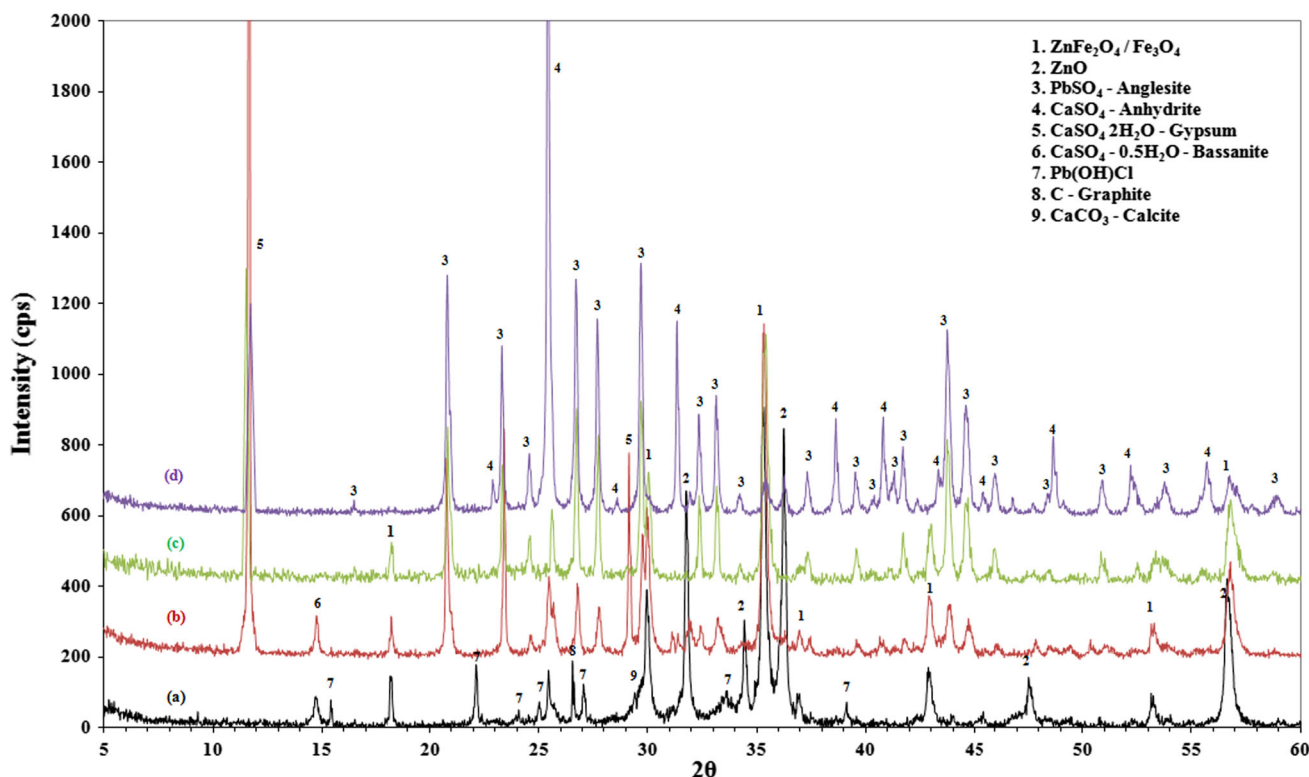At the beginning of each leaching run, 400 ml of solution were placed into the reaction vessel. When the desired

Fig. 5 Mineralogical phases of leach residues produced at successive leach steps: *a* water-washed EAF dust (1st step), *b* 25 °C leach residue (2nd step), *c* 95 °C leach residue (3rd step), *d* 95 °C leach residue (4th step)

temperature was reached, the appropriate amount of dust was added to make a pulp with the predetermined pulp density value. At the end of the run, the slurry was vacuum filtered into a Buchner flask, through a Whatman Filter Paper Cat No 1442-090. The filtrate was transferred and made up to 500 ml in a volumetric flask for Zn, Fe, Cd, Pb, Ca and Si analyses by atomic absorption spectrophotometry (AAS). The results of the analyses were always referred to the initial volume of 400 ml. The resulting leach residue was washed with distilled water by repulping, dried at 95 °C for about 12 h and weighed.

The pregnant solution and the leach residue of each test were analyzed chemically by atomic absorption spectrophotometer (AAS). The mineralogical analysis was carried out by XRD. When necessary, the morphology of the dust and the leach residues were also examined by scanning electron microscopy (SEM).

Results and Discussion

EAF Dust Characterization

The chemical composition of the dust used is shown in Table 2. Figure 1 gives the mineralogical analysis of the

dust. Iron was detected mainly in two forms, as magnetite (Fe_3O_4) and as zinc ferrite or franklinite ($ZnO \cdot Fe_2O_3$). Zinc occurs as free zinc oxide or zincite (ZnO) and also as zinc ferrite ($ZnO \cdot Fe_2O_3$). Minor constituents of the dust involve PbO, CaO, $Ca(OH)_2$, NaCl and quartz (SiO_2). Particle size analysis of the EAF dust, as given in Fig. 2, shows that 50 % of the particles were below 19.3 μm while almost 90 % were below 100 μm.

1st Step: Water-Washing of the EAF Dust Prior to Acid Leaching

In order to avoid chloride ions in the leach liquor and, also, overconsumption of sulphuric acid due to the high calcium content of the dust sample, it was decided to wash the dust with water, prior to sulphuric acid leaching. It was thus necessary to determine the conditions at which washing was more effective, especially for calcium removal, without losses of other metals, such as zinc, lead and cadmium.

Equilibrium pH, in the range from 6.5 to 12.8, and pulp density, in the range from 1 to 20 %, were studied as factors, whereas parameters, fixed at certain values, were: temperature at 25 °C, residence time at 60 min and stirring speed at 500 rpm. Responses under investigation were calcium, zinc, lead and cadmium percent extraction.
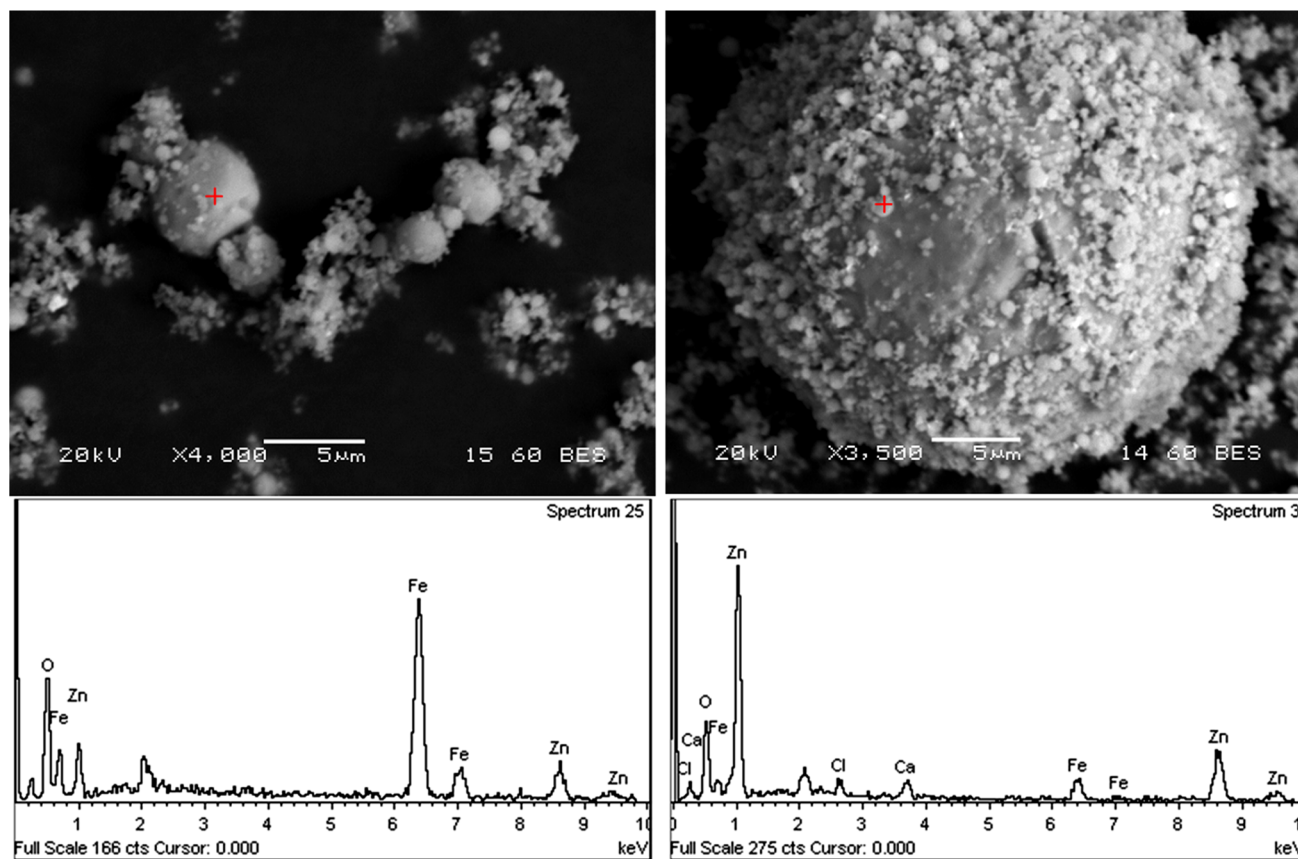
Fig. 6 SEM images of washed EAF dust. A *sphere* of zinc ferrite (*left*) and fine particles of zinc oxide on the surface of a much bigger spherical particle of zinc ferrite (*right*)

