Electroleaching and electrodeposition of zinc in a single-cell process for the treatment of solid waste

Pascaline Guillaume [a], Nathalie Leclerc [a,*], François Lapicque [b], Clotilde Boulanger [a]

[a] *Laboratoire d'Electrochimie des Matériaux (Groupe du Laboratoire de Chimie du Solide Minéral), UMR CNRS 7555, Université Paul Verlaine,*
1 Bd Arago, Metz Technopôle, CP 87811, 57 078 Metz Cedex 3, France
[b] *Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC, BP 20451, F-54001 Nancy, France*

Abstract

This work deals with zinc beneficiation of industrial solid waste by an electrochemical technique combining electroleaching and electrodeposition in a single-cell process. This technique is based on leaching of the solid waste by the protons generated at the anode and migration of the resulting ions toward the cathode where deposition takes place.

A laboratory cell was built for testing the method. It consisted of three compartments, two electrode compartments and a solid waste chamber placed between these. Catholyte and anolyte were sulphuric/sulphate solutions at optimised concentrations. Experiments were first carried out using a zinc solution and an inert matrix in the central compartment, then using a synthetic waste prepared by dispersing zinc oxide in silicon dioxide. Best performance was obtained with treatment duration of 6 h, at 4.5 A dm^{-2} and with catholyte circulation. In this case, a 97% of zinc oxide lixiviation and 75% of zinc-plated were achieved.
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1. Introduction

Industrial activity generates large amounts of solid waste containing heavy metals such as zinc and lead. For example: electric arc furnace dust [1], household alkaline batteries [2], are some zinc rich by-products. Processes used for treating this kind of materials are pyrometallurgical or hydrometallurgical. Generally, the pyrometallurgical way is more expensive than the other one and does not allow a total recovery of metals. Hydrometallurgical treatments are cheaper, can be operated under milder conditions, but involve a number of steps, frequently including leaching and electrowinning [3]. In this work, we proposed to combine the two operations in a single-cell process: electroleaching–electrodeposition treatment.

Electrokinetic processes have been used and studied for soil and groundwater remediation for two decades and the mechanisms involved have been well described in the literature [4–10].

Some authors have also investigated the use of such techniques for metal recovery from ocean nodules [11–15], ores [16–19], or for waste treatment and valorization [20–27]. Sabba and Akretche [28,29] proposed an electrokinetic process for copper dissolution from ores in ammoniacal media. High selectivity of the electroleaching was obtained using ion exchange membranes.

The method described in this article is based on electroleaching of a metal oxide (ZnO) and recovery of the leached metals by electrodeposition in a single-cell process, i.e. without transport of solids or fluids from one chamber to another by pumps or other mechanical processes. The process relies upon application of an electric field to the solid waste to be treated. Protons generated at the anode by water oxidation, migrate towards the cathode: they react with metal oxides or salts contained in the solid placed between the electrodes. Metal ions are formed and migrate to the cathode where they reduce to form a deposit. The final product is zinc metal and can be directly recovered.

A laboratory cell was built for testing the method in discontinuous (batch) operation. It consisted of modular number of compartments, and for the present study, the two electrode

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* Corresponding author. Tel: +33 387 547 415; fax: +33 387 315 460.
E-mail address: leclerc@univ-metz.fr (N. Leclerc).

compartments encompassed the solid waste chamber. After preliminary tests conducted without leaching operation, experiments were carried out using a synthetic waste prepared by dispersing zinc oxide in sand, acting as the inert support.

2. Theoretical

2.1. Principle of treatment

The principle of the treatment is given in Fig. 1. When a dc voltage is applied, the reaction occurring at the anode placed in compartment (A), is water oxidation:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{1}$$

Protons generated by reaction (1) migrate towards the cathode under the action of the electric field. In central compartment (B) they react with zinc oxide through the leaching operation:
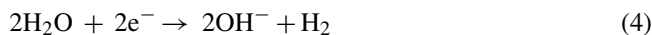
$$ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O \tag{2}$$

Zn^{2+} ions produced by the above process migrate towards the cathode compartment (C). At the cathode surface two reactions can take place:

- Zinc reduction:
$$Zn^{2+} + 2e^- \rightarrow Zn^0 \tag{3}$$

- Water reduction:
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{4}$$

Reaction (4) has to be minimised to avoid formation of little soluble $Zn(OH)_2$:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{5}$$

To prevent formation of the precipitate, a sulphuric acid solution was used as the catholyte. In such cases, the side hydrogen formation is due to by proton discharge at the cathode:

