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RECOVERY OF Zn FROM ACID MINE WATER AND ELECTRIC ARC FURNACE DUST IN AN INTEGRATED PROCESS

Abstract

In this paper, the purification of acid mine water and the treatment of electric arc furnace dust (EAFD) are integrated into one process with the aim of recovering the Zn content of both effluent and waste. Zinc recovery can reduce the cost of their environmental management: purified acid mine water is discharged after removing all metals; EAFD ceases to be hazardous waste; and Zn is valorised.

The process consists of the recovery of Zn as zinc oxide and its purification into commercial products. First, EAFD is leached with acid water and the dissolved metals are selectively precipitated as hydroxides. After EADF leaching, ferrous iron is bio-oxidized and Fe and Al are then precipitated; in the following stage, Cu, Ni, Co and Cd are cemented and finally Zn is precipitated as ZnO. In order to purify water that finally is discharged to a river, lime is used as the neutralizing agent, which results in a precipitate of mainly gypsum, MnO, and ZnO. From the impure zinc oxide produced, various alternatives for the attainment of commercial products, such as basic zinc carbonate and electrolytic zinc, are studied in this work.

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1. Introduction.

The aim of this paper is to study the integration into a single process of two operations of cleanup and reclamation: the purification of acid mine water and the valorisation of electric arc furnace dust (EAFD).

Acid mine drainage (AMD) from mining operations is one of the most difficult environmental problems faced by the sulphide mining industry. Acid mine drainage is a contaminated effluent that results from the oxidation of iron-sulphide minerals exposed to air, water and extremophile microorganisms naturally present in the area (Johnson and Halberg, 2003). The nature and the extent of this contamination is highly variable, depending on such factors as the nature of the ore body and associated geological strata, climate and mining engineering constraints. Water draining mines and mine spoils are often acidic, and frequently contain elevated concentrations of heavy metals, such as copper, zinc, aluminium and manganese. These metals were originated from dissolved sulphides and are held in solution due to their solubility in acidic liquors. However, in most cases, iron is the dominant metal present in AMD. Iron may be present in both ferrous and ferric form. Soluble ferric iron imparts the characteristic red colour to extremely acidic mine waters while orange-yellow ferric iron sediments are common in streams of higher pH. The adverse environmental impacts resulting from AMD can lead to substantial financial hardships for a mining company. Obviously, this problem worsens after a mine is closed and abandoned.

After the closure of Aznalcollar Mines (Spain), the Administration has managed and controlled the effluents generated as a consequence of former mining activity. The treatment consists of pumping wastewater to a plant for oxidation and neutralization, which results in an effluent suitable for discharge into a public waterway and in a thick pulp that contains, in the form of hydroxides, all the heavy metals initially present in the water.

Some 7200 m³/day of effluent that contains about 1 g/L of zinc and significant amounts of sulphate, ferrous, ferric, calcium, magnesium, copper, aluminium, and manganese ions are treated. Table 1 shows the characteristics of water treated in Aznalcollar Mine, Aznalcollar Mine Water (AMW). It is noteworthy that Zn²⁺ concentration exceeds 1000 g/m³. The various uses in which zinc is employed, with an overall annual production worldwide of over 7 Mt (Adriano, 2001), confers it high economic value, and hence its recovery could reduce the cost of the environmental management of this effluent. In this vein, in order to recovery Zn from this effluent, a treatment based on a solvent

extraction (SX) followed by electrowinning has been developed (Avila et al, 2011 and Valiente et al, 2008). A pre-treatment stage consisting of the bio-oxidation of ferrous iron followed by an alkaline precipitation was employed because the great amount of iron in the effluent was incompatible with both the SX and the EW processes. The whole process was successfully tested in a pilot plant and a recovery of 90% of Zn was achieved. However, a preliminary economical evaluation prompted certain misgivings about the necessary initial investment, derived from the low capacity of Zn production. For this reason, an increase in the zinc production capacity is considered through the integration of two processes: the recovery of Zn from AMD and the hydrometallurgical treatment of EAFD.

Electric arc furnace dust is a waste from the steel-making industry, from iron scrap in an electric arc furnace. The management EAFD constitutes another major problem from an environmental point of view. During the scrap-fusing process in an electric arc furnace (EAF), many components of the charge, including iron, zinc, cadmium and lead, are volatilised and enter to the vapour phase. When the vapour is cooled and collected, a large quantity of dust is generated. When galvanized scrap is used in the EAF, most of the zinc from the steel scrap ends up in the dust and fumes due to its low solubility in molten steel and slag (Oustadakis, 2010). The largest metallic portion of the EAFD is comprised of zinc and iron. The content of Zn varies between 7 and 40%, depending on the ratio of galvanized scrap utilized (Orhan, 2005; Pereira, 2007; Salihoglu and Pinarli, 2008). Due to its chemical and physical properties, the EAFD was categorized as hazardous waste according to the European Waste Catalogue of 2002 (EWC 2002). In Andalusia (Spain), this hazardous waste is stabilized prior to permanent disposal. Table 2 shows the composition of the EAFD produced by Siderurgica Sevillana Company (Andalusia, Spain). It can be observed that the zinc content exceeds 24%. Given the high price of zinc (London Metal Exchange), it is paradoxical that primary ores (sulphides) whose zinc contents are lower than 3% are being processed, when wastes exceeding 25% of Zn are being landfilled.

Two major technological processes are used for the extraction of zinc from EAFD; pyrometallurgical and hydrometallurgical methods. Pyrometallurgical methods require certain reducing agents and relatively high temperatures to produce raw zinc oxide of low commercial value (Matsuno et al, 1995 and Harp et al, 1990). The hydrometallurgical processing of EAFD is aimed at the recovery of Zn and at leaving a residue that can be recycled into the EAFD unit. Many leaching media have been tested,

including sulphuric acid (Havlík et al, 2006 and Oustadakis et al, 2010), sodium hydroxide (Youcai and Stanforth, 2000), and ammonium chloride (Ruiz et al, 2007). In previous work, the authors studied the leaching of the EAFD generated by Siderurgica Sevillana Company both in an acid medium and in an alkaline medium (Palencia et al, 1999). Both methods were found viable from a technical point of view.