When the dust was added into the water, the pH raised immediately to 12.8. To keep the equilibrium pH constant at the predetermined value throughout the test, concentrated nitric acid was used, rather than sulphuric acid, in order to avoid the formation of gypsum and the contamination of the dust with this precipitate.

Figure 3 shows the effect of equilibrium pH on the above responses. Calcium could be leached out in the pH range 6.5–11.0 by around 53 %, according to the reaction:

$$CaO_{(s)} + H_2O \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$
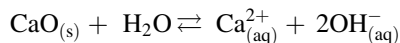
At pH higher than 11.0, calcium precipitated as calcium hydroxide whereas lead started dissolving as it formed soluble species with hydroxide ions [23]. Neither zinc nor iron was extracted under the experimental conditions used. From the above, it is obvious that water washing of the dust should take place with equilibrium pH in the range 9.0–11.0 and, preferably, at around 10.0.

The variation of calcium and other metals extraction with pulp density during water-washing of the dust is presented in Fig. 4. As was expected, the maximum calcium removal, around 70 %, was achieved with 1 %. Though this is not a practical value for the leach pulp density, it reveals the maximum percent removal of calcium by leaching the dust with water and, consequently, the percent of the calcium content that occurs in the dust as free calcium oxide. The rest 30 % of calcium occurs as insoluble in water compounds, such as portlandite [Ca(OH)$_2$], gypsum (CaSO$_4$) and calcite (CaCO$_3$).

Conclusively, single stage water leaching of the dust at ambient temperature, equilibrium pH around 10.0 and 20 % pulp density washed out the chloride salts and eliminated most of the free calcium oxide of the dust. However, a high calcium content and its mineralogical forms in any EAF dust is an issue of concern, in the case of acid leaching.

The chemical analysis of the washed dust, after drying at 95 °C for approximately 12 h, was Zn = 29.1 %, Pb = 5.4 %, Fe = 18.6 %, Cd = 0.1 % and Ca = 5.7 %. The analysis of the water after leaching was Ca^{2+} = 8.1 g/l, Zn^{2+} = 1.2 mg/l, Fe^{3+} = 0.2 mg/l, Cd^{2+} = 0.2 mg/l and Pb^{2+} = 1.2 mg/l. If needed, calcium can be removed from the water as calcium hydroxide by precipitation at pH around 13.0.

As seen in Fig. 5a, the remaining calcium in the washed dust was identified as calcium hydroxide and calcium
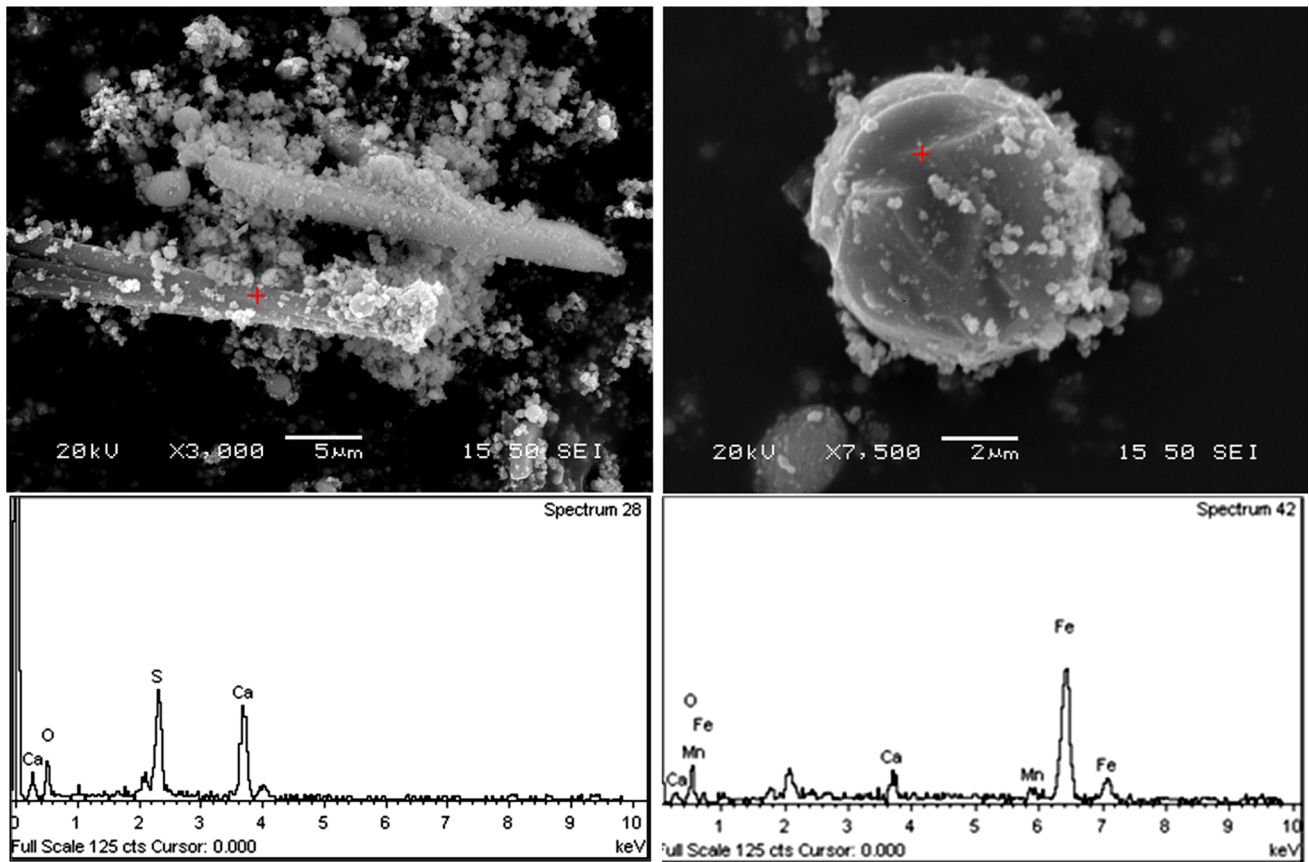
Fig. 7 SEM images of washed EAF dust. Plates of calcium sulphate (*left*) and a spherical particle of magnetite (*right*)

