Recovery of Zn from unsorted spent batteries using solvent extraction and electrodeposition

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ABSTRACT

This study focused on the selective recovery of zinc (Zn) from a leaching solution emerging from a sulfuric acid leaching process applied to unsorted spent batteries. Precipitation and solvent extraction were investigated. According to our results, solvent extraction using Cyanex 272 allowed for the selective removal of Zn from the solution containing high amounts of metals (~19.4 g Zn/L; ~23.4 g Mn/L, ~3.27 g Cd/L, ~3.19 g Ni/L, and ~0.25 g Co/L). According to the results, the solvent extraction process was capable of recovering 97.6% of Zn from this leaching solution under the following conditions: two stages of extraction in the presence of an organic solution made of Cyanex 272 (30%, v/v) and tributylphosphate (TBP - 2%, v/v) in kerosene, pH = 2.2, organic/aqueous (O/A) ratio = 2/1 and T = 50°C. The Zn present in the organic phase was then stripped using 0.4 M H₂SO₄ with an O/A ratio fixed at 2/1. This stripping step allowed for the recovery of 81.8% of the Zn initially present in the organic phase. Subsequently, 82.4% of the Zn stripped in the aqueous solution was then electrically deposited after 3 h at pH = 2 with a current density fixed at 360 A/m².

Keywords: Unsorted spent battery; Precipitation; Electrodeposition; Solvent extraction; Zinc.
INTRODUCTION

Recently, the increase in electronic device consumption has led to an increase in the amounts of spent batteries disposed in landfill sites. In 2004, among the 229 million alkaline battery units (Zn-MnO₂) sold in Canada, only 4.7 million units were recycled (RIS International, 2007). For zinc-carbon (Zn-C) batteries, 1.4 million units were recycled in 2004, whereas approximately 71 million units were sold during the same period. The market for secondary batteries (rechargeable batteries), including nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH) and lithium-ion (Li-ion), is less important than the market for primary batteries (non-rechargeable batteries). In the secondary batteries market, Ni-Cd batteries were the most sold in 2004 with 12.8 million units followed by Ni-MH with 4.1 million units and Li-ion cell with 1.5 million units (RIS International, 2007). According to Bonhomme et al. (2013), only 12% of spent batteries removed from service were recycled in Canada in 2010, whereas the other 88% were disposed in landfill sites or incinerated. However, the inappropriate management of large amounts of spent batteries represents a major threat for the environment due to the presence of toxic metals such as Cd, Co, Cu, Ni and Zn, and the risks associated with their potential dispersion through the soil and ground water.

In accordance with an environmental policy in Canada, the government applied the Extended Producers Responsibility Program to the waste primary and secondary batteries management, which means the battery’s producers take part in the battery recycling process (RIS International, 2007). Moreover, a non-profit organization named “Call2Recycle” was created by the Canadian Government to collect and promote the recycling of spent batteries with no cost for the municipalities, industries and consumers (Call2Recycle, 2012). This project was adopted by the Canadian government to restrict the amounts of spent batteries entering landfill sites and to
encourage the reuse of the metals contained in spent batteries as secondary raw materials (Call2Recycle, 2012). Thus, the development of physical, thermal, biological and/or chemical processes able to recycle the metals present in spent batteries, especially a process that is suitable for all of the types of spent batteries (alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion, etc.) is required.

Over the last several years, pyrometallurgical and hydrometallurgical processes have been widely developed to recover the valuable metals from spent batteries. Hydrometallurgical processes are more suitable to recover the low-grade metals such as Zn and Mn from spent batteries, whereas pyrometallurgical processes are more appropriate for the recovery of high-grade materials, such as gold, silver, cobalt and others, due to the high costs related to the consumption of energy. The other advantages of hydrometallurgical over pyrometallurgical processes are 1) lower energy consumption and 2) lower production of greenhouse gases (Yazici et al. 2013). Several researchers have shown the effectiveness of inorganic acids (H$_2$SO$_4$, HCl) and/or reducing agents (oxalic acid, carbohydrates, H$_2$O$_2$, SO$_2$/NH$_3$) in efficiently solubilizing the valuable metals present in spent batteries (Ferella et al. 2010; Furnali et al. 2009; Li and Xi 2005; Sayilgan et al. 2009). Currently, the main techniques used for the recovery of metal from acidic solutions include precipitation, ion-exchange, solvent extraction and/or electrodeposition. Among these methods, solvent extraction and precipitation seemed to be more appropriate for the recovery of metals from concentrated solutions while ion-exchange and electrodeposition were applied to more diluted solutions (Habashi 1999). Economically, these processes vary in feasibility; ion exchange was the most expensive, whereas selective precipitation was considered as the least expensive. The use of solvent extraction to recover metals from solutions containing various metals in high concentrations offers several advantages, such as its ease of operation, time-efficiency (equilibrium is quickly reached) and low costs compared to ion exchange.
For these reasons, it seemed reasonable to use solvent extraction and/or selective precipitation to selectively recover the Zn from acidic solutions containing others metals such as Co, Cd, Mn, Ni and Fe in high concentrations.