In this paper, EAFD has been leached with acid mine water from Aznalcollar Mine, and thereby incorporated into the water treatment process with the following advantages:

1. The capacity of Zn production increases, which may include some 4500 t / a.
2. A synergistic effect on the environmental management of AMD and EAFD is triggered, which enables an economic recovery in both cases and therefore a reduction in management costs.
3. The integrated treatment significantly improves the quality of environmental management in both cases.

The criteria for integrating both treatments are the following:

1. The final water quality and the minimization of purification costs.
2. The final solid residue composition. Possibility of non-hazardous waste and minimization of waste management costs.
3. Maximization of zinc production.

The process consists of two essential stages: the concentration of Zn as zinc oxide and its purification as commercial products. In the first stage, EAFD is leached with acid water and the dissolved metals are selectively precipitated as hydroxides. In order to enable the selective precipitation, ferrous iron in solution must be oxidized to ferric iron; to this end a bio-oxidation stage is included. After bio-oxidation, Fe and Al are precipitated; Cu, Ni, Co and Cd are then cemented, and finally Zn is precipitated as impure ZnO. Since one of the objectives of this work is the purification of water to be discharged into the river, neutralization is performed with lime, thus resulting in a precipitate containing gypsum and a decrease in sulphate concentration. From the zinc oxide obtained through this sequence of operations, various alternative methods to attain commercial products, such as basic zinc carbonate and electrolytic zinc, are also studied in this work. The overall capacity of treatment is determined by the data included in Table 3.

2. Experimental.

2.1 Washing of EAFD.

Electric arc furnace dust is washed with water in the range of pH 7-12 in order to remove undesirable soluble compounds. The discontinuous washing tests are performed in 1-litre stirred-tank reactors at room temperature for 2 hours. Given the lime content of EAFD, in each test the pH of pulp is kept constant by controlling the dosage of sulphuric acid 1:1. The pulp density is 20%.

2.2 Acid leaching of EAFD.

The leaching of EAFD with mine water (acidified with sulphuric acid) is studied in stirred-tank reactors of 1-litre and 7-litre capacities. The leaching time is 1 hour because longer times do not significantly improve the extraction.

To study the influence of the acidity, a pH electrode and a dosage pump are connected to a data acquisition system. The pH is kept constant by the automatically controlled addition of acid. Temperature, pH and pulp density are the variables studied.

2.2.1. Acid-leaching residue characterization

The leaching residue is characterized in order to ascertain its hazardousness. Leaching tests for evaluating risk in solid-waste management decision-making, UNE-EN ITR-M-015, *Daphnia magna* immobilisation test (ISO 6341-2012), and Luminescent bacteria test (ISO 11348-3-2007) were performed.

2.3. Bio-oxidation.

Ferrous iron bio-oxidation of solutions obtained by mixing leaching liquors of EAFD and AMW in the ratio 1:45 is carried out in a continuous flooded packed-bed bio-reactor (Mazuelos et al, 2000).

The bioreactor is a column filled with 7-mm siliceous stone particles. The column has a height of 1200 mm and a diameter of 43 mm and has inlets for liquid medium and for air at the bottom. It has three holes at different heights labelled 1, 2 and 3 at 350, 770 and 1200 mm from the base, respectively. These can be used to test different bed heights or to obtain samples of fluid at intermediate positions.

2.4. Precipitation of iron and aluminium.

Precipitation by alkanisation with lime in stirred-tank reactors of 7-litre capacity is studied. Lime is dosed in a controlled manner to prevent coprecipitation phenomena and the formation of colloidal precipitates.

2.5. Cementation.

Cementation of Cu^{2+} , Ni^{2+} and Cd^{2+} with zinc powder is assayed in a column packed with a bed of Zn particles (0.3 - 1.5 mm in size) and in 1-litre stirred-tank reactors (1-3% pulp density).

2.6 Selective precipitation of Zn.

Selective precipitation of ZnO is carried out by controlled alkalisation with lime in stirred-tank reactors of 7-litre capacity.

2.7. Precipitation of Zn as basic carbonate.

The attainment of basic zinc carbonate beginning with impure ZnO has been tested. The procedure takes place in two stages:

- The impure precipitate of ZnO is redissolved by controlled addition of sulphuric acid up to pH 3 in a stirred-tank reactor. Operation time is 30 minutes and temperature is 20°C.
- Liquor alkalisation is performed by addition of 1M CaCO_3 solution addition in a stirred-tank reactor. Operation time is 40 minutes and temperature is 70°C.

2.8. Electrolysis of Zn in alkaline medium.

The attainment of metallic Zn from the impure ZnO precipitate is studied. The procedure is comprised of two steps:

- Dissolution of impure ZnO precipitate in strong alkaline medium (NaOH 300 g / L).
- Electrolysis of liquor.

Electrolysis is conducted in a 250 mL electrolytic cell, equipped with a magnetic stirring and heating system, in which three electrodes of stainless steel grade 316 are inserted. Electrodes are 4 mm thick; two of these act as anodes and the other as a cathode. The sunken area has a width of 59 mm and a height of 47 mm, giving a total cathode area of 61.6 cm^2 . The electrode gap is maintained constant at 5 mm with spacers of silicone.

The anodes and cathode are connected to a regulated power supply (maximum current 10 A, variable voltage). An ammeter is connected in series to measure the electric current in the circuit. Samples of electrolyte are periodically taken in order to determine Zn content and to calculate the current efficiency, the energy consumption and the net cathodic current density. Temperature is 20°C.

2.9. Analysis.

Fe^{2+} concentration is determined by standard potassium dichromate solution in an automatic titrator with 0.05N $\text{K}_2\text{Cr}_2\text{O}_7$. Metal concentrations are determined by AAS.