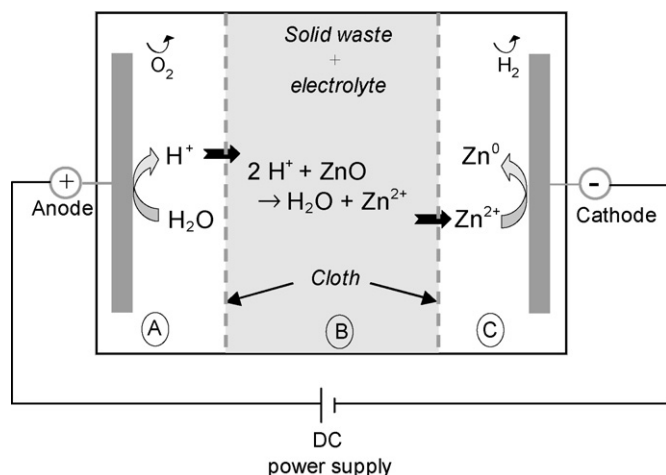$$2H + 2e^- \rightarrow H_2 \tag{4'}$$

Fig. 1. Principle of electroleaching–electrodeposition in a single-cell process.

2.2. Calculations

2.2.1. Transference numbers

The electromigration efficiency is related to the transference number t_i. It is defined as the fraction of the total current carried by ionic species i:

$$t_i = \frac{Z_i U_i C_i}{\sum_i Z_i U_i C_i} \tag{6}$$

where Z_i is the valence, C_i the concentration and U_i is the mobility of i.

Electromigration may be poorly efficient for ions with very low t_i values. For the present work, transference numbers of the various species have to obey the following constraints:

- t_{H^+} must be high in compartment (A) for the sake of efficient transport of H^+ to the leaching compartment (B)
- $t_{Zn^{2+}}$ must be high in compartment (B) for efficient Zn^{2+} migration to the electrodeposition compartment (C): this corresponds to t_{H^+} as low as possible in this compartment.

2.2.2. Yields calculation

Leaching yield (LY) relates to the efficiency of electroleaching operation and was calculated as follows:

$$LY\,(\%) = \left(\frac{1 - n_{f,ZnO}}{n_{i,ZnO}} \right) \times 100 \tag{7}$$

where $n_{i,ZnO}$ is the mole number of zinc oxide initially introduced in compartment (B) and $n_{f,ZnO}$ the mole number of ZnO at the end of the treatment.

Current efficiency was determined as the ratio of the weight of zinc W_1 deposited at the cathode with electrical charge Q, to the theoretical weight of deposited metal W_2 calculated by using Faraday's law:

$$W_2 = \frac{M_{Zn} Q}{Z_{Zn} F} \tag{8}$$

where F is the Faraday's constant, M_{Zn} the molar weight of zinc ($65.38\,\text{g mol}^{-1}$), and Z_{Zn} is the valence of zinc, i.e. 2. For the present case of galvanostatic runs, Q is the product of the applied current I and the period of time, t. Eq. (10) gives the current efficiency (CE):

$$CE\,(\%) = \left(\frac{W_1}{W_2} \right) \times 100 \tag{9}$$

The deposition yield (DY) is the fraction of zinc deposited. This rate was calculated as

$$DY\,(\%) = \left(\frac{n_{Zn^0}}{n_{t,Zn^{2+}}} \right) \times 100 \tag{10}$$

where n_{Zn^0} is the mole number of zinc deposited and $n_{t,Zn^{2+}}$ the mole number of Zn^{2+} ions (including leached ZnO), i.e. the difference $(n_{i,ZnO} - n_{f,ZnO})$.

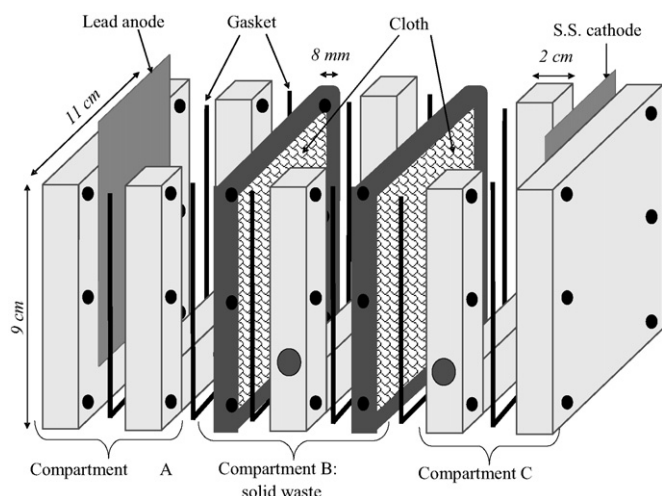All the yields defined above can be calculated at the end of the discontinuous process or at intermediate times.