Solvent extraction was first applied in a hydrometallurgical process in 1947 for the Manhattan project (Freitas et al. 2007). Currently, many types of organic solvent, such as D2EHPA (di-2-ethylhexyl)phosphoric acid extractant) and Cyanex 272 (dialkyl phosphinic acid extractant), have been widely used at an industrial scale to selectively recover metals from industrial solutions. Those organic solvents have a specific function group that is used to selectively recover the metal from the pregnant leach solution (PLS). The selectivity of the organic solvent depends on many factors, including the electron density of the oxygen atoms of the reagents, the acidity and the strength and geometry of bonds formed in the inner coordinated sphere (Karstten et al. 2014). Recently, solvent extraction has been widely used for the selective recovery of metals from PLS obtained from the leaching of valuable metals from spent batteries. Provazi et al. (2011) showed that valuable metals present in unsorted spent batteries (alkaline, Zn-C, Ni-Cd, Ni-MH and Li-ion batteries) can be selectively recovered from an acidic leachate (H$_2$SO$_4$ at 1 M) using solvent extraction. The valuable metals were selectively extracted from the sulfuric acid solution by Cyanex 272 depending on the pH of the mixture. According to their results, 99% of Ti$^{4+}$ was extracted at pH = 1.0, 99% of Zn was extracted at pH = 2.5, 85% of Ni was extracted at pH = 3.0 and 80% of Cd and La were co-extracted at pH = 3.5. The other metals, such as Fe, Ce, Mn, Cr and Co, were extracted at pH = 7.0 with the extraction efficiencies higher than 88%.

According to Innocenzi and Veglio (2012), 99% of Zn could be selectively extracted from a PLS (40 g/L Ni, 20 g/L Mn and 10 g/L Zn) at pH = 2 using Cyanex 272 while Mn was completely extracted at pH = 7 (experimental conditions: Organic/Aqueous (O/A) ratio of 1/1; 2.42 M of

(Habashi 1999).
Cyanex 272 diluted in n-dodecane). The mixture of two organic solvents was also studied to increase the performance of Zn separation from Mn. Biswas et al. (2016) applied a mixture of PC88A (2-ethylexyl hydrogen 2-ethylhexyl phosphonate extractant) and Cyanex 272 to separate Zn from Mn. With this mixture, the Zn$^{2+}$ ions could be selectively extracted from the aqueous sulfate solution containing Mn$^{2+}$ (7.0 g/L) and Zn$^{2+}$ (2.2 g/L) at pH = 2 in the presence of 4% (v/v) of extractant in kerosene solution (reaction time = 10 min, O/A ratio = 1/1 (v/v), agitation = 300 strokes/min, T = 25°C). Their results indicated that a pH of 2.0 is suitable to separate Zn$^{2+}$ from Mn$^{2+}$. Indeed, the mixture of PC88A and Cyanex 272 could extract 60% of Zn from a PLS.

The originality of the present study is based on the use of a Cyanex 272 solvent extraction to selectively recover Zn from a PLS emerging from the recycling of unsorted spent batteries (alkaline, Zn-C, Li-ion, Ni-Cd, Ni-MH and Li-M). This PLS contained huge amounts of metals (Zn, Fe, Cd, Mn, Ni, Co, etc.), requiring the development of a purification process train to selectively recover Zn while minimizing the loss of the other valuable metals that could be recovered from the PLS. The present work was focused on the selective recovery of Zn from the PLS by comparing the performances of the selective precipitation and solvent extraction. The influence of solvent extraction parameters (pH, phase modifier concentration, reaction time, etc.) was also investigated.

This study aims to:

- Selective recover the Zn from the PLS by comparing the performances of the selective precipitation and solvent extraction (Cyanex 272 was used as an organic solvent);
- Investigate the influence of solvent extraction parameters (pH, phase modifier concentration, reaction time, etc.) on the recovery of Zn;
- Investigate the recovery of Zn by electrodeposition.

The recovery of residual metals (Mn, Cd, Ni, etc.) from the leaching solution will be also investigated in future work using other type of organic solvents.
BACKGROUND

Solvent extraction mechanisms

Cyanex 272 is an ester organic solvent formed by the reaction of an alcohol with inorganic acid (Habashi 1999). The group function of Cyanex 272 is a phosphinic acid. The metals present in aqueous solutions are extracted through a cationic exchange mechanism by the reaction described in Equation 1 (Coll et al. 2012).

\[
\text{Zn}^{2+} + 2 \text{RH} = \text{ZnR}_2 + 2 \text{H}^+ \]  

(1)

Where RH represents the cationic extractant.

Kerosene was usually used as a diluent due to its low dielectric constant leading to less polymerization of the extractant during the cationic exchange mechanism. Furthermore, it can diminish the viscosity of the organic solvent (Jay 2004).

Cyanex 272 can be used with PLS at low pH, which is useful for the selective recovery of metals from sulfuric acid leachates. This organic solvent can extract a variety of cationic metals. The selective extraction of metals from a solution containing sulfates using Cyanex 272 extractant at pH values ranging from 0.5 to 8.0 follows this sequence: \( \text{Fe}^{3+} > \text{V}^{4+} > \text{Zn}^{2+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ni}^{2+} \) (Cytec 2008).
Two parameters could be used to determine the capacity of an organic solvent to separate metals: the distribution coefficient and the separation factor. The distribution coefficient was determined using Equation 2 (Owusu 1998).

\[ D_M = \frac{[M_{\text{org}}]}{[M_{\text{aq}}]} \]  

(2)

Where \( D_M \) represents the distribution coefficient, \([M_{\text{org}}]\) represents the concentration of metal ions in the organic phase and \([M_{\text{aq}}]\) represents the concentration of metal ions in the aqueous phase.

The separation factor between two metals was calculated using Equation 3 (Habashi 1999).

\[ \beta_{A/B} = \frac{D_{MA}}{D_{MB}} \]  

(3)

Where \( \beta_{A/B} \) represents the separation factor and \( D_{MA} \) and \( D_{MB} \) represent the distribution coefficients of metal A and metal B, respectively.