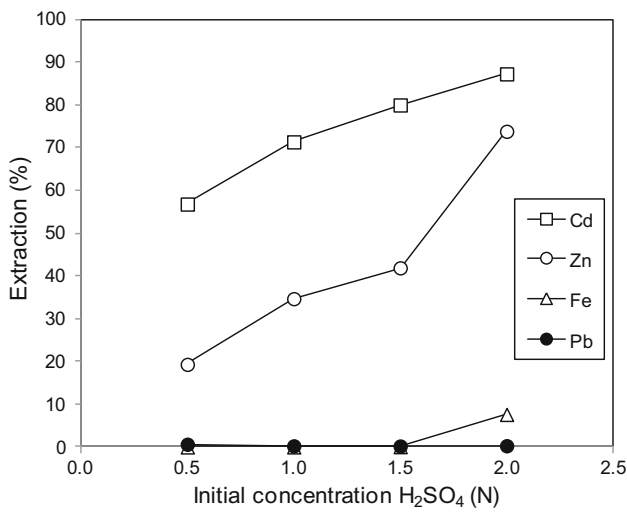**Fig. 8** 2nd step leaching. Extraction (%) of metals versus initial sulphuric acid concentration (25 °C, 20 % pulp density, 20 min)
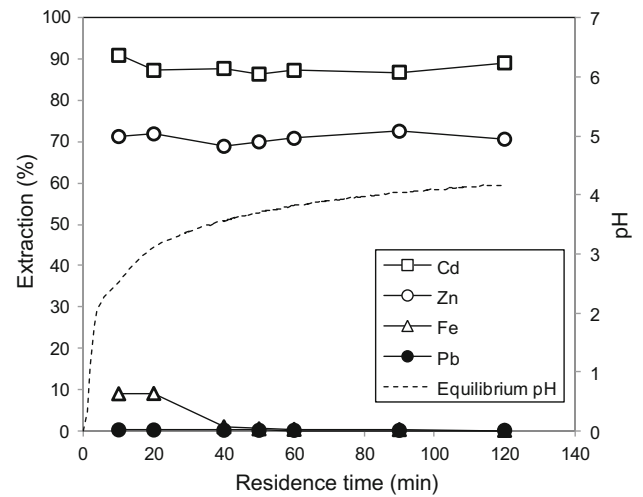
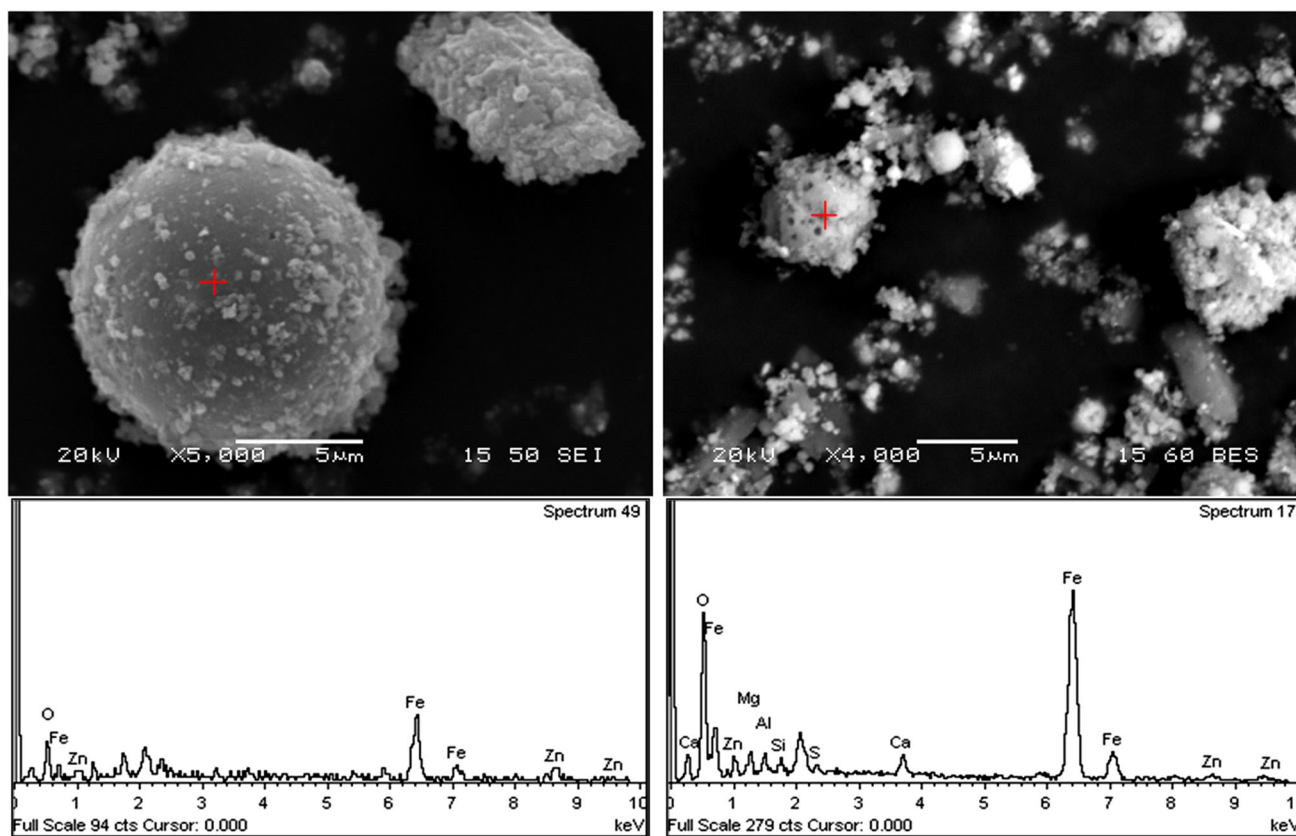**Fig. 9** 2nd step leaching. Extraction (%) of metals versus residence time (25 °C, 2N H_2SO_4, 20 % pulp density)

Fig. 10 SEM images of the 2nd step residue (25 °C, 2N H_2SO_4, 20 % pulp density, 10 min). Spherical grain of zinc ferrite (*left*), magnetite crystal (*right*)

sulphate, anhydrite and hydrated, whereas lead as a phase containing hydroxyl ions, because of the high pH (10.0) of washing, and chloride ions, that originated from the dissolution of sodium chloride. Figures 6 and 7 give SEM images of the main phases present in the dust after leaching with water.

2nd Step: Leaching of the Washed EAF Dust with Sulphuric Acid at 25 °C

The aim of this step was to determine the conditions, other than the temperature, at which as much zinc as possible could be recovered with the least possible amount of iron dissolved. Obviously, that would correspond to the free zinc oxide dissolution.

For this reason, it was decided to study first the effect of the initial sulphuric acid concentration on the percentage extraction of zinc, cadmium, iron and lead. The acid concentration varied in the range from 0.5N to 2N. Variables

used as parameters, fixed at certain values, were: temperature at 25 °C, pulp density at 20 %, a value close to the industrially applied, residence time at 20 min and stirring speed at 500 rpm.

As shown in Fig. 8, no lead was leached at those conditions, as expected. Iron was co-dissolved when the initial acid concentration was higher than 1.5N. Zinc and cadmium percent extraction increased with acid concentration, reaching 74 and 87 %, correspondingly, with 2N initial sulphuric acid concentration after 20 min of leaching. The corresponding iron co-dissolution was around 8 %.