Fig. 2. Laboratory cell for combined electroleaching –electrodeposition.

3. Experimental details

3.1. Synthetic waste

The synthetic waste was obtained by blending 990 g metal-free sand (Sarah Eggert) and 110 g ZnO (Acros Organics) for 6 h in a ball mill. For controlling homogeneity, six samples of 1 g were taken from the obtained solid mixture for characterisation. Grain size distribution of the obtained solid mixture was as follows: over 250 µm, 10 wt.% 90–250 µm, 65 wt.% 45–90µm, 20%, and 5 wt.% below 45µm. Samples were leached with hot hydrochloric acid (6 M) and zinc concentration was determined by atomic absorption spectrometry (AA 240 FS, Varian), to control the homogeneity of the solid blend.

3.2. Electroleaching–electrodeposition cell

All experiments were carried out in a laboratory-built cell schematically shown in Fig. 2. It is made of PVC and can be constituted by a variable number of compartments. To allow fluid circulation each compartment was provided with two holes: one on the top of one side and a second on the bottom of the other side. The compartments were 9 cm high and 7 cm broad. The thickness of the electrode compartment was 2 cm, whereas the waste

chamber was 2.5 cm thick. Anodic and cathodic compartments were filled with 125 cm^3 solutions, whereas 100 cm^3 liquid plus 133 g of solid were introduced into the waste compartment. This chamber was separated from the two others by a polypropylene cloth (Sefar Fyltis). The cloth was 0.5 mm thick, with pore size below 45 µm. The electrodes were plates with an active area of 53 cm^2: the anode was out of lead and the cathode out of 316 stainless steel. The cell was mounted by inserting O-ring between the various compartments and the cell assembly was carried out with bolts regularly located in the PVC components. The electrodes were connected to a dc power supply.

3.3. Experimental conditions

Previous works carried out separately on electroleaching [30,31] and electrodeposition [32] allowed the best electrolyte compositions to be defined as follows:

- anolyte: H_2SO_4 0.2N;
- waste electrolyte: H_2SO_4 0.02 N and $ZnSO_4$ 0.2 M, in the presence of the ZnO-sand solid mixture (presence of electrolyte in the central chamber was found to be necessary for the sake of sufficient electrical conductivity and reasonable ohmic drops in the early stages of the batch run);
- catholyte: H_2SO_4 1N and $ZnSO_4$ 0.2 or 0.5 M.

It was previously shown that the use of 4.5 A/dm^2 as current density allow leaching yields of ZnO higher than 90%. The catholyte composition was selected after thorough investigations of zinc deposition in a Hull cell using 20 different solutions with different Zn^{2+} and H^+ concentrations [32]. Examination of the deposits obtained at 4.5 A/dm^2 revealed the satisfactory morphology of the produced metal that consists of regular platelets of a good compactness, without dendrites or powdery structures.

In this work, the results of four experiments are reported. Their operational conditions are listed in Table 1. Experiments 1 and 2 were carried out with a $ZnSO_4$ solution impregnating inert sand in the waste chamber for investigation of the only electrodeposition step in the laboratory cell. Experiments 3 and 4 were carried out with ZnO-sand blend described above for investigation of combined electroleaching–electrodeposition steps.