The development of a solvent extraction process from a given pregnant leach solution should take into account several operating parameters. Indeed, various factors, such as the temperature, the flow rate, the acidity (pH), the O/A ratio, the phase modifier and so forth, should be
optimized depending on the composition of the PLS. According to Hutton-Ashkenny et al. (2015) a phase modifier should be added to prevent formation of crude material and to facilitate the O/A phase separation. This organic compound is meant to prevent the formation of a third phase between the organic and the aqueous phases, which is mainly caused by the limited solubility of the metal-ligand complex in the organic phase (Jha et al. 2006). From the literature, it appeared that the tributylphosphate (TBP) modifier interacts with metals and allows for the formation of adducts by replacing water molecules (Jay 2004). Subsequently, this modifier could enhance the metal extraction rate and reduce the water solubility of the complex. The operation of the solvent extraction phase at low pH enhances the reaction kinetics and decreases the retention time required for the O/A phase separation (Hutton-Ashkenny et al. 2015).

**Electrodeposition**

In electrochemical processes, the displacement of electrons is supplied by electron-donating species. Considering the standard electrode potential \( E^0 \) of the couple \( \text{Zn}^{2+}/\text{Zn}^0 \) \( (E^0 = -0.76 \, \text{V}) \), which is lower than the electrode potential of water decomposition \( (E^0 = 0.00 \, \text{V}) \), the ions \( \text{Zn}^{2+} \) will be reduced and deposited on the cathode during the electrodeposition process as revealed by Equation 4 (Scott et al. 1987). Parasite reactions related to the decomposition of water will occur at the cathode (Equation 5) and at the anode (Equation 6), decreasing the performances of \( \text{Zn}^{2+} \) ions reduction (Scott et al. 1987).

\[
\begin{align*}
\text{Cathodic reactions:} \\
\text{Zn}^{2+} + 2 \, \text{e}^- &= \text{Zn}(s), \quad E_0 = -0.76 \, \text{V} \quad (4) \\
2 \, \text{H}^+ + 2 \, \text{e}^- &= \text{H}_2(g), \quad E_0 = 0.00 \, \text{V} \quad (5)
\end{align*}
\]
Anodic reaction:

$$2\ H^+ + 2\ e^- + \frac{1}{2}\ O_2(g) = H_2O(l), \quad E_0 = -1.229\ V$$ (6)

The cathode current efficiency (CE) corresponds to the ratio of the mass of metal actually deposited on the cathode and the theoretical mass of metal that can be deposited on a cathode surface (Fatmehsari et al. 2009). This parameter indicates the current actually used for depositing the Zn$^{2+}$ ions from the total current applied (Carillo-Abad et al. 2015). Thus, an electrodeposition process with higher current efficiency (CE) shows the greater performances of metal of interest deposition (Fatmehsari et al. 2009).

$$CE = \frac{W'}{W} \times 100$$ (7)

Where $w'$ represents the mass of metal of interest actually deposited on a cathode and $w$ represents the theoretical mass of the metal of interest that could be deposited on a cathode.

**MATERIALS AND METHODS**

**Preparation of the pregnant leach solution**

**Preparation of real pregnant leach solution (PLSr) emerging from unsorted spent batteries**

Spent batteries, including Zn-MnO$_2$, Zn-C, Ni-Cd, Ni-MH, Li-ion and lithium iron, were retrieved from a spent batteries collection point located at the National Institute of Scientific
Research (Quebec, Canada). The unsorted spent batteries were frozen in liquid nitrogen and were then immediately dismantled to prevent the potential explosion of Li-M and Ni-MH batteries. The undesirable coarse particles (iron scraps, paper and plastic) present in the spent batteries were removed by screening through 1-mm and 2-mm aperture sieves. Finally, the black powder was ground using a pulverizer (Fritsch pulverisette, Serial no. 06 2000/01908, Germany). Then, 109 g of the black powder was mixed with 1 L of the leaching solution containing 1.34 M H$_2$SO$_4$ (Fisher, Canada) and 48 g of sodium meta-bisulfite (Na$_2$S$_2$O$_5$ – Fisher, Canada) for 45 mins. The optimal leaching conditions were obtained from a previous work (Tanong et al., 2017). After 45 min at room temperature, the solid was separated from the PLS by filtration. The composition of the PLS$_r$ obtained from the leaching process was characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 725-ES) apparatus. The real leach solution was used for the experiments carried out on the selective precipitation of metals and solvent extraction to validate assays with the synthetic pregnant leach solution.

**Preparation of the synthetic pregnant leach solution (PLS$_s$)**

PLS$_s$ was prepared based on the characterization results of the PLS$_r$ emerging from the metals leaching from unsorted spent batteries. According to the results, the metallic species present in the PLS$_r$ in small amounts (less than 1% of Ca, Li, Cu, Al, etc.) were neglected for the preparation of the PLS$_s$. The synthetic solution was used in the optimization of the experimental conditions in solvent extraction experiments.

The main metals, such as Mn, Zn, Ni, Cd, Fe and Co, were considered for the preparation of the synthetic solution. Analytical grade powders of ZnSO$_4$.7H$_2$O, MnSO$_4$.H$_2$O, CdSO$_4$.H$_2$O, CoSO$_4$.7H$_2$O and K$_2$SO$_4$ (Laboratoire MAT, Canada) were dissolved in distilled water to prepare a PLS$_s$. Concentrated H$_2$SO$_4$ was used to adjust the pH of the solution to approximately 1.00.
The pH was measured with a Fisher Scientific pH meter (model Accumet AR15), which was calibrated before each series of experiments. For the first series of solvent extraction experiments, a powder of FeSO$_4$.7H$_2$O (Laboratoire MAT, Quebec, Canada) was not added because the Fe was already removed by precipitation at pH = 4. However, a defined quantity of FeSO$_4$.7H$_2$O was added to the synthetic solution for the second series of solvent extraction assays to determine if this metal could be eliminated from the PLS$_r$ and from the organic phase using a selective stripping method.