To examine whether zinc, cadmium and iron extraction would increase further with the residence time, for kinetic reasons, at 2N sulphuric acid, the residence time was studied as a variable in the range from 10 to 120 min. As depicted in Fig. 9, both zinc and cadmium extraction reached equilibrium within 10 min. The fast kinetics was attributed to the fact that both zinc and cadmium, which entered the solution, came from their corresponding simple
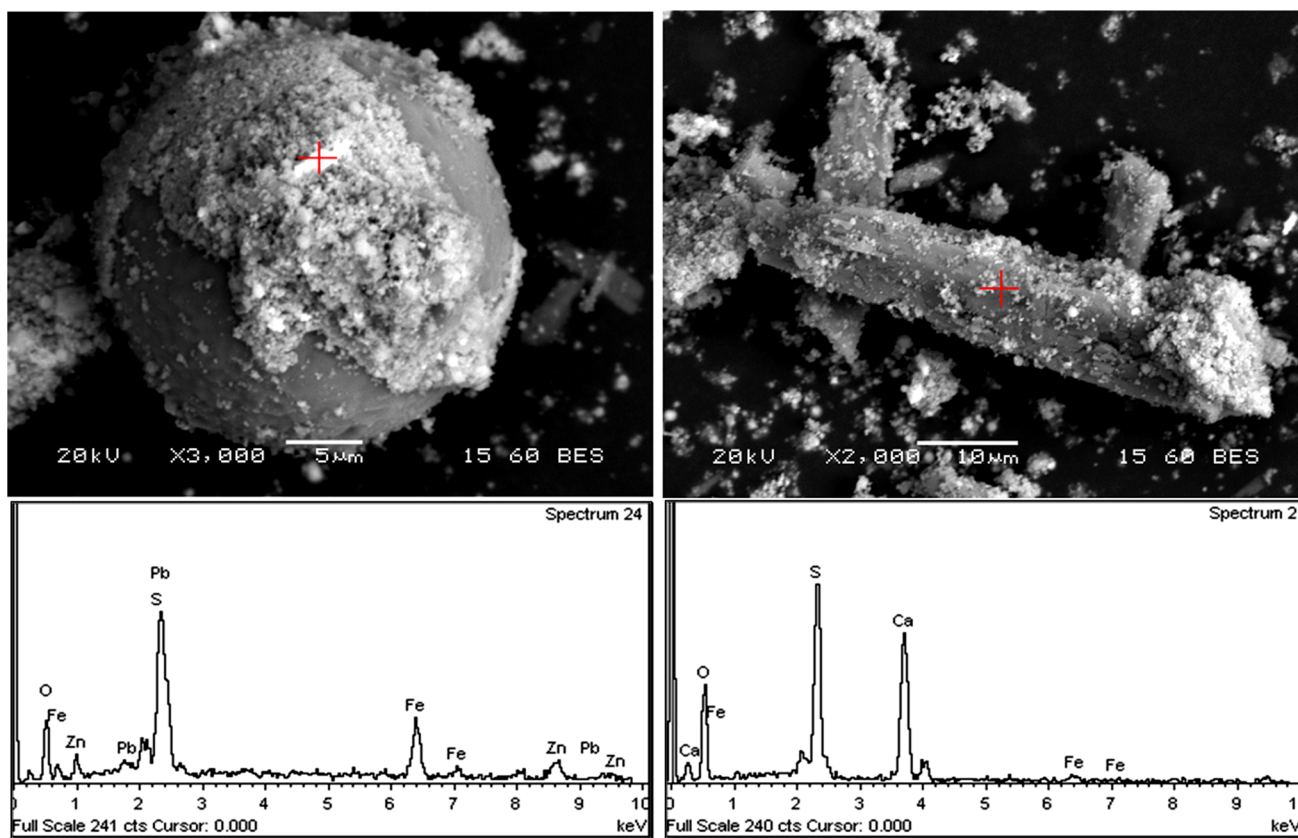
Fig. 11 SEM images of the 2nd step residue (25 °C, 2N H₂SO₄, 20 % pulp density, 10 min). A white crystal of lead sulphate (*left*), a plate of calcium sulphate (*right*)
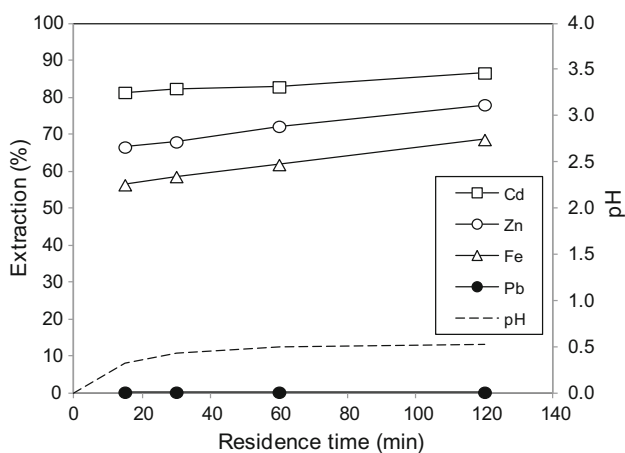

Fig. 12 3rd step leaching. Extraction (%) of metals versus residence time (95 °C, 3N H₂SO₄, 20 % pulp density)

(not complex) oxides. Iron co-dissolution was also fast, reaching 10 % within 10 min. It is noteworthy, however, that, after 20 min, iron started to precipitate with its concentration reducing to about 0.4 g/l in 40 min and to 0.06 g/l in 120 min. The iron precipitation, as hydroxide, was obviously due to the increase of pH, as seen in Fig. 9, because of the reaction of the free sulphuric acid with the neutralizing constituents of the dust, such as Ca(OH)$_2$, CaCO$_3$, etc.

The results suggest that, in order to achieve the maximum extraction of zinc and cadmium with no iron in the pregnant solution at 25 °C, using 20 % pulp density, leaching should be conducted with 2N initial sulphuric acid concentration for 10 min, followed by pH adjustment to 4.0. The chemical analysis of the produced leach residue, under the above conditions, was Zn = 12.9 %, Pb = 6.1 %,
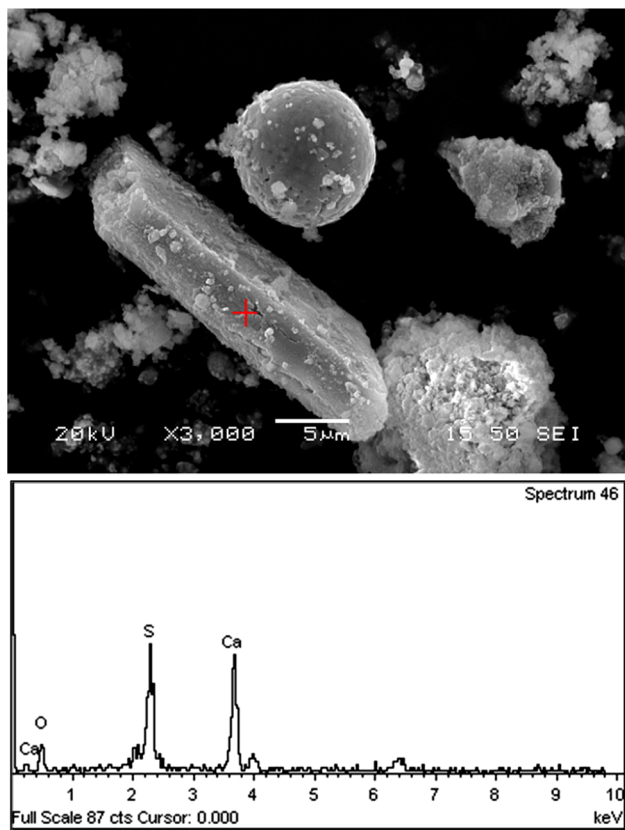
Fig. 13 SEM image of the 3rd step residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A plate of calcium sulphate

Fig. 14 SEM image of the 3rd step residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A white crystal of lead sulphate

Fe = 23.1 %, Cd = 0.02 % and Ca = 8.9 %. The dry weight of the 2nd step leach residue was found to be approximately 67 % of the initial dry mass of the washed dust.

The mineralogical analysis of the leach residue (Fig. 5b) showed that the free zinc oxide had almost quantitatively been dissolved. The only zinc containing phase was zinc ferrite. Other principal phases of the residue included calcium sulphate and lead sulphate, products of the reactions of calcium and lead compounds with sulphuric acid. Figure 10 gives SEM images of a spherical particle of zinc ferrite ($ZnO \cdot Fe_2O_3$), on the left, and a spherical particle of magnetite ($FeO \cdot Fe_2O_3$), on the right. Figure 11 shows a fine white crystal of lead sulphate ($PbSO_4$), deposited on the surface of a big zinc ferrite grain, on the left and an oblong calcium sulphate ($CaSO_4$) crystal, on the right.
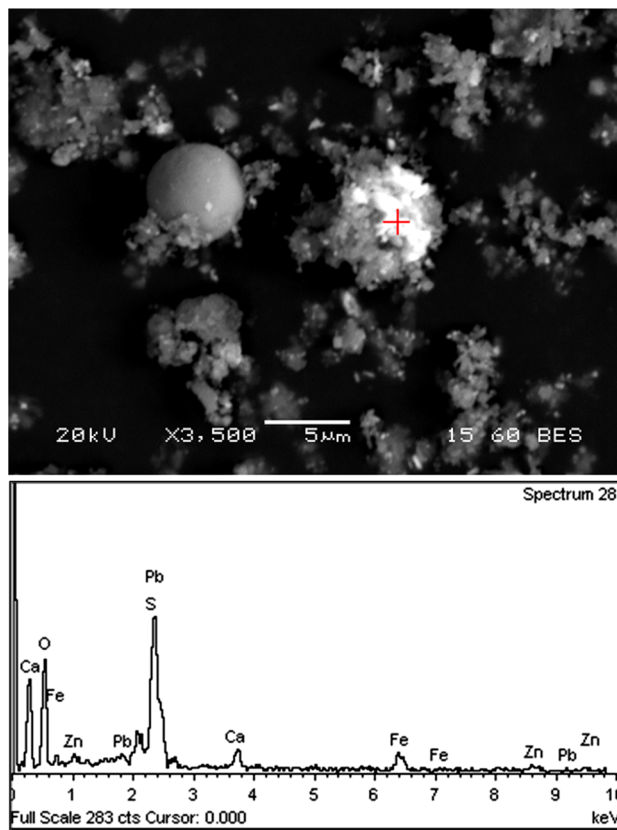
3rd Step: Hot Leaching of the 2nd Step Leach Residue