Table 1
Operational conditions

|	Anodic compartment (A)	Waste chamber (B)	Cathodic compartment (C)
Without electroleaching			
Experiment 1	H_2SO_4 0.2N; no fluid circulation	Sand (133 g); $ZnSO_4$ 1.4 M; H_2SO_4 0.02N; no fluid circulation	$ZnSO_4$ 0.2 M; H_2SO_4 1N; no fluid circulation
Experiment 2	H_2SO_4 0.2N; no fluid circulation	Sand (133 g); $ZnSO_4$ 1.4 M; H_2SO_4 0.02N; no fluid circulation	$ZnSO_4$ 0.5 M; H_2SO_4 1N, no fluid circulation
With electroleaching			
Experiment 3	H_2SO_4 0.2N; no fluid circulation	Synthetic waste (133 g); $ZnSO_4$ 0.2 M; H_2SO_4 0.02N; fluid circulation	$ZnSO_4$ 0.5 M; H_2SO_4 1N; no fluid circulation
Experiment 4	H_2SO_4 0.2N; no fluid circulation	Synthetic waste (133 g); $ZnSO_4$ 0.2 M; H_2SO_4 0.02N; fluid circulation	$ZnSO_4$ 0.5 M; H_2SO_4 1N; fluid circulation
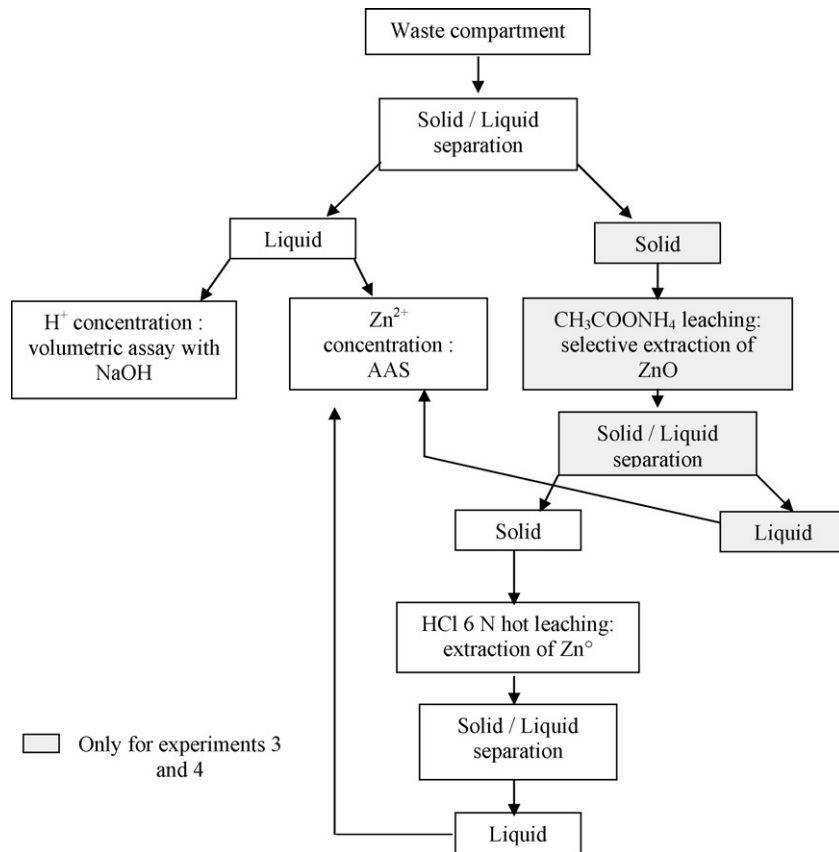
Fig. 3. Analytical procedure used in the waste compartment.

3.4. Analytical

At formerly defined times the liquid of each compartment was sampled for determination of zinc and H^+ concentrations: Zn assay was achieved by atomic absorption spectroscopy and H^+ concentration was obtained by volumetric titration with freshly calibrated NaOH solutions. At the end of each experiment, the three compartments were simultaneously emptied, and the final concentrations of zinc ions and H^+ were determined. Zinc electrodeposited on the cathode was digested by hydrochloric concentrated acid. Besides, Fig. 3 reports the procedure used for zinc speciation in the waste chamber.

4. Investigations without electroleaching

The initial concentration of zinc sulphate in the central compartment was fixed at 1.4 M so that the concentration of zinc ions in the various compartments was large enough for effective deposition and satisfactory morphology of the deposit. In addition, the order of magnitude of the Zn concentration was similar to that for electroleaching experiments described in Section 5.

4.1. Evolution of species amount in each compartment

The variations of the mole number of zinc and H^+ in each compartment with time for experiment 1 are reported in Figs. 4 and 5.

• Compartment (B) (waste)