**Precipitation**

For the first series of solvent extraction experiments, Fe was selectively removed from the PLS$_r$ by precipitation after the addition of H$_2$O$_2$ to oxidize Fe$^{2+}$ ions to Fe$^{3+}$ ions and the addition of NaOH until pH = 4.00 to precipitate Fe as Fe(OH)$_3$. Indeed, according to the Pourbaix diagram, the precipitation of iron is better at pH 4.00 once oxidized in its trivalent form. Various amounts of H$_2$O$_2$, corresponding to 1s, 1.25s and 2s where s is equal to the stoichiometric amount required to oxidize all of the Fe present in PLS$_r$, were added to compare the Fe removal efficiencies. Filtration on G6-Glass fiber filter (Fisher Scientific, porosity = 1.5 μm) was used to separate the aqueous and solid phases after precipitation and decantation during 30 min. The aqueous phase was then collected and transferred to the next experiments carried out to selectively recover the other metals, including Zn, using solvent extraction.

The selective precipitation of valuable metals initially present in the PLS$_r$ was carried out at ambient temperature in 500-mL Erlenmeyer flasks. All assays were conducted in triplicate with a working volume of 200 mL. During the precipitation, the PLS$_r$ was continuously mixed at 250 rotations per minute (rpm) using a magnetic agitator and a Teflon-coated stirring bar. The selective precipitation of Zn, Mn, Cd, Ni and Co was studied by adjusting the pH of the PLS$_r$ at
During the first series of experiments, a solution of NaOH (40 g/L, Fisher, Canada) was gradually added to adjust the pH of the PLS$_r$. However, for the second series of experiments, a NaOH solution was stepwise added to the PLS$_r$ until pH = 4.00 and a powder of Na$_2$CO$_3$ (Fisher, Canada) was then used to increase the pH to precipitate the metals as carbonates.

Solvent extraction

Preparation of the organic solvent

The extractant Cyanex 272 used in this study was provided by Cytec Canada Inc. (Ontario, Canada). This extractant was composed of 85% of bis(2,4,4-trimethylpentyl) phosphinic acid and had a specific gravity of 0.92 g/cm$^3$ at 24°C. The organic solvent was prepared before each series of solvent extraction experiments in a 1-L glass tanks by mixing 20% (v/v) Cyanex 272; 2-5% (v/v) TBP (tributylphosphate, 97%, Sigma Aldrich, Canada) and 75% (v/v) kerosene (Recochem. Inc., Canada).

Solvent extraction procedure

Solvent extraction experiments were carried out in 250-mL beakers at 50°C (Cytec, 2008). The aqueous phase was mixed with the organic phase with an O/A ratio of 2/1 (v/v), which corresponded to the limit of organic loading. The maximum organic loading was fixed at approximately 65% by the company Cytec to prevent the precipitation of metals. These two phases were then mixed at 400 rpm. With an O/A ratio of 2/1 and an initial concentration of 19.4 g Zn/L, the percentage of Cyanex 272 that should be used to completely extract all of the Zn$^{2+}$ ions present in PLS$_s$ was estimated at 17.0% (v/v). However, 20% vol. of Cyanex 272 was chosen due to its ease of preparation.
The first set of extraction experiments, performed in triplicate, successively determined the influence of different parameters, such as pH (1.5, 2.0, 2.5, 3.0 and 4.0) (Cytec, 2008), equilibration time (5, 10, 20, 30 and 60 min) and [TBP] (0, 2 and 5% (v/v)) (Cytec, 2008) on the selective extraction of Zn from the PLS. The equilibrium pH was controlled during the experiments by adding a concentrated solution of NaOH (10 M) and/or a dilute solution of H$_2$SO$_4$ (1 M). Subsequently, the mixture was transferred to a funnel to separate the organic phase from the aqueous phase. The organic phase was then transferred to the stripping procedure to recover the Zn extracted. Once the appropriate extraction conditions were determined, the extraction process was repeated in triplicate to verify its effectiveness and reproducibility with the real pregnant leach solution.

**Stripping procedure of the organic solvent**

The organic phase emerging from the solvent extraction step (metals-Cyanex272) was sent to the stripping step to transfer the metals of interest into an aqueous phase. The stripping step was carried out in a 250-mL beaker by applying a solution of sulfuric acid (0.4 M and 0.5 M) with an O/A ratio of 2/1 (v/v). The organic and aqueous phases were mixed for 10 min at 400 rpm, and the temperature was kept constant at 50°C through the experiments. Two stripping stages were conducted to ensure that all of the Zn was recovered from the organic phase. For each stage of stripping, a fresh solution of H$_2$SO$_4$ was added to the organic phase after separation of the two phases. During the extraction step, the Fe$^{2+}$ ions were co-extracted with the Zn$^{2+}$ ions in the organic phase, which was inevitable due to its affinity for the functional group of Cyanex 272 at pH lower than the optimal pH for Zn extraction. For this reason, a solution of H$_2$SO$_4$ (1 M) with an O/A ratio of 2/1 (v/v) was applied to strip all of the Fe$^{2+}$ ions from the organic phase after the stripping stages applied for the recovery of Zn$^{2+}$ ions. The stripping conditions used for the Fe$^{2+}$
ions were similar those used for the Zn$^{2+}$ ion stripping except for the acid concentration (0.4 – 0.5 M for Zn$^{2+}$ ions versus 1.0 M for Fe$^{2+}$ ions). Only one stage of stripping was required for the recovery of Fe$^{2+}$ ions. This stripped organic solvent was then reused for the next extraction cycle.