3. Results and discussion

3.1 Washing of EAFD.

Chlorides present in EAFD may cause disturbances in the equilibrium of the different stages of the process and, finally, appear in the effluent. A previous wash step can avoid them entering into the circuit. Table 4 shows the results of washing tests with acidified water at different pH values. In accordance with these results, pH= 10 is chosen for the washing step because the goal is achieved without the removal of Zn.

3.2. Acid leaching of EAFD.

Three variables have been studied for the leaching of EAFD: pulp density, temperature, and acid concentration. It was found that pulp density and temperature do not significantly affect the extraction of zinc from EAFD, on the condition that the availability of acid is not limiting.

Table 5 shows results of tests performed at 20% of pulp density and 20°C. It can be observed that the Zn extraction depends on the acidity of the medium. At pH=4, the iron extraction is practically nil, but zinc extraction is only 51%. An increase in the available acidity can increase Zn extraction, although Fe extraction is also increased. This is counterproductive because the leached Fe will have to be precipitated later.

The consumption of acid also depends on the level of acidity due to the significant removal of iron and manganese.

Moreover, an excess of acidity generates silicic acid, which becomes silica gel and significantly disrupts the operations of solid/liquid separation.

3.2.1 Acid-leaching residue characterization.

Table 6 shows the chemical composition of residue resulting from the acid leaching at pH 1.3 of EAFD and the results of normalized leaching tests. The residue contains significant proportions of heavy metals: especially Zn due to refractoriness of zinc ferrites, and Pb, as lead sulphate. Both substances are very insoluble, but low solubility does not prevent development of small quantities of the order of parts per million in the case of Zn and two orders of magnitude lower for Pb, as is revealed by the standard leaching test.

The Luminescent bacteria test performed on the leaching residue gives $EC_{50}=200,000$ mg/l, and the *Daphnia magna* immobilization gives $CL_{50}=6,192$ mg/L: values much higher than $EC_{50}=3,000$ mg/L and $CL_{50}=750$ mg/L, below which waste is considered “ecotoxic” (attribute H14). In accordance with current legislation (Regulation (EC) No

1272/2008), the solid residue remaining after acid leaching is considered a non-hazardous waste.

3.3 Bio-oxidation.

The objective of this stage is to achieve complete oxidation of Fe (II) present in the liquor that results from mixing the acid leach liquor with AMW. The typical concentration of Fe (II) in this mixture is 600 ppm. The hydraulic loading (liquid flow per unit transverse area of empty reactor) in all cases is less than $0.5 \text{ m}^3 / \text{h} \cdot \text{m}^2$. This parameter is fundamental for the scaling up and determines, for a particular flow to be treated, the surface area occupied by the commercial bioreactor.

With the aim of minimizing the size of the bioreactor, and given the low concentration of Fe (II) in the liquor, it has been decided to increase the aforementioned hydraulic loading and test the increase of flow until incomplete conversion of Fe (II) is reached.

Table 7 shows the main results in the bio-oxidation study. The mean residence time (T_R) has been calculated in relation to the liquid volume in the reactor.

Ferrous iron concentration at outputs 1, 2 and 3 is controlled during reactor operation; and, from these concentrations, the conversion of ferrous to ferric iron at each height of bed (X_1 , X_2 and X_3) has been calculated, in order to establish the oxidative capacity as a function of the different conditions assayed.

For inflows less than 1500 mL/h, the conversion is complete at output 1. Inflows less than 2700 mL/h ensure a complete conversion at output 2. The reactor reaches the objective of complete conversion at 3700 mL/h ($2.552 \text{ m}^3 / \text{h} \cdot \text{m}^2$), although this level of flow involves the entire bed.

3.4. Precipitation Equilibrium.

Figure 1 shows the equilibrium concentrations in the precipitation of metals as hydroxides versus pH. From this graph, a number of considerations can be obtained:

1. The selective separation of Fe, Al, and Cu seems possible before Zn precipitation.
2. Ni must be separated before Zn because their curves coincide in the final stretch.
3. If Zn concentration in water is set at 0.1 ppm, Cd partially precipitates together with Zn.
4. Mn precipitates at a higher pH than Zn, thereby allowing their selective separation.
5. The precipitation of Mg is relatively close to that of Mn, although at a higher pH.

From these considerations, the following treatment strategy arises:

1. Selective precipitation of Fe and Al as hydroxides at controlled pH.

2. Cementation of Cu, Cd, and Ni with metallic zinc.
3. Selective precipitation of Zn as oxide

3.4.1. Selective precipitation of Fe and Al.

For selective precipitation of Fe and Al, it is necessary reach a pH = 5 in order to ensure the complete removal of Al. The precipitate obtained mainly consists of gypsum and hydroxides of iron and aluminium. Table 8 shows the typical composition of the precipitated Fe-Al, as well as the rate of retention of each element in the precipitate. It should be noticed that Fe, As, Cr, and Al are removed from the solution. Surprisingly, 90% of Cu is eliminated when it should not precipitate at pH=5. Approximately 5% of zinc present in the liquor is retained in the precipitate of hydroxides by an adsorption phenomenon.

3.4.2. Cementation.

Both Cu^{2+} and Cd^{2+} co-precipitate with Zn^{2+} as hydroxides (Figure 1), and hence it is necessary to separate them before the zinc precipitation step. Cementation with metallic Zn is the method of separation, in accordance with:



The cementation is tested in a column packed with a bed of Zn particles (0.3 - 1.5 mm in size). In all cases, the kinetics is too slow, especially in the case of cadmium, which imposes large column sizes that are not currently operating.

Cementation in pulp, using metallic zinc powder, gives much better results. Table 9 shows the residual concentrations in liquor after cementation with pulp densities of 1 and 3% for times below 15 minutes. The high Zn demand over the stoichiometric makes it necessary to work with a recirculation loop. Zn is partially returned to the tank after being separated from the liquor by sedimentation. In this way, it is possible to operate at high pulp density and keep the consumption of zinc at the same order of magnitude as that required stoichiometrically.