The zinc ions initially present in this compartment migrate to the cathode compartment and diffuse to the anodic one. Consequently the mole number of Zn species in compartment (B), decreased rapidly for 200 min before reaching a steady value at approximately 0.15 mol. H^+ quantity increased then stabilised at around 0.08 mol in the same periods of time.
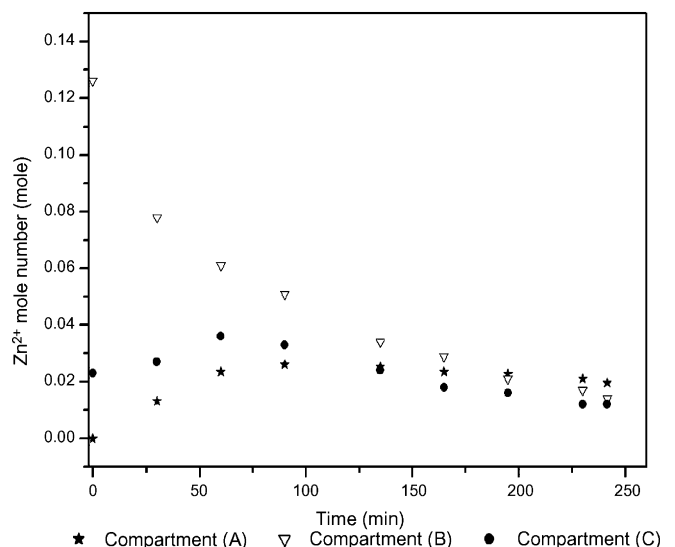

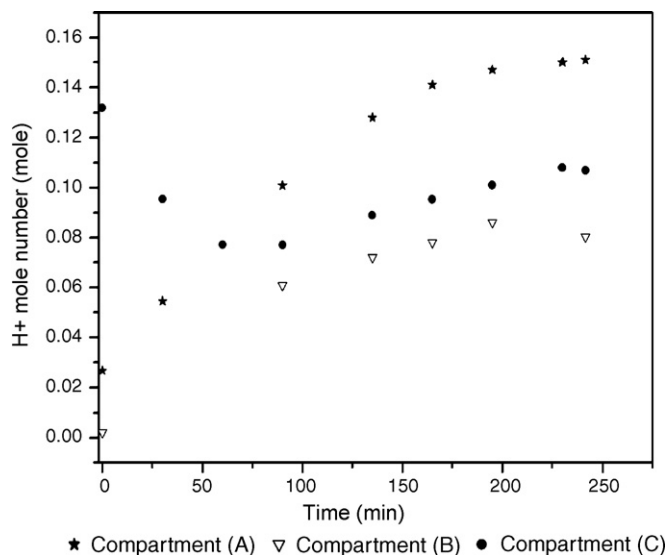Fig. 4. Time variation of the zinc mole number in each compartment.

Fig. 5. Time variation of the H$^+$ mole number in each compartment.

- Compartment (A) (anode)

  Zn^{2+} regularly accumulated by diffusion from compartment (B) during the first hour and its amount reached a steady level at 0.025 mol. The number of moles of H$^+$ logically increased all along the run because of the continuous water electrolysis.
- Compartment (C) (cathode)

  For the first hour, the amount of zinc slightly increased whereas the concentration of H$^+$ decreased accordingly. After 1 h, this trend was reversed.

Figs. 6 and 7 show the time variations of the total mole numbers of Zn^{2+} and H$^+$ – integrating the contributions of each compartment – in comparison with the initial mole numbers for experiments 1 and 2, respectively. It can be seen that during
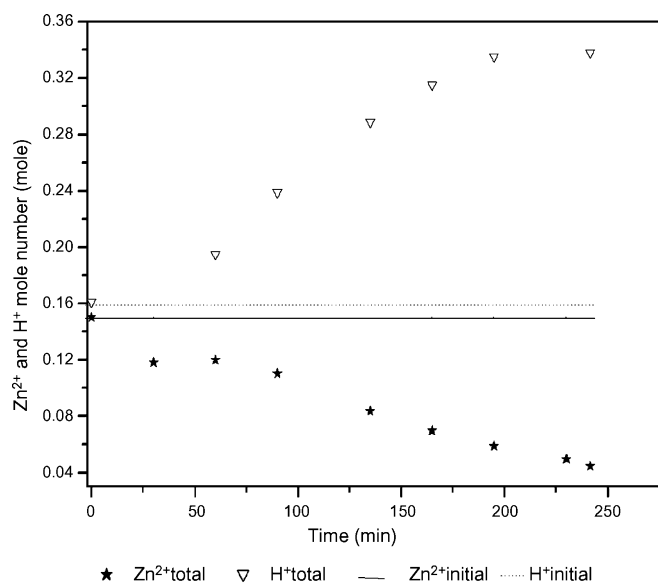