**Electrochemical experiment**

The electrodeposition experiments were carried out in a reactor made of acrylic with a dimension of 3.5 cm (width), 13.5 cm (length) and 17 cm (depth). A stainless steel electrode was used as the cathode and a Ti/IrO$_2$ electrode was used as the anode. The surface area available for the deposition of Zn was estimated at 110 cm$^2$ and the distance between the electrodes was equal to 1 cm. A quantity of 500 mL of the solution emerging from the stripping steps carried out to recover the Zn solution was used in the electrochemical experiment. The initial pH of this solution was adjusted at 2.0, 2.5 or 3.0 by the addition of a solution of NaOH. No alkaline solution was added to control the pH during the electrodeposition process and the final pH was measured at the end of each experiment. Once introduced in the reactor, the PLS, was continuously mixed by allowing a water recirculation into the system. The current density was fixed at 360 A/m$^2$, and the experiments were carried out at ambient temperature. The electrochemical experiments were conducted for 3 h, and 1 mL of sample was collected after 5, 10, 20, 30, 60, 120 and 180 min to select the optimal reaction time. A decrease of the potential value with time was observed during the experiment. The residual concentrations of Zn were measured in each sample to evaluate the performance of Zn deposition with time. Additionally, at the end of electrodeposition experiment, the cathode was washed by an exact volume of 5% HNO$_3$ to determine the impurities present in the Zn metallic obtained. The purity of Zn powder was also evaluated by scanning electron microscope (SEM).
Analytical techniques

The aqueous samples were analyzed by ICP-AES (Inductively coupled plasma - atomic emission spectroscopy, Varian 725-ES) (Tanong et al., 2017). The samples emerging from the precipitation and electrodeposition experiments were filtered through a G6 glass fiber paper (G6, Fisher brand, Fisher Scientific, Canada) to remove the solid particles (pore size = 1.5 µm) and then preserved in 5% HNO₃ before analysis. The aqueous samples emerging from the solvent extraction experiments were preserved in 5% HNO₃ before analysis.

The purity of Zn metallic from electrodeposition experiment was determined using a scanning electron microscope (SEM, Carl Zeiss EVO®50) equipped with an X-ray energy dispersion spectrometer (EDS, Oxford Instrument, INCA x-sight EDS). The metal images were generated with a Quadra-Pole Backscatter detector at - 20 kV accelerating voltage with a current beam of 100 µA and analyzed with EDS to confirm the presence of other metals.

RESULTS AND DISCUSSION

Characterization of the PLSᵣ and the PLSₛ

Table 1 presents the characteristics of the PLSᵣ resulting from the leaching process (H₂SO₄ + Na₂S₂O₅) applied to unsorted spent batteries (alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion and Li-M) used for the precipitation experiments. This table also shows the composition of the synthetic solution used for the solvent extraction assays. The composition of both the PLSᵣ and the PLSₛ were quite similar, except for the concentration of Fe (0.53 g/L in PLSᵣ versus 0.005 g/L in PLSₛ). Indeed, Fe ions were removed by selective precipitation before they were reintroduced into the PLSₛ during the solvent extraction process, which explains why the concentration of Fe was lower in the synthetic solution. Initially, the PLSᵣ contained 27.5 ± 2.4 g Mn/L,
19.9 ± 1.8 g Zn/L, 3.17 ± 0.24 g Cd/L, 3.51 ± 0.30 g Ni/L, 0.26 ± 0.02 g Co/L and 0.53 ± 0.05 g Fe/L. The high concentration of potassium found in the PLS (4.58 ± 0.12 g K/L) was due to the use of KOH as the electrolyte in the production of alkaline batteries.

**Metal selective recovery using precipitation**

Precipitation of Fe from the solution containing Zn, Cd, Mn, Ni and Co.

An initial series of experiments was conducted to determine if Fe ions can be selectively removed from the PLS by precipitation as hydroxides at pH = 4.0 after oxidation of ferrous ions (Fe$^{2+}$) to ferric ions (Fe$^{3+}$). Table 2 presents the metal removal yields obtained at pH = 4.0 depending on the amounts of H$_2$O$_2$ added to the PLS (1s, 1.25s and 2s where s is equal to the stoichiometry value required to oxidize all ferrous ions present in the PLS). According to these results, an increase in the amount of H$_2$O$_2$ added from 1s to 1.25s led to an increase in the removal of Fe from 69.3 ± 12.3% to 92.4 ± 1.8%, whereas its increase from 1.25s to 2s did not lead to an increase in Fe removal yield. The highest Fe removal efficiencies were obtained with the amount of H$_2$O$_2$ is equal to 1.25s. According to these results, the precipitation of Fe as ferric hydroxide (Fe(OH)$_3$) when using 1.25 times of H$_2$O$_2$ stoichiometry at pH = 4.0 was highly efficient, reaching 92.4% removal of Fe. Under these operating conditions, we noticed that only 2.78% of Co, 3.30% of Mn, 2.72% Ni, 3.14% of Cd and 4.29% of Zn were removed from the PLS, which was quite favorable for the selective recovery of these valuable metals, especially Zn.
Precipitation of metal as hydroxides

A second series of experiments was conducted to determine if the valuable metals present in the PLSr could be selectively removed from the solution by successive additions of a solution of NaOH to precipitate the metals as hydroxides (Equation 8).

\[ M^{2+} + 2 \text{OH}^- \rightarrow M(\text{OH})_2 \]  

where \( M \) represents the metals present in the PLSr, such as Zn, Cd, Ni and Co.