3.4.3. Precipitation of ZnO.

Once Fe, Al, Cu, Ni, and Cd are separated, the objective becomes the selective separation of Zn from Mn in the form of ZnO. Figure 2 shows the actual evolution of Zn and Mn concentrations versus pH in a test of precipitation with lime. Figure 2 also includes the theoretical curve of Mn precipitation.

As can be seen, the precipitation of Mn takes place at a pH lower than that predicted by equilibrium data; it should begin at pH 8.8 and it actually performs for the entire range, although more significantly at pH 6. The explanation for this phenomenon lies in the

conditions of precipitation and in an oxidation reaction, which changes the nature of the manganese precipitate.

During precipitation, every drop of alkali causes a local and sharp increase of pH in the neighbourhood, and metal hydroxides indiscriminately precipitate. When the agitation establishes the actual pH of solution again, soluble hydroxides are redissolved. The Mn is also redissolved, but not completely, as it reacts with the oxygen dissolved in water, according to the following reaction:



The MnO_2 formed is more refractory to acid dissolution than Mn(OH)_2 , and hence a part of Mn is effectively kidnapped at pH values well below the equilibrium of precipitation.

Several precipitation tests in presence of air, oxygen and hydrogen peroxide have been performed with the aim of oxidising Mn(OH)_2 and of preventing its passage to solution by acid dissolution of precipitation residue. Moreover, precipitation in an inert atmosphere has also been tested in order to prevent the aforementioned oxidation reaction.

The redissolution of zinc hydroxide precipitate obtained in oxidizing conditions is not entirely selective, since 30% of Mn is also dissolved. The results obtained in an inert atmosphere have not been successful due to the difficulties in completely preventing the presence of oxygen in the precipitation reactor. Therefore, the need to purify ZnO arises.

Table 10 shows the analysis of precipitates obtained at pH 8.2, 9.1 and 9.6. Figure 3 shows Zn concentration in liquor as a function of the pH reached as well as the values calculated from thermodynamic data.

With a final pH=8.2, the precipitation gives a high-grade Zn product with minority components as gypsum and other metallic hydroxides. This facilitates the subsequent purification stages, but the liquor cannot be considered purified water due to the presence of approximately 5 ppm of Zn. The attainment of purified water requires a new precipitation stage with lime at pH=10.5 in the supernatant liquor.

3.5. Preparation of commercial products.

3.5.1. Basic zinc carbonate.

One commercial product considered is basic zinc carbonate ($\text{ZnCO}_3 \cdot 2\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$). It is an insoluble compound, which is obtained according to the following reaction:



The proposed procedure starts with a step of dissolution of the zinc oxide precipitate with sulphuric acid. The residue of this stage, mainly consisting of gypsum and hydroxides of manganese, is sent to the iron precipitation step for the purge and recovery of the remaining zinc. The pregnant liquor is treated with a sodium carbonate solution at 70°C to promote the selective precipitation of basic zinc carbonate. The residual liquor, which still contains some amount of zinc, is sent to the stage of ZnO precipitation for its recovery.

Figure 4 summarizes the results of obtaining basic zinc carbonate. The x-axis represents the ratio between the mass of sodium carbonate added and the mass of ZnO precipitated. The y-axes represent the pH values on the left and the fraction of Zn and Mn precipitates on the right.

In Figure 4, it can be observed that the precipitation of Zn shows a linear evolution with the addition of carbonate; however, Mn precipitation shows no such evolution. Up to pH=6, Mn precipitation is less than 5%; above this pH value, the manganese precipitation rises rapidly.

This difference in the precipitation of the two metals is useful to define conditions for obtaining a product with a very low Mn content. According to the results and in order to reach this goal, the level of Zn precipitation should not exceed 90%. The pH must be the control variable, with a final setpoint of pH=6.

Zinc remaining in the solution should be recovered by returning to the stage of Zn precipitation. Table 11 shows the composition of the product obtained when 80% of Zn is precipitated as basic zinc carbonate.

3.5.2. Electrolytic Zinc.

ZnO precipitate is dissolved when there is an excess of NaOH (about 300 g/L), according to the following reaction:



An insoluble residue mainly consisting of gypsum, lime and manganese hydroxide is generated and it is returned to the Fe-Al precipitation stage for purging and for incorporation of the residual Zn to the circuit.

The fertile liquor, consisting of 20-30 g/L of Zn^{2+} , is electrolysed according to the following reactions:

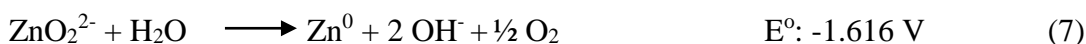
Cathodic reaction:



Anodic reaction:



Overall reaction (5)+(6):



If this reaction is added to the alkaline redissolution of ZnO (reaction 4), the following overall reaction is obtained:



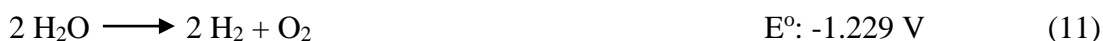
That is, the theoretical consumption of NaOH is zero since the need of this reagent for the dissolution of ZnO is covered with its production in electrolysis.

The main secondary electrolytic reaction is the formation of hydrogen at the cathode.

The anodic reaction is that of the oxygen generation:



The sum of these two, (9)+(10), gives the overall secondary reaction:



In this reaction, alkali is not consumed; however it does cause a decrease in current efficiency because, in theory, it takes place at a potential lower than the potential of the main reaction.

The cell potential necessary for the electrolytic discharge of hydrogen depends greatly on the nature of the cathode used; materials such as Pt, Au, and Pd have overpotentials below -0.1V, while Pb and Hg have values above -0.9V. In the present case, regardless of the material to use as a cathode, zinc has a cathodic overpotential of -0.8V, which overrides the initial advantage that the equilibrium potentials give to water decomposition.