The aim of this step was to dissolve the zinc ferrite of the leach residue produced at the end of the 2nd step leaching, at 25 °C. From the literature [24, 25], it is well known that hot acid conditions are required for zinc ferrite dissolution. Also, previous research work of the authors [26] has shown that an initial sulphuric acid concentration of 2N was inadequate to dissolve the zinc ferrite, even at 95 °C. Based on the above data, temperature was chosen as a parameter, fixed at 95 °C, the highest possible level for atmospheric pressure leaching, and 3N was chosen as the lowest possible level for the initial sulphuric acid concentration. Pulp density was also fixed at 20 %, as in previous runs. Residence time was studied as the only
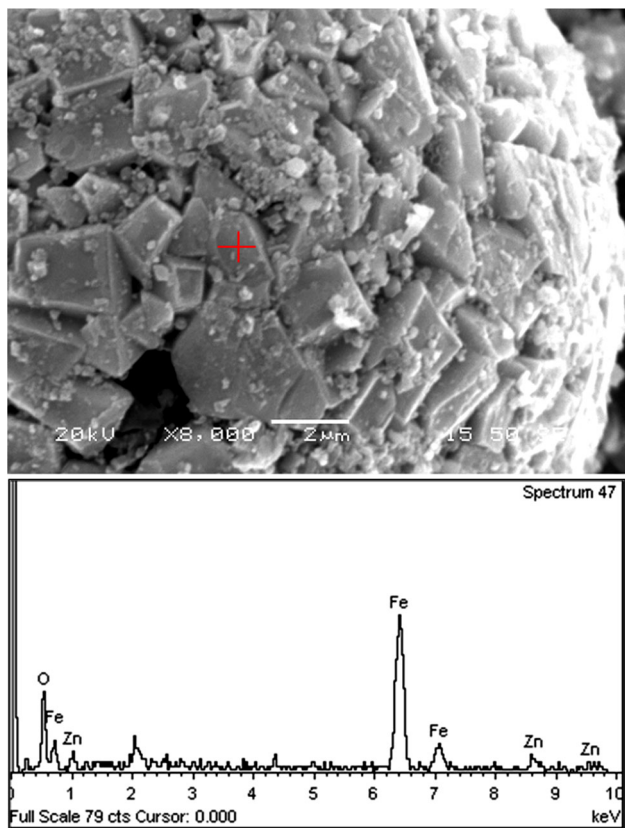
Fig. 15 SEM image of the 3rd step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A corroded spherical grain of zinc ferrite
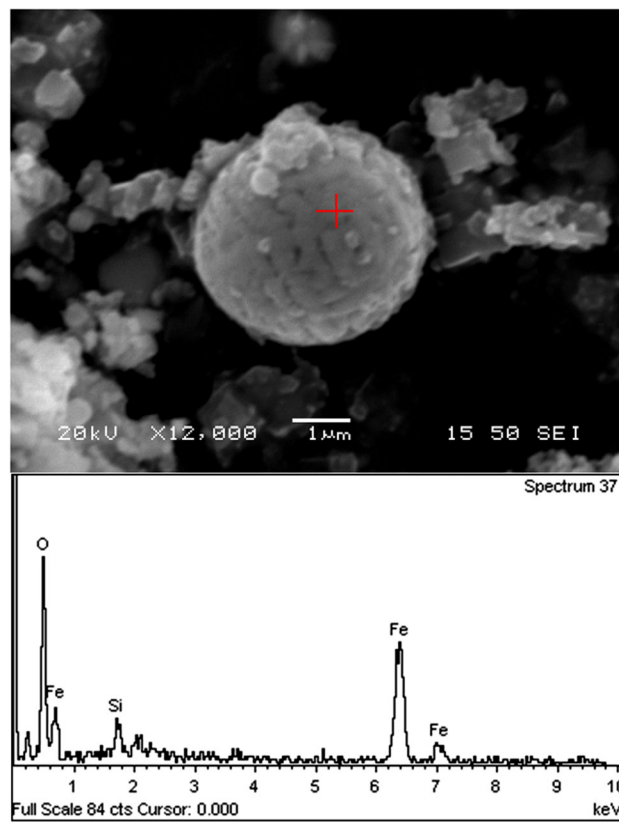

Fig. 16 SEM image of the 3rd step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A corroded by the acid spherical grain of magnetite

independent variable (factor). Responses under investigation were %Zn extraction, %Cd extraction, %Fe co-dissolution and %Pb extraction. As can be seen in Fig. 12, the extraction of zinc, cadmium and the iron co-dissolution increased with time. Zinc was recovered by 78 % after 120 min of leaching. At the same residence time, cadmium extraction reached around 87 % and the iron co-dissolution 68 %. The similar slopes of the curves for zinc and iron dissolution with time denote congruency of dissolution for these two metals, which, in turn, indicates that zinc and iron dissolve from the same mineralogical phase, that of zinc ferrite.

The dry weight of the produced leach residue was found to be approximately 60 % of the initial dry mass of the 2nd step leach residue. The chemical analysis of the residue was Zn = 4.5 %, Pb = 10.7 %, Fe = 15.2 %, Cd = 0.007 % and Ca = 16.1 %.
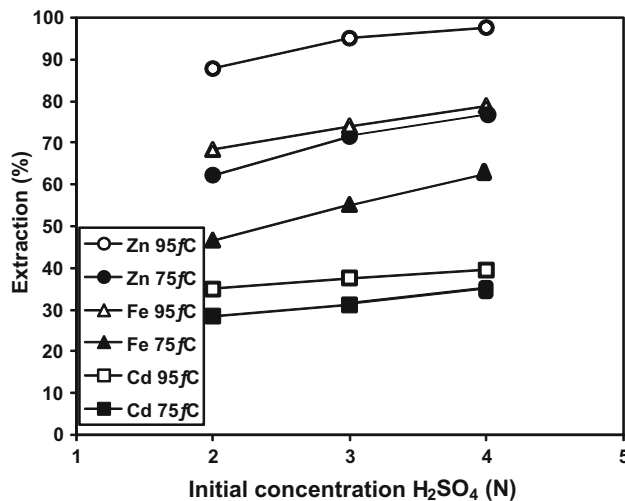

Fig. 17 4th step leaching. Extraction (%) of metals versus the initial H_2SO_4 concentration (75 and 95 °C, 20 % pulp density, 120 min)
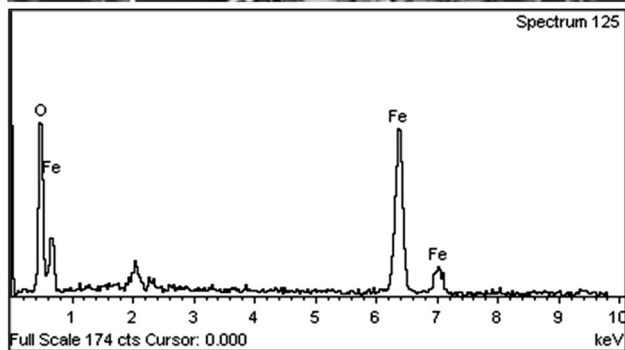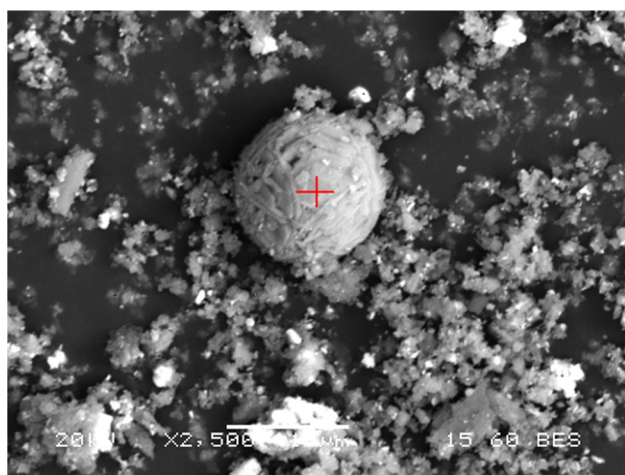
Fig. 18 SEM image of the 4th step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A corroded by the acid spherical grain of magnetite

Fig. 19 SEM image of the 4th step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). An aggregate of lead sulphate crystallites

As observed in its X-ray diffraction spectrum in Fig. 5c, zinc ferrite and magnetite do not constitute major phases any more, in contrast to calcium sulphate and lead sulphate, which become the principal constituents of the residue. Microscopic examination showed that gypsum, in the form of elongated plates (Fig. 13) is the most abundant crystalline phase in the residue. Figure 14 shows white particles of lead sulphate whereas Figs. 15 and 16 depict corroded by the leaching agent spherical grains of zinc ferrite and magnetite, correspondingly.