Fig. 1 presents the residual concentrations of the metals initially present in the PLSr, including Zn measured in the supernatant after precipitation at different pH using NaOH. According to these results, the precipitation of Zn was quite negligible in the pH range of 1 to 4. Indeed, according to the results presented in Fig. 1a, the precipitation of Zn started at pH = 4 and was complete at pH = 8. From the results presented in Fig. 1a and Fig. 1b, we can notice that the same precipitation behaviors were observed for Ni, Cd and Mn. Indeed, the concentration of these metals measured in the supernatant were stable in the pH range of 1 to 4 (from 3.17 g/L to 2.82 g/L for Cd, from 27.5 g/L to 24.6 g/L for Mn, and from 3.51 g/L to 3.12 g/L for Ni).

Between pH 1 and 4, the concentrations of Co and Fe slightly decreased from 0.26 to 0.23 g Co/L and from 0.53 to 0.37 g Fe/L. The concentrations of Cd, Mn and Ni started to decrease in the pH range of 4 and 6, and a complete precipitation of these metals was observed at pH = 12. Therefore, precipitation using a solution of NaOH was not suitable for the selective
recovery of Zn present in a leaching solution containing high concentrations of Cd, Ni and Mn. For example, 15.7% of Zn was precipitated at pH = 5.0, while approximately 13.2% of Ni, 12.4% of Co, 12.0% of Cd, 39.7% of Fe and 11.0% of Mn had co-precipitated.

Precipitation of metal carbonates

As the selective recovery of the Zn present in PLSr containing high amounts of Cd, Ni and Mn using precipitation of metals as hydroxides was inefficient, additional experiments were performed in the presence of NaOH and Na2CO3. The objective of this third series of experiments was to determine if Zn can be selectively recovered from the PLSr as zinc carbonate (Equation 9).

\[
x M^{x+}(aq) + y CO_3^{2-}(aq) \leftrightarrow M_x(CO_3)_y(s)
\] (9)

where M represents the metals present in the PLSr, such as Zn, Cd, Mn, Ni and Co.

Fig. 1c and Fig. 1d present the residual concentrations of the metals initially present in the PLSr, including Zn, measured in the supernatant after precipitation at different pH using NaOH and Na2CO3. The results from these precipitation tests showed the same tendency as the experiments conducted in the previous section in the presence of only NaOH. Between pH 1 and 4, the metals initially present in the PLSr (Cd, Ni, Zn, Co, Fe and Mn) did not precipitate or slowly precipitated (only Fe); they started to precipitate pH between 4 and 6. At pH = 5, approximately 24.0% of Zn was precipitated as carbonates, while 20.9% of Cd, 19.7% Ni, 20.1% Co and 19.3% Mn precipitated at the same condition. According to these results, the selective precipitation of
Zn as carbonates from the PLS<sub>r</sub> was not efficient at pH near 5. Notably, most of the metals present in the PLS<sub>r</sub> were mostly precipitated at pH = 7. These results implied that Zn could not be selectively precipitate from the leaching solution when using a combination of NaOH (until pH = 4) and Na<sub>2</sub>CO<sub>3</sub> due to the large amounts of Mn, Ni and Cd initially present in the PLS<sub>r</sub>. Similar results were found in the study conducted by Provazi et al. (2011) where the selective precipitation of valuable metals from a leaching solution emerging from the solubilization of metals from a mixture of spent batteries was not achieved. In their study, the combination of H<sub>2</sub>O<sub>2</sub> and NaOH was applied to selectively precipitate the valuable metals from the leaching solution at different pH values. According to their results, the metals present in high concentrations co-precipitated with the metals present in low concentrations, which rendered the selective recovery of each metal difficult. As the precipitation of metals as hydroxides and carbonates was not successful to selectively recover Zn from the PLS<sub>r</sub>, solvent extraction was studied as an alternative option. These results will be discussed in the following section.

**Solvent extraction**

In the following section, all of the results were expressed for the treatment of one liter of synthetic solution containing 3.27 g of Cd, 3.64 g of K, 23.4 g of Mn, 3.19 g of Ni, 19.4 g of Zn and 0.25 g of Co, even if the experiments were actually performed in smaller volumes.