Alkaline redissolution of ZnO gives Zn extractions between 70 and 90%, without Mn in solution. Assays, which simulate the return of alkaline leaching residue to the Fe precipitation stage, have been carried out. This residue has been treated with the liquor coming from bio-oxidation. In all cases, Zn extraction has been higher than 99.5%; this ensures the recovery of the entire content of Zn.

Figure 5 shows the response curve for a linear sweep voltammetry for a standard electrolyte (20.5 g/L of Zn and 300 g/L of NaOH). From a voltage of 2V, the intensity significantly begins to flow through the circuit. Above 2V, the increase in intensity is linear with potential. This suggests that the electrodes are not passivated and that there is no additional polarization from a decrease of concentrations (relatively fast potential

sweep). Under the conditions tested, the minimum overpotential for the discharge of zinc is approximately 0.4V.

Figure 6 shows the influence of potential on current efficiency. The influence of the degree of electrolyte depletion is shown for each potential value.

In test conditions, a voltage of 2.4V is necessary in order to operate with a current efficiency higher than 90%. For higher values of potential, the efficiency decreases significantly. At 2.4V, the current density is around 300 A/m² and energy consumption 2 kW • h / kg Zn.

Table 12 shows the composition of the Zn deposit obtained at this potential. It is a continuous sheet of Zn easily removable from the electrode.

4. Conclusions.

As a summary, Figure 7 shows the flowchart of the overall process considering the various product alternatives. Separation stages shown in the diagram have been thoroughly studied but are not included in this article. The proposed process recovers zinc content of both EAFD and AMW as ZnO, which is valorised as the high-grade commercial products electrolytic zinc and basic zinc carbonate, thereby enabling a reduction in management cost. From an environmental point of view, two objectives are achieved: water purification is attained, and the waste ceases to be classified as a hazardous waste. The solid residue remaining after the acid-leaching stage is considered non-hazardous in accordance with European Legislation.

In this way, not only is inertization waste prevented and costs of water purification are reduced, but better use of natural resources is also made.

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Table 1: Chemical composition of water from Aznalcollar Mine.

[Fe] (mg/L)	[Zn] (mg/L)	[Al] (mg/L)	[Mn] (mg/L)	[Cu] (mg/L)	[Ni] (mg/L)	[Ca] (mg/L)	[Mg] (mg/L)	pH
488	1,185	54.8	253	4.6	2.7	488	1,828	2.96

Table 2: Composition of the EAFD generated by Siderurgica Sevillana Company.

Fe (%)	Zn (%)	Pb (%)	Al (%)	Mn (%)	Na (%)	Ca (%)	K (%)	Cu (%)	Cr (%)	Cl ⁻ (%)	CO ₃ ²⁻ (%)	SO ₄ ²⁻ (%)
25.3	24.1	1.9	0.6	2.1	4.16	4.9	1.7	0.3	0.2	3.3	1.5	1.6

Table 3: Data used to determine the overall capacity of treatment.

AMD
Average flow = 300 m ³ / h
Operation time = 9 months / year
Water volume water = 1,944 10 ⁶ m ³ /year
Mean [Zn ²⁺] = 1 kg/m ³
Zn recovery = 99.9%
Zn production = 1,944 t/year
EAFD
Production = 14,000 t / year
Zn content = 25 %
Minimum Zn extraction = 65%
Minimum Zn production = 2,275t/year

Table 4: Washing of EAFD at different pH values. Wash water composition.

pH	Zn (ppm)	Mn (ppm)	Mg (ppm)	Ca (ppm)	Cu (ppm)	Pb (ppm)	Na (g/L)	K (g/L)	Cl (g/L)	Acid (g/kg)
7.0	365	10.6	155	774	<0.05	2.5	3.13	3.22	6.19	33.1
8.0	7.2	3.3	78	800	<0.05	0.2	3.21	2.92	6.36	37.4
9.0	0.1	0.18	71	820	<0.05	0.3	3.16	2.94	6.19	25.7
10.0	0.1	0.07	15	860	<0.05	0.3	3.12	2.92	6.25	26.8
11.0	0.3	0.03	0.37	880	<0.05	0.2	3.14	2.90	5.33	22.8
12.1	0.4	0.03	0	650	<0.05	8.5	2.36	3.11	6.40	0

Table 5: Leaching results of tests performed at 20% of pulp density and at 20°C.

Acidity (pH or g/L)		Extraction (%)			Weight loss (%)	Acid consumption g/Kg	Density (g/l)
Initial	Final	Zn	Fe	Mn			
pH 4	pH 4	51.5	0,06	5.3	3.1	278	1058
pH 3	pH 3	62.2	5,9	14.8	20.3	446	1090
pH 2	pH 2	66.5	6,8	16.5	26.9	464	1102
pH 1	pH 1	68.7	9,3	19.4	27.5	534	1105
25 g/l	4	69.7	11,5	24.9	28.0	561	1116
50 g/l	36	72.4	16,5	26.8	29.5	647	1170
75 g/l	53	71.2	13,2	29.4	32.0	739	1200

Table 6: Chemical composition of residue and normalized leaching tests

	pH 1.3 leaching residue (%)	pH 0.7 UNE-EN (mg/L)	pH 1.3 UNE-EN (mg/L)	pH 2.0 UNE-EN (mg/L)
Zn	11.34	5.93	20.82	9.8
Al	0.458	< 0.02	< 0.02	< 0.02
Ca	6.28	615.73	555	612.41
Cd	0.008	0.088	0.074	0.072
Cr	0.262	0.032	0.039	< 0.02
Cu	< 0.0013	< 0.03	< 0.03	< 0.03
Fe	33.16	0.035	< 0.02	< 0.02
Mg	1.05	1.74	1.89	1.44
Mn	2.38	0.124	0.356	0.638
Ni	0.022	< 0.06	< 0.06	< 0.06
As	0.445	< 0.03	< 0.03	< 0.03
Se	< 0.0013	< 0.03	< 0.03	< 0.03
Sb	0.007	< 0.08	< 0.08	< 0.08
Pb	2.58	0.189	0.238	0.055
Be	-	< 0.01	< 0.01	< 0.01
Tl	-	< 0.03	< 0.03	< 0.03
Co	-	< 0.02	< 0.02	< 0.02
Hg	-	< 0.03	< 0.03	< 0.03
Na	0.445	-	-	-
pH	-	5.37	5.25	5.76
Conductivity	-	2.83	2.78	2.8