It is apparent from Fig. 12 that under the conditions used, zinc ferrite dissolution could not be completed in one stage. For this reason, it was decided to submit the residue to further hot leaching, as described below.

4th Step: Hot Leaching of the 3rd Leach Residue

The aim of this step was to determine the leaching conditions at which zinc recovery would be maximized.
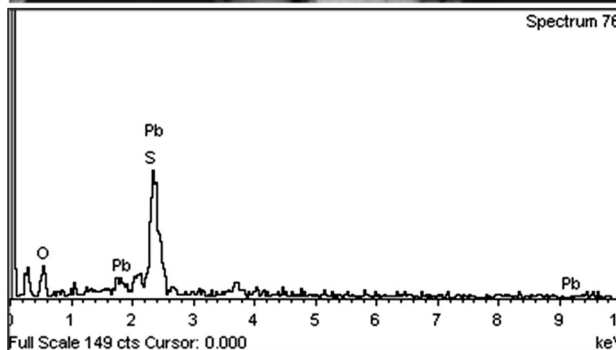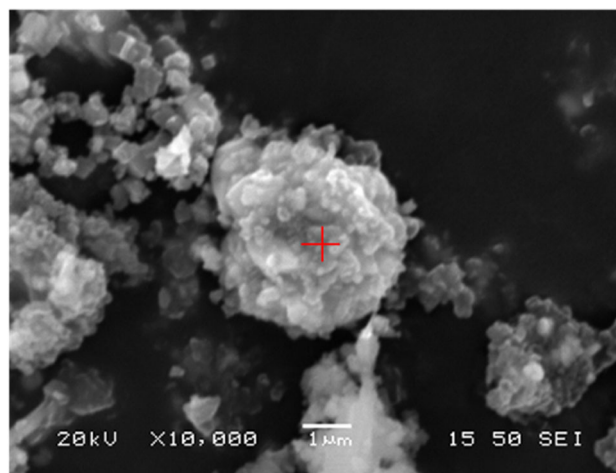
The effect of the initial sulphuric acid concentration on the metals extraction was examined for concentrations from 2N to 4N, at two levels of temperature, 75 and 95 °C, while pulp density was kept constant at 20 %, residence time at 120 min and stirring speed at 500 rpm.

Figure 17 shows the obtained results. As expected, for all metals, except Pb, which remains undissolved, their extraction increased with increasing temperature and acid concentration. It is to be noted that cadmium extraction increased only slightly with temperature and the initial acid concentration, not exceeding 40 %. This low extraction was attributed to the fact that the 3rd step leach residue had almost been depleted of cadmium and, thus, the kinetics of its further dissolution was very low. There also seems to exist no interaction between the acid concentration and the temperature, namely those factors are independent, as the increase of the percent extraction of the metals by increasing the temperature does not depend on the level of the initial sulphuric acid concentration. As
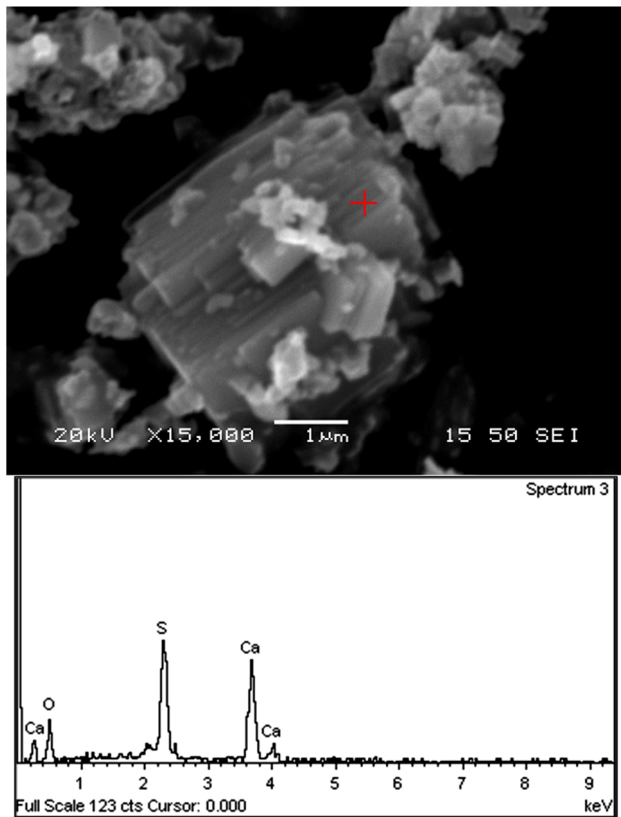
Fig. 20 SEM image of the 4th step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A calcium sulphate crystal
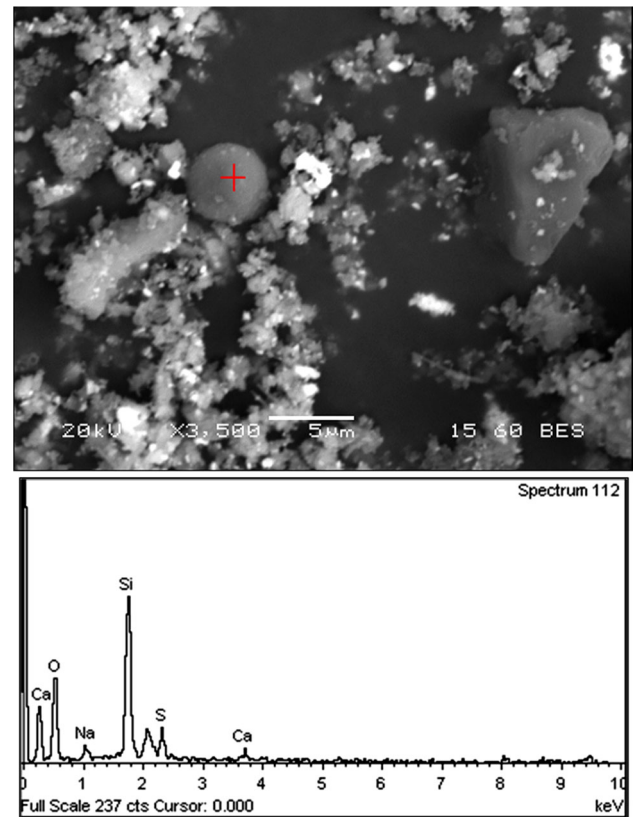

Fig. 21 SEM images of the 4th step leach residue (95 °C, 3N H_2SO_4, 20 % pulp density, 120 min). A silica grain

already pointed out in 3.4, the similar slopes of the curves for zinc and iron extraction confirm that zinc and iron dissolved from the same mineralogical phase, that of zinc ferrite.

Conclusively, leaching the 3rd step leach residue with initial sulphuric acid concentration in the range 3N–4N, at 95 °C for 120 min and with a pulp density 20 %, the percent zinc extraction lay in the range 97–99 %, with iron co-dissolution around 80 %. Apparently, the rest 20 % of the iron, remaining in the leach residue, is in the form of magnetite (Fe_3O_4).

The dry weight of the 4th step leach residue was around 30 % of the initial dry mass of the 3rd step leach residue.

Its chemical analysis was Zn = 0.8 %, Fe = 4.8 %, Cd = 0.004 %, Pb = 15.4 % and Ca = 15.8 %.

As can be seen in Fig. 5d, the 4th step residue consisted mainly of $PbSO_4$ and $CaSO_4$. The ambiguity whether the low peaks, designated by one, would be attributed to zinc ferrite or to magnetite, was resolved by SEM. No zinc ferrite was observed under the microscope, whereas some magnetite particles showed up (Fig. 18). Figure 19 shows an aggregate of lead sulphate crystallites. Figure 20 shows a calcium sulphate crystal and Fig. 21 a silica grain, a minor unleachable phase of the EAF dust.