**Extraction pH isotherm**

Fig. 2 presents the extraction pH isotherms obtained for Zn, Cd, Co, Mn and Ni that were used to determine the optimal pH for selective recovery of Zn from the synthetic solution. According to these results, it can be noticed that the extraction rate of Zn from the synthetic solution increased with an increase in the pH values. At pH = 3, approximately 85.8% of Zn (16.5 g) was extracted, whereas almost all of the Zn initially present in the solution was extracted (17.5 g) at pH = 3.5.
with a recovery of 90.2%. These isotherms were constructed to determine the equilibrium pH values at which the Mn, Cd and Ni could be co-extracted with Zn in the organic phase. From the results presented in Fig. 2, the unwanted metals were co-extracted with Zn in the organic phase from pH 2.0 to 3.5 for Mn and from pH 3.0 to 3.5 for Cd and Ni. At pH = 3.5, 17.5 g of Zn were transferred to the organic phase with high amounts of Mn (4.59 g), Cd (0.46 g), Ni (0.44 g) and Co (0.05 g). Similar results were obtained in the studies conducted by Salgado et al. (2003), under similar operating conditions (20% of Cyanex 272 at 50°C). According to these studies, approximately 60% of the Zn was extracted at the equilibrium pH of 2 whereas 57.1% of Zn was extracted at the same equilibrium pH in the present study. However, some experimental conditions were slightly different from our study, such as the initial concentration of Zn and the O/A ratio used. In the study conducted by Salgado et al. (2003), the initial concentration of Zn and the O/A ratio were 5.24 g/L and 1/1 (v/v), while in our study, they were equal to 19.4 g/L and 2/1 (v/v), respectively. This observation implied that the optimal equilibrium pH seemed to be independent of the initial concentration of Zn and the O/A ratio if the amount of Cyanex 272 used is sufficient. Based on Fig. 2, the highest Zn extraction rates were obtained at pH values between 3.0 and 3.5. However, according to a personal discussion with the Cytec company, the extraction efficiencies should not exceed 60-65% to prevent metal precipitation in the organic phase. It seemed that the highest purity of Zn extracted in the organic phase was obtained at pH approximately 1.5 (Fig. 2) as the co-extraction of Mn, Cd, Co and Ni were insignificant. However, the amounts of Zn extracted in the organic phase were very low (4.3 g) at pH = 1.5. It appeared that a solvent extraction carried out at pH between 2.0 and 2.5 was a good compromise in terms of amounts of Zn extracted and purity of Zn in the organic phase. The highest separation factors observed between Zn$^{2+}$ and Mn$^{2+}$ using Cyanex 272 were obtained for similar pH values.
in the studies conducted by Salgado et al. (2003) and Nathsaruma and Devi (2006). Therefore, solvent extraction conditions in this stage were chosen as follows: $T = 50^\circ\text{C}$, O/A ratio = 2/1, 20% vol. Cyanex 272 and 2% vol. TBP in kerosene, residence time = 10 min, and pH = 2.2.

Effect of TBP concentration

The effect of the TBP concentration on the extraction efficiencies was studied, and the results are revealed in Table 3. These experiments were conducted in triplicate by varying the TBP concentration, while the other parameters remained constant (O/A ratio = 2/1, 20% vol. Cyanex 272 in kerosene, residence time = 10 min, pH = 2.5, $T = 50^\circ\text{C}$). According to a Student’s $t$-test (results not shown), the removal of Zn from the synthetic solution seemed to be insignificantly influenced by the amount of TBP added in the organic phase ([TBP] between 0 and 5% (v/v). However, the quantity of TBP added in the organic solvent seemed to have a significant effect on the extraction rates obtained for Cd, Co and Ni between 0 and 2% (v/v) and for Cd, Co, Mn and Ni between 0 and 5% (v/v). According to these results, Zn extraction efficiencies obtained when using 0%, 2% and 5% TBP were equal to 54.4% (10.6 g), 59.7% (11.6 g) and 49.2% (9.54 g), respectively, while approximately 2.98% (0.70 g), 9.20% (2.15 g) and 6.26% (1.47 g) of Mn were co-extracted in the organic phase. Eskandari and Najafabadi (2016) highlighted the insignificant effect of TBP concentration (2.5 – 10%) on Zn extraction efficiencies by D2EHPA, which was similar to our results. Therefore, the TBP addition in this study could be beneficial, as it improved the separation of both the organic and aqueous phases.

For all of the aforementioned reasons, the use of 2% vol. TBP was chosen for the remaining experiments. When using 2% vol. TBP, 59.7% of Zn (11.6 g) were transferred from the PLS, to the organic phase, whereas approximately 0.33 g of Cd, 0.03 g of Co, 2.15 g of Mn and 0.31 g of Ni were co-extracted.
Effect of reaction time

Table 4 presents the kinetics of metal extraction efficiencies from the synthetic solution obtained with the Cyanex 272-TBP-Kerosene system using the following experimental conditions: O/A ratio = 2/1, pH = 2.2, 20% vol. Cyanex 272; 2% vol. TBP, T = 50°C. According to the results presented in Table 4, the Zn was mostly extracted within 5 min. However, it seemed that the equilibrium between the two phases (organic and aqueous) was not stable for the other metals initially present in the PLSs. After 5 min, the standard deviation values obtained for Mn²⁺, Cd²⁺, Co²⁺ and Ni²⁺ were highly different from their average values, indicating that the system was not stable for these compounds. The effect of contacting time on solvent extraction efficiency was also studied by Gupta et al. (2002), which highlighted that the equilibrium was reached after only 2 min when they extracted a volume of 10 mL of the aqueous phase. Their research also showed that a prolonged reaction time did not have an adverse effect on the extraction efficiency.

Generally, the equilibrium of a solvent extraction process can be achieved in a short period of time, which was also confirmed by the study of Hereijgers et al. (2016). According to these authors, the equilibrium extraction of cobalt using Cyanex 272 was attained after less than 1 min.

To ensure that the equilibrium of the reaction was attained and to reduce the costs (shaking and maintaining the temperature at 50°C), a reaction time of 10 min was selected in our study as suggested by Haghshenas et al. (2009).