Table 7: Bio-oxidation results

Flow rate (mL/h)	T _R (min)	X ₁ (%)	X ₂ (%)	X ₃ (%)	Hydraulic loading (m ³ /h·m ²)
700	47.4	100.0	100.0	100.0	0.483
1100	30.2	100.0	100.0	100.0	0.759
1500	22.1	100.0	100.0	100.0	1.034
1900	17.5	85.8	100.0	100.0	1.310
2700	12.3	85.9	100.0	100.0	1.862
3000	11.1	79.1	98.8	100.0	2.069
3700	9.0	63.6	96.0	100.0	2.552
3750	8.9	63.0	96.0	99.1	2.586

Table 8: Typical analysis of Fe-Al precipitate and % of removal from solution

	Zn	Al	Ca	Cd	Cr	Cu	Fe
Precipitate composition (%)	1.35	0.95	14.5	0.006	0.035	0.18	9.1
Removal from solution (%)	4.3	96.9	--	8.1	98.6	90.7	100.0
	Mg	Mn	Ni	As	Se	Sb	Hg
Precipitate composition (%)	0.01	0.18	0.002	0.002	< 0.0004	< 0.001	< 0.0004
Removal from solution (%)	0	4.4	5.2	100	--	--	--

Table 9: Evolution of Cu and Cd concentrations in pulp cementation tests

Time (min)	1% Zn		3% Zn	
	[Cu ²⁺] (ppm)	[Cd ²⁺] (ppm)	[Cu ²⁺] (ppm)	[Cd ²⁺] (ppm)
0	10.37	6.40	10.37	6.40
1	0.10	0.68	< 0.03	0.06
2	< 0.03	0.06	< 0.03	0.05
3	< 0.03	0.05	< 0.03	< 0.04
5	< 0.03	< 0.04	< 0.03	< 0.04
10	< 0.03	< 0.04	< 0.03	< 0.04
15	< 0.03	< 0.04	< 0.03	< 0.04

Table 10: Analysis of ZnO precipitate obtained at different pH values

Element	pH 8.2 (%)	pH 9.1 (%)	pH 9.6 (%)
Zn	28.75	21.81	13.65
Al	0.007	0.011	0.005
Ca	7.800	9.562	13.00
Cd	0.027	0.026	0.008
Cr	0.001	< 0.001	< 0.001
Cu	0.014	< 0.0015	< 0.0015
Fe	0.015	0.025	0.017
Mg	1.951	3.386	4.680
Mn	1.951	2.245	1.720
Ni	0.038	0.030	0.020

Table 11: Zinc carbonate composition (80% of Zn precipitation)

Element	Zn	Al	Ca	Cd	Cr	Cu	Fe
(%)	58.94	0.181	0.009	0.006	< 0.0002	0.001	0.008
Element	Mg	Mn	Ni	Na	Se	Sb	Pb
(%)	0.017	0.053	0.036	0.061	< 0.0004	< 0.001	< 0.0011

Table 12: Electrolytic zinc analysis

Zn	99.72
Al	0.003
Ca	0.012
Cd	< 0.0007
Cr	0.012
Cu	< 0.0007
Fe	0.023
Mg	< 0.0002
Mn	< 0.0002
Ni	< 0.0015
Se	< 0.0007
Sb	< 0.002
Pb	< 0.0021
Na	0.040
Hg	< 0.0003

Figure 1: Theoretical equilibria for hydroxide precipitation

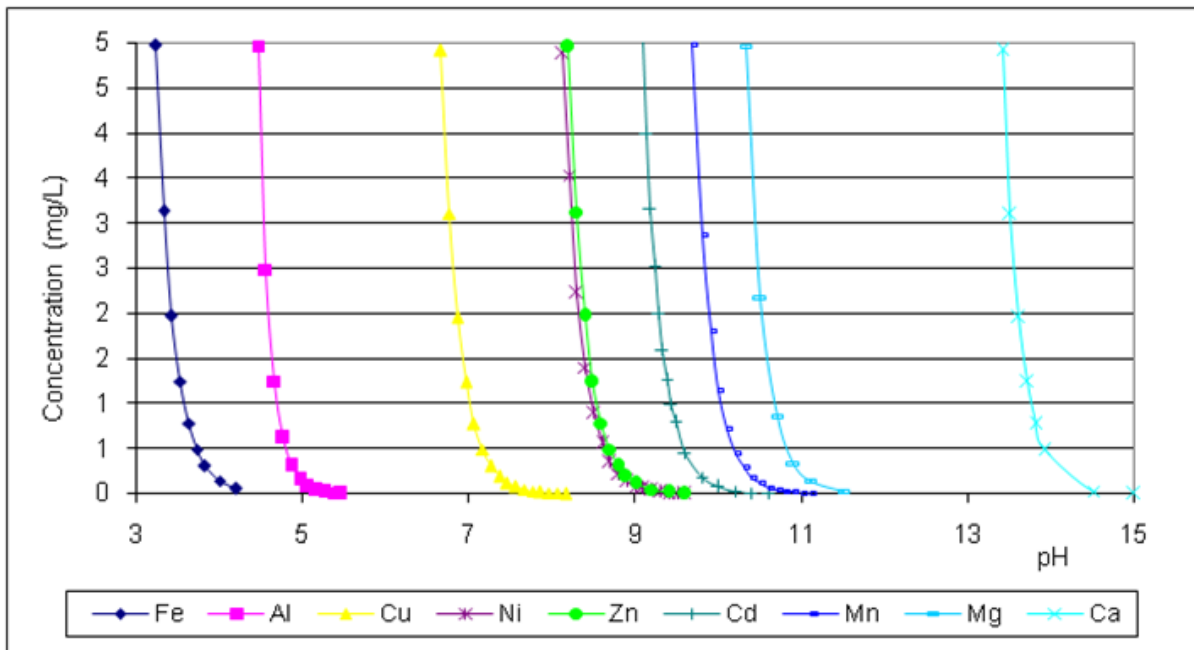


Figure 2: Evolution of Zn and Mn concentration versus pH and theoretical Mn precipitation curve