Under the optimum experimental conditions that were determined and applied for each of the four steps described
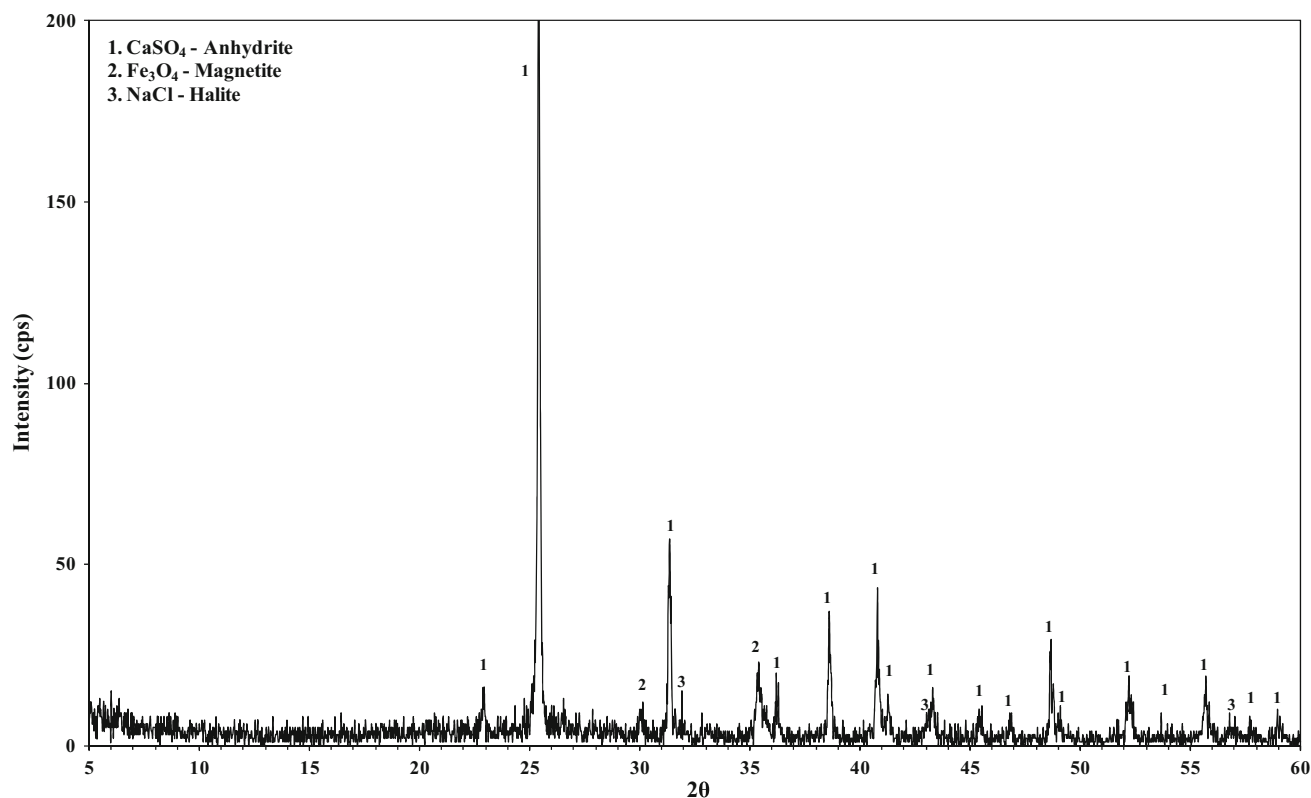
Fig. 22 XRD pattern of the residue remaining after leaching with NaCl the lead sulphate leach residue

in the foregoing, zinc and cadmium recoveries were finally around 97 % for both metals.

Recovery of Lead as Lead Sulphide

As stated in 3.5, the final residue of the sulphuric acid leaching of the EAF dust, under the experimental conditions applied, contains mainly around 15 % lead, as lead sulphate, and 16 % calcium, as calcium sulphate. Though this material is a source of lead, it is not attractive for lead smelters because of its relatively low content. It is not attractive for cement kilns either because lead sulphate increases the hardening time of cement. For those reasons, it was decided to just test the possibility of producing lead

sulphide, a saleable product, form the above residue, even though a detailed study was outside the scope of this work. Based on literature [21, 22, 27], the final residue was submitted to leaching by a solution containing 400 g/l NaCl, at 95 °C, with 10 % pulp density and for 180 min. At those conditions, lead was recovered in the solution, as lead chloride, by 90 % within 60 min. Co-extraction of iron and calcium was limited to 2 and 6 %, correspondingly. The chemical analysis of the leadferous solution produced was $Pb^{2+} = 9.0$ g/l, $Fe^{3+} = 0.06$ g/l and $Ca^{2+} = 0.63$ g/l. The chemical analysis of the produced residue was $Zn = 1.3$ %, $Fe = 6.6$ %, $Pb = 0.53$ % and $Ca = 19.5$ %. Its XRD pattern, in Fig. 22, shows that the only detectable phases were calcium sulphate, unleached
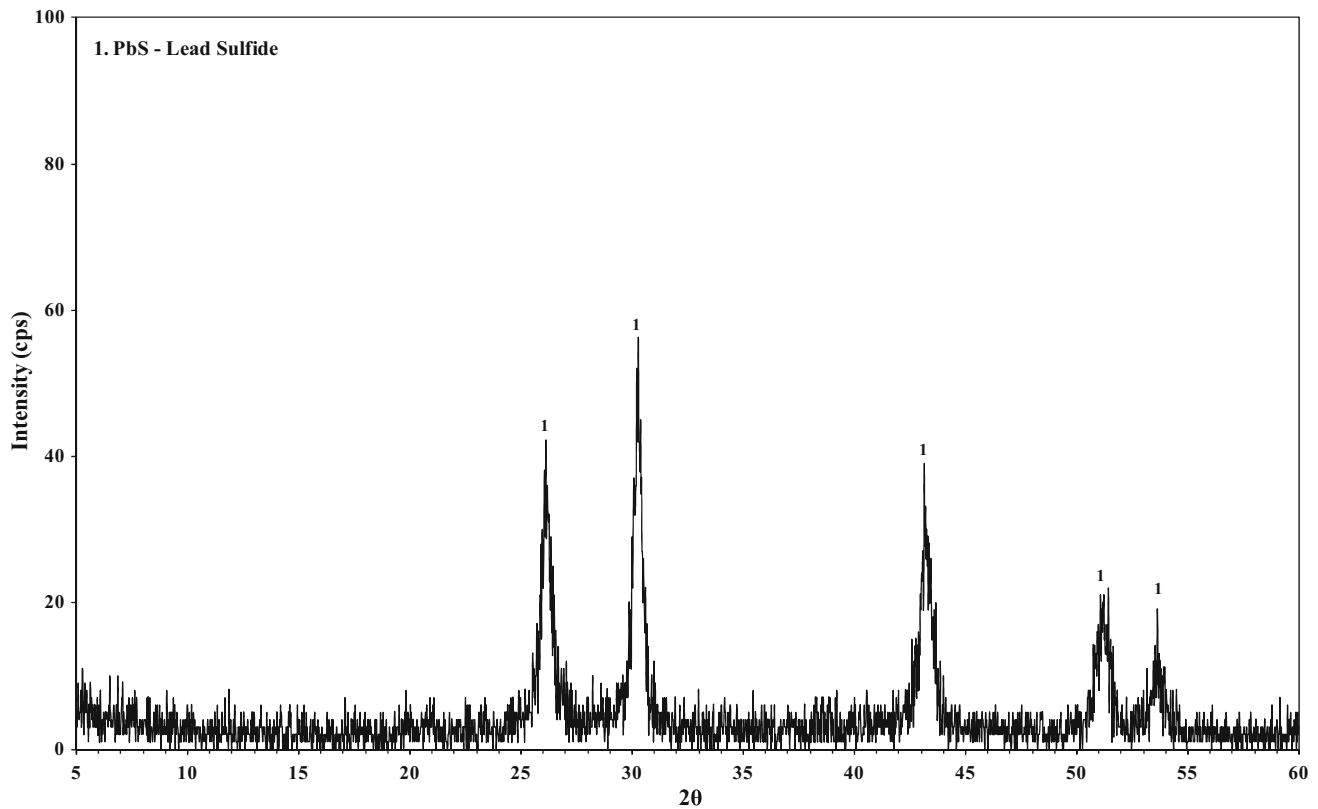
Fig. 23 XRD pattern of the lead sulphide, precipitated at 25 °C

magnetite form the initial EAF dust and sodium chloride due to inadequate rinsing with water.