Fig. 6. Time variation of the total mole numbers of Zn^{2+} and H$^+$ in experiment 1 and comparison with the initial mole numbers (dotted lines).
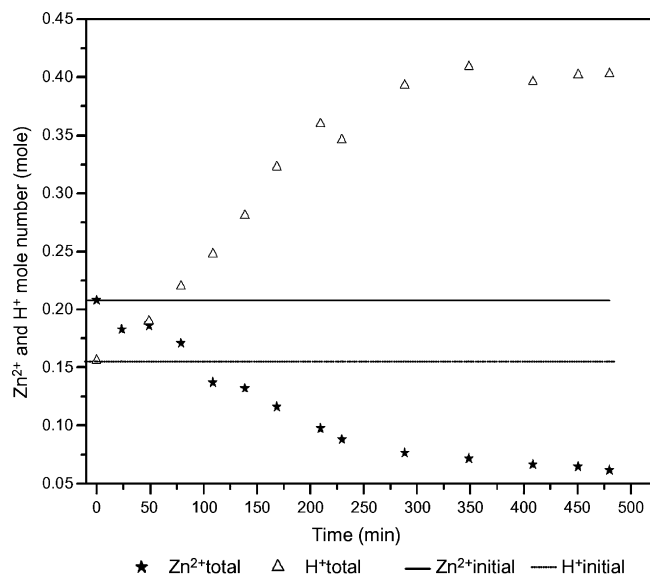

Fig. 7. Time variation of the total mole number of Zn^{2+} and H$^+$ in experiment 2 and comparison with the initial mole numbers (dotted lines).

the 200 first minutes, for both experiments, the amount of zinc rapidly decreased whereas the mole number of H$^+$ increased; after this first period, the two mole numbers stabilised. This means that zinc deposition occurred mainly in the first 200 min. Beyond this time limit, zinc deposition occurred only with very low yields, and the flux of protons reduced at the cathode compensated the flux of H$^+$ produced at the anode.

4.2. Zinc mass balance

Table 2 gives zinc mass balance for experiments 1 and 2. For the same duration of experiment, one can see that using a higher Zn^{2+} concentration in the cathode chamber allowed a higher amount of deposited zinc, with higher current efficiency. For experiment 2, only 0.7 g of zinc was plated between 4 and 8 h, expressing that the current efficiency dramatically decreased in this time period. Therefore it can be concluded that the deposition experiment does not have to be carried out for time periods over 4 h.

5. Combined electroleaching/electrodeposition

The cell voltage usually decreased with time by occurrence of oxide leaching, passing from 30 V in the first minutes, to 8 V or so for the major part of the run. Figs. 8 and 9 report the

Table 2
Zinc mass balance for experiments 1 and 2

	Experiment 1	Experiment 2	
Catholyte composition	ZnSO$_4$ 0.2 M; H$_2$SO$_4$ 1N	ZnSO$_4$ 0.5 M; H$_2$SO$_4$ 1N	
Time of experiment (h)	4	4	8
Zinc-plated (g)	6.1	7.8	8.5
Deposition yield (%)	68	57	68
Current efficiency (%)	52	70	36

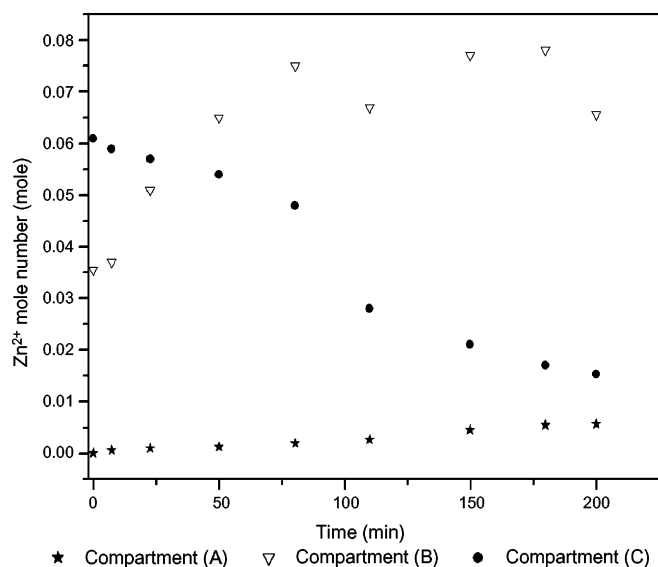Fig. 8. Variation of the Zn^{2+} mole number in the three compartments (experiment 3).

Fig. 10. Variation of the H^+ mole number in the three compartments (experiment 4).

variations of zinc amount in each compartment for experiments 3 and 4. These two experiments differed from each other by their duration and the presence of catholyte circulation ensured by a peristaltic pumps at 250 rpm or not. The operations were stopped as soon as formation of zinc dendrites was detected.