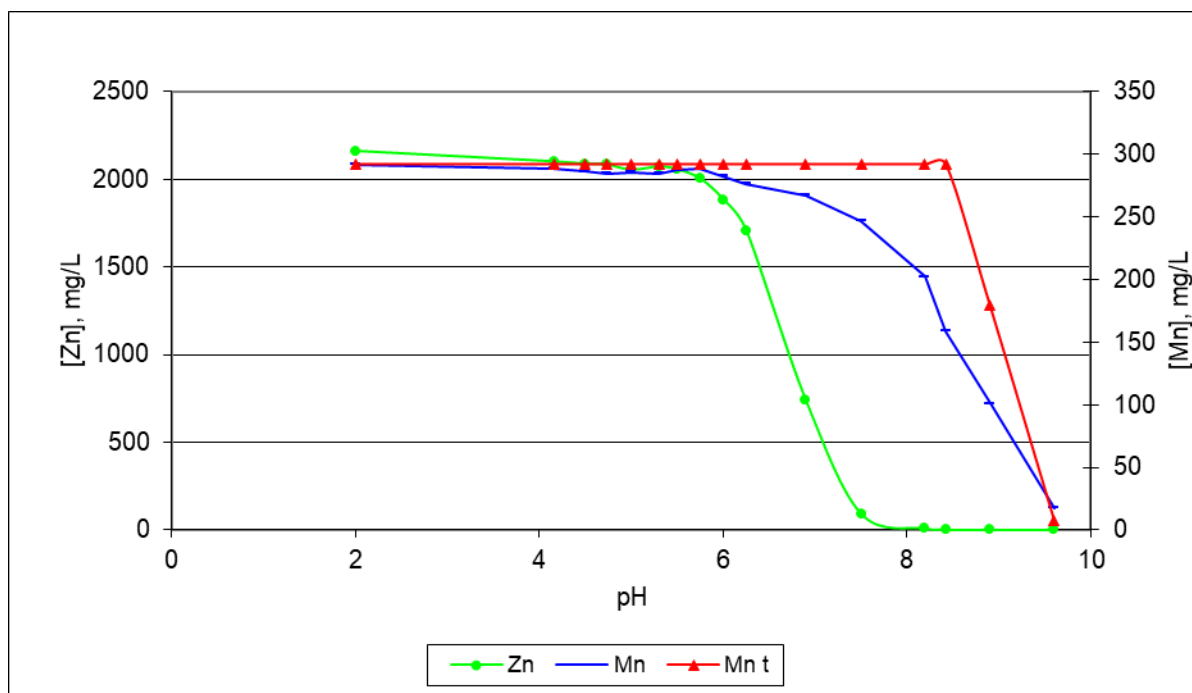


Figure 3: Influence of pH on final zinc concentration in solution. Theoretical and experimental values.

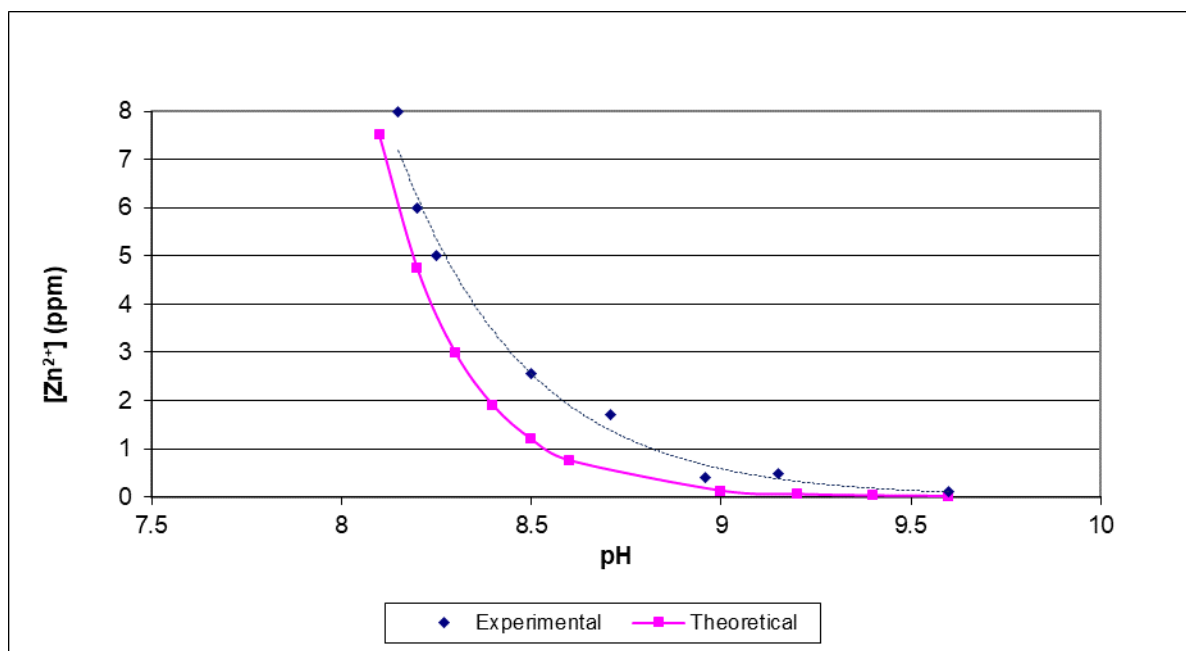


Figure 4: Basic zinc carbonate precipitation. X-axis represents the ratio between the mass of sodium carbonate added and the mass of ZnO precipitated. Y-axes represent the pH values on the left and the fraction of Zn and Mn precipitates on the right.