The lead in the afore-mentioned solution was subsequently precipitated, as lead sulphide (Fig. 23), a dark grey precipitate, at room temperature, in 1 h, by adding a quantity of sodium sulphide a little higher than the stoichiometrically required.

Optimization experiments regarding both lead sulphate leaching with NaCl and lead precipitation as lead sulphide are certainly required before finalizing these processes.

## Purification of Zincferous Leach Solutions and Recovery of Zinc and Cadmium

In the framework of the present study, some tests were also conducted regarding the removal of iron from the zincferous leach solutions, as a chemical precipitate, and also the recovery of zinc and cadmium from the purified solutions, using established techniques [6]. The results cannot be included here, due to space limitations.

Conceptual Flowsheet

Based on the data presented above, the following flowsheet layout, shown in Fig. 24, is proposed for an integrated hydrometallurgical method treating directly, at atmospheric pressure an EAF dust with chemical and mineralogical characteristics similar to those of the dust used in the present work. It should be stressed, however, that a small pilot plant, operating in a continuous feeding mode, would be necessary to confirm or modify the proposed layout and also to produce data for a reliable pre-feasibility study.

Fig. 24 Conceptual flowsheet of the proposed hydrometallurgical method for direct leaching of EAF dust with dilute sulphuric acid at atmospheric pressure
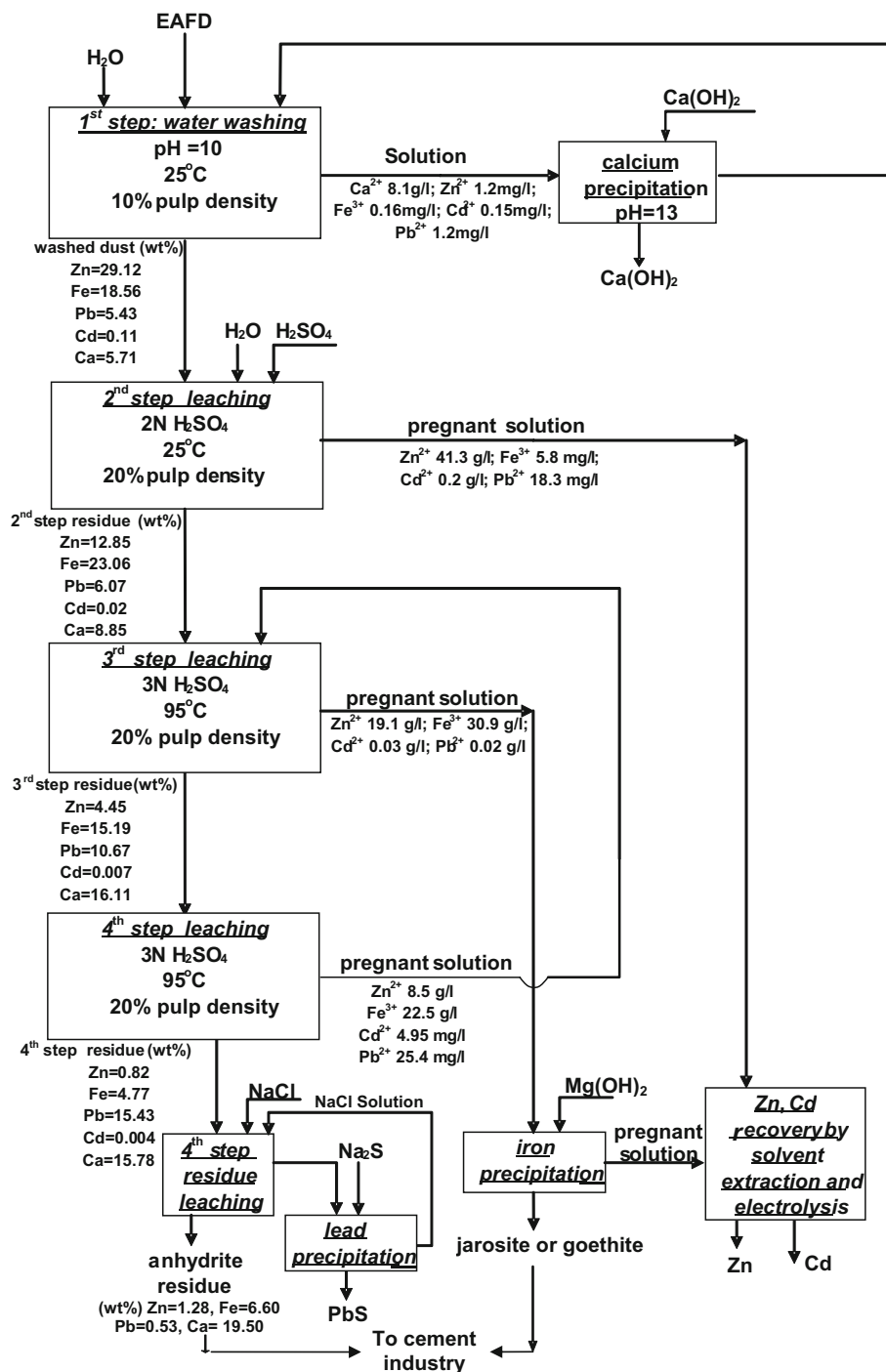
Conclusions

The present research has shown that a purely hydrometallurgical method, able to treat the Electric Arc Furnace Dust directly, at atmospheric pressure, with dilute sulphuric acid solution, is possible.

The method can efficiently extract, in the form of saleable products, all the useful metals contained in the dust, namely zinc, cadmium and lead.

The method includes the following steps:

1. Leaching of the dust with water at ambient temperature and equilibrium pH equal to 10 (1st step). At those conditions, more than 50 % of the calcium in the dust, contained as free calcium oxide, dissolved in water without co-dissolution of any other metal of the dust.
2. Leaching of the washed dust with dilute sulphuric acid ($\sim$2N) at ambient temperature and final pH adjustment

to 4.0 (2nd step). At those conditions, almost complete dissolution of the free zinc oxide was accomplished in 10 min. The recoveries for zinc and cadmium were 70 and 90 % correspondingly. This extraction was absolutely selective against lead and iron. The pregnant solution can directly be treated for zinc and cadmium recovery.

3. Leaching of the 2nd step leach residue with dilute sulphuric acid ($\sim$3N) at 95 °C, in two stages (3rd step and 4th step). At those conditions, almost all zinc ferrite was dissolved within 120 min. The total percent extraction values were 97 % for zinc and 97 % for cadmium. The 4th step leach residue consisted mainly of calcium sulphate, lead sulphate and magnetite. Its chemical analysis was Zn = 0.8 %, apparently in unleached zinc ferrite, Cd = 0.004 %, Pb = 15.4 %, as lead sulphate, Fe = 4.8 %, as magnetite and zinc ferrite, and Ca = 15.8 % as calcium anhydrite. Its dry weight was approximately 27 % of the initial dry mass of the dust which was treated.

4. Removal of iron from the pregnant solution as jarosite or as goethite and subsequent recovery of zinc and cadmium by established methods.

5. Extraction of lead from the 4th step leach residue by leaching with sodium chloride solution at 95 °C and its subsequent precipitation, as lead sulphide, by the addition of sodium sulphide, at ambient temperature. The residue from the sodium chloride leaching contained: Zn = 1.3 %, Fe = 6.6 %, Pb = 0.5 % and Ca = 19.5 %. Its dry weight was about 20 % of the dry weight of the initial dust treated. It is worthy of note that this residue is acceptable as a raw material in the Greek cement industry.

A reliable evaluation of the economics of the proposed hydrometallurgical method could be based only on data from continuous operation of a pilot-plant, even of a small size. Despite the lack of such data, there are some obvious advantages of the method over the industrially applied pyrometallurgical methods for the treatment of EAF dust. More specifically, the temperature used is much lower, there is no need for pelletizing or any other preparation of the dust and the solids produced are either commodities (zinc, cadmium, lead sulphide) or chargeable to cement industry (iron precipitate). It is thus very possible that the hydrometallurgical method could be appropriate for the treatment of low annual capacities of dust, for which the pyrometallurgical methods are definitely uneconomic.

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