Experiments showed that with forced circulation of catholyte, the electroleaching/electrowinning operation can be carried out for longer periods of time. This is probably due to the destruction of formed dendrites by the catholyte flow.

Fig. 9 shows that during the third first hours, the zinc amount in compartment (B) was observed to increase, and to decrease beyond this time. This variation corresponds to accumulation of Zn^{2+} by ZnO leaching followed by Zn^{2+} migration to compartment (C), prior to its electrochemical reduction to metal zinc.
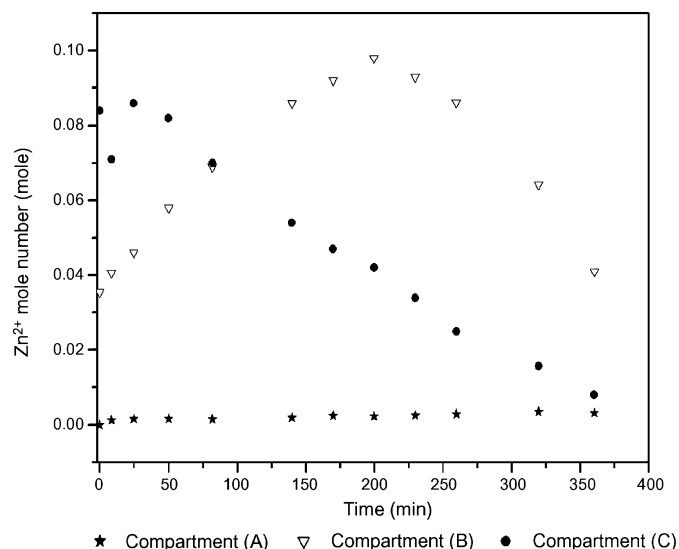
This is in agreement with the observations that one can make in Fig. 10. During the first period (3 h) H^+ mole number decreased in (C): this is due to the H^+ reduction that occurred when the Zn^{2+} concentration is too low. After this lapse of time the amount of H^+ stabilised in (C), corresponding to efficient Zn^{2+} reduction at the cathode. In the same time, H^+ mole number weakly increased in (B) because of the low consumption of this ion for ZnO leaching. Fig. 11(A–C) reporting the evolution of the transference number of the two cations in each compartment, confirms the global interpretation.

The operation time of experiment 3 was probably too short to allow significant migration of zinc to compartment (C) and quantitative zinc metal deposition.

It can be observed in Table 3 that the catholyte circulation, therefore the time period of the run, had a positive influence on leaching and deposition yields. For conditions summarised in Fig. 12, ZnO leaching yield was 97% and zinc could be plated with a deposition yield of 75%, with a current efficiency equal to 60% in the 6-h operation.

Besides, the metal produced in experiment 4 was of satisfactory quality, as it is shown in Fig. 13.

The power consumption for treatment of ZnO to electroplated zinc was found at 23.7 kWh/kg. This value is in good agreement with the works of Page et al. [18]. This specific power is far larger than required for zinc electrodeposition from sulphate-sulphuric

Fig. 9. Variation of the Zn^{2+} mole number in the three compartments (experiment 4).