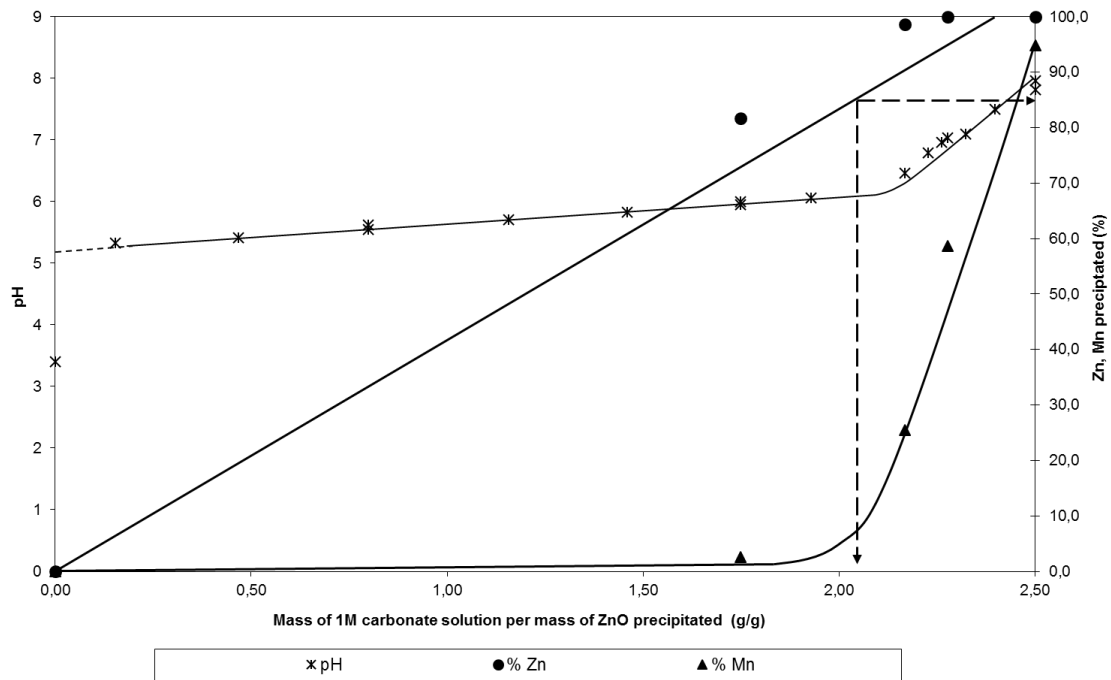


Figure 5: Linear sweep voltammetry for a standard electrolyte (20.5 g/L of Zn and 300 g/L of NaOH).

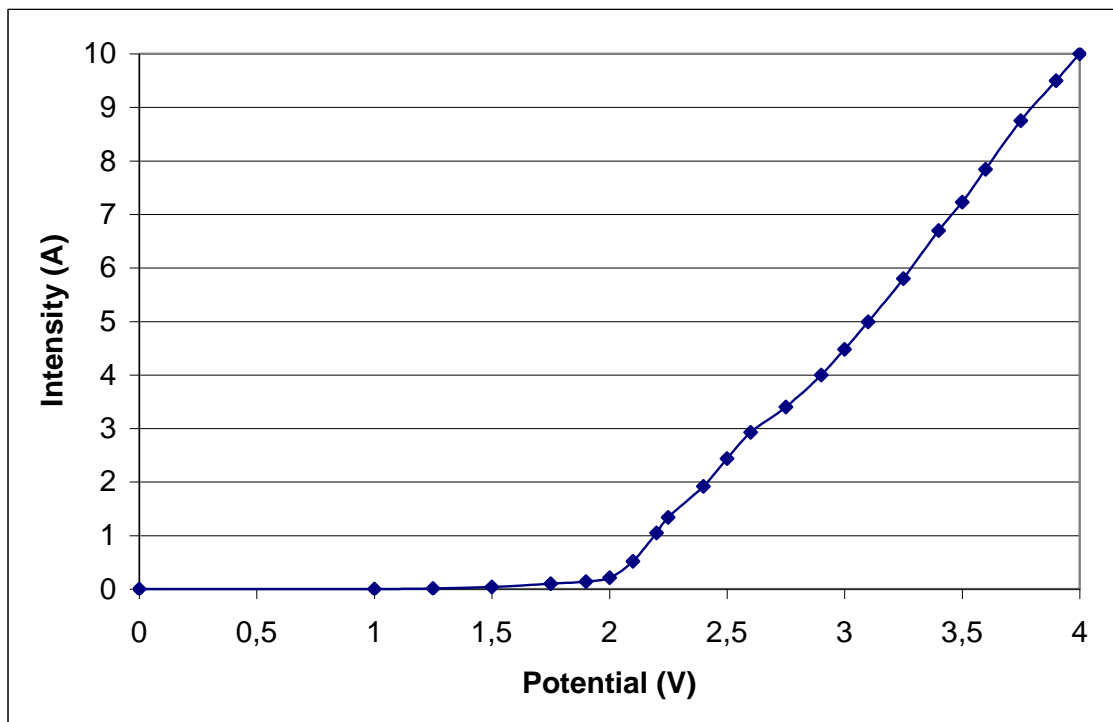


Figure 6: Influence of the potential and the degree of electrolyte exhaustion on current density.