Table 3
Zinc mass balance for experiments 3 and 4

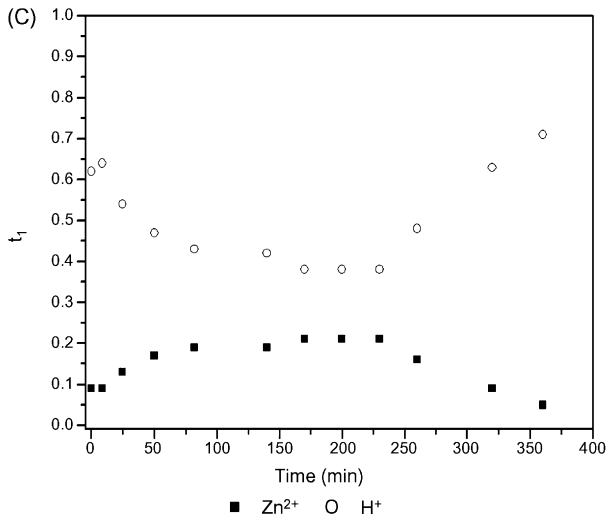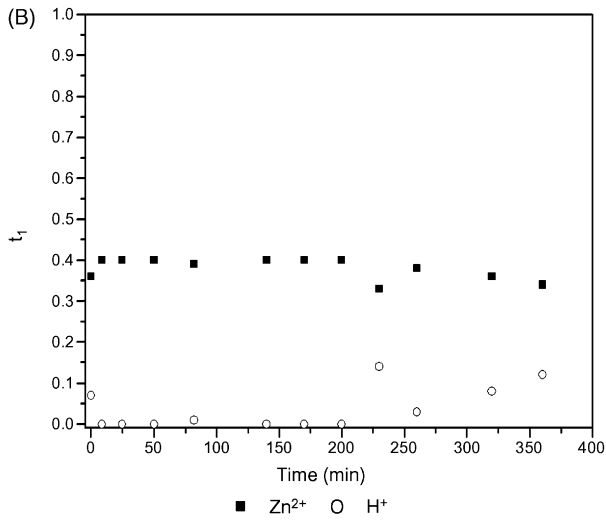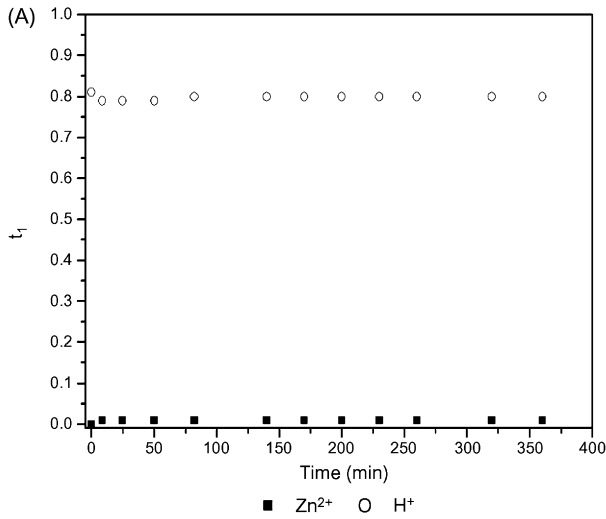|	Experiment 3	Experiment 4
Catholyte circulation	No	Yes
Time of experiment (h)	3.3	6
Leaching yield (%)	83	97
Zinc-plated (g)	6.4	10.5
Deposition yield (%)	48	75
Current efficiency (%)	66	60
Power consumption (kWh/kg)	28.9	23.7

Fig. 11. (A–C) Variation of the Zn^{2+} and H^+ transference numbers in the three compartments (experiment 4).
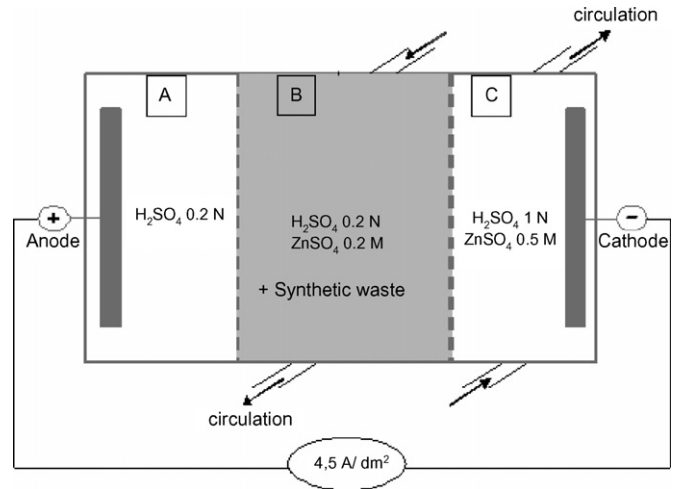

Fig. 12. Cell configuration.

Fig. 13. Aspect of the zinc coated cathode at the end of experiment 3.

medium, near 3.5 kWh/kg [33], although the power consumption involved in the leaching operation was not accounted for in their investigation dealing with deposition process. The design of the cell, governing the significance of the ohmic drops in the various chambers, has to be optimised for further development.

6. Conclusion

The present work was aimed at demonstrating the feasibility of a single-cell process for zinc recovery by electroleach-

ing/electrodeposition. After investigating the effect of the catholyte composition on both the deposition yield and the current efficiency without electroleaching operation, we had applied the optimal conditions on the combined operations.

Applying a current density at the two electrodes 4.5 A/dm^2 for 6 h, in the three-compartment cell allowed the treatment of 13.3 g ZnO dispersed in inert matrix: the leaching yield attained 97 and 70% of the leached zinc could be recovered in the form of compact metal.

This technique is now being developed for investigations of real metal oxides and salts such as roasted fractions of zinc sulphide, and zinc rich wastes like spent Zn–MnO$_2$ batteries.

Acknowledgements

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