Distribution coefficient and the separation factor of Zn, Mn and Cd in Cyanex 272

Table 5 reveals the distribution coefficient of Zn, Mn and Cd and the separation factors of Zn from Mn and Cd at different pH values applying Equations 2 and 3. The $D_{Zn}$ values obtained were equal to 0.33, 1.54, 2.35, 40.5 and 330 for the experiments performed at pH 1.5, 2.0, 2.5, 3.0 and 3.5, respectively. According to these results, it could be noticed that the $D_{Zn}$ values
increased with increasing pH of the aqueous phase (3.5 > 3.0 > 2.5 > 2.0 > 1.5); indicating that larger amounts of Zn were transferred to the organic phase when the pH of the aqueous phase was increased from 1.5 to 3.5. This observation corresponded to the results obtained by Hosseini (Hosseini et al. 2010). Considering the $\beta_{Zn/Mn}$ (separation factor between Zn and Mn) and $\beta_{Zn/Cd}$ (separation factor between Zn and Cd), these factors increased with pH values until the equilibrium pH reached 3.0. Indeed, the highest values of $\beta_{Zn/Mn}$ and $\beta_{Zn/Cd}$ were obtained at pH = 3.0, with values reaching 538 and 643, respectively. These high values of $\beta_{Zn/Mn}$ and $\beta_{Zn/Cd}$ indicated that the separation of Zn from Mn and Cd was efficient using Cyanex 272 at pH = 3.0. Beyond pH = 3.0, the $\beta_{Zn/Mn}$ and $\beta_{Zn/Cd}$ values decreased due to the co-extraction of Mn and Cd in the organic phase. In their study, Chen et al. (2015) observed the variation of $\beta_{Co/Ni}$ values at different equilibrium pH values (15% vol. Mextral in kerosene and A/O ratio = 1/1 at ambient temperature). Based on their results, the values of $\beta_{Co/Ni}$ increased with the increase of the pH value until the equilibrium pH reached 4.5 and then decreased until the pH values reached 6.0. Similar trends of these variations in $\beta_{Zn/Mn}$ values with the pH were also observed in the study conducted by Fleitlikh et al. (2011) with a mixture of Cyanex 302 (0.4 M), TAA (tert-amyl alcohol) (0.5 M) and 10% n-octanol in kerosene. Indeed, the $\beta_{Zn/Mn}$ value increased from 94 to 980 when the pH increased from 4.39 to 6.34 (leach solution: 8.65 g/L Zn$^{2+}$, 3.15 g/L Mn$^{2+}$, 10 min extraction time at 22°C).

The separation factors between Zn$^{2+}$ and Cd$^{2+}$ as well as Zn$^{2+}$ and Mn$^{2+}$ increased with the increase in pH values when the pH was lower than 3.0. From these results, it appeared that the operating pH should not be higher than 3.0 and should be maintained between 2.0 and 2.5 to prevent precipitation of metals in the organic phase. Thus, these conditions allow for the
selective transfer of Zn from PLS to the organic phase without co-extracting other metals in huge amounts.

Effect of the extraction stage number

Three extraction stages were conducted to determine the effectiveness of Zn extraction from the PLSs. Table 6 shows the residual amounts of Zn present in the PLSs obtained after each stage of extraction. The Zn extraction efficiencies from the PLSs obtained after the first, the second and the third stage reached 68.4%, 99.2% and 99.9%, respectively, whereas small amounts of Cd, Co, Mn and Ni were co-extracted. Thus, two extraction steps were used for the remaining experiments.

Effectiveness of Zn extraction

According to the results mentioned above, the selective extraction of Zn from the synthetic solution was highly favorable after two extraction stages with an O/A ratio of 2/1, 20% vol. Cyanex 272 in kerosene, 2% vol. TBP, a residence time of 10 min, a pH = 2.2 and a temperature of 50°C. Indeed, under such operating conditions, highly effective separations of Zn from the PLSs containing high amounts of Mn, Cd, Ni and Co were obtained. It was important to apply this solvent extraction process to the real leaching solution (PLSr). Therefore, the above operating conditions were applied to the PLSr in triplicate to verify the effectiveness and the reproducibility of the solvent extraction process we developed. Moreover, these additional experiments were performed on the PLSr without performing the precipitation of Fe to verify if this step could be replaced by a selective stripping method, which was simpler. The higher percentage of Cyanex 272 (30% vol.) was applied because of the increased Zn concentration and the presence of Fe in the PLSr. The results obtained are summarized in Table 7. According to these results, it was found that approximately 72.0% (14.91 g) of the Zn were extracted from the
the first stage of extraction and that almost all of the Zn (97.6%) was extracted after
the second extraction stage. After two extraction stages, the Zn extraction yield reached 97.6%
(19.61 g) whereas 98.8% of Fe (0.49 g), 7.13% of Cd (0.85 g), 2.35% of Co (0.004 g), 4.12% of
Mn (1.61 g) and 7.28% of Ni (0.41 g) were also co-extracted with Zn during its transfer to the
organic phase.

Stripping experiments

Extraction experiments using Cyanex 272 as the organic solvent were conducted in triplicate on
the real leachate following the operational conditions described in the previous section. Stripping
experiments were then performed on the organic phase to selectively recover the Zn using
different concentrations of a solution of H$_2$SO$_4$ (0.15 M - 0.40 M and 1.00 M). The results
obtained from the stripping experiments are expressed for the treatment of 1 L of the PLS$_r$ and
are presented in Table 8. The amounts of Zn recovered from the organic phase initially
containing 19.6 g of Zn were estimated at 12.9 and 16.0 g for stripping experiments performed at
H$_2$SO$_4$ concentrations of 0.15 M and 0.40 M, respectively. According to these results, an
increase in the concentration of H$_2$SO$_4$ concentration from 0.15 M to 0.40 M led to an increase in
the amount of Zn recovered from the organic phase without modifying the amount of Fe
transferred to the stripping solution. The best stripping efficiencies were obtained when applying
0.4 M of H$_2$SO$_4$, reaching 81.8% after one stripping stage (16.0 g) and 88.5% after two stripping
stages (17.3 g) (results not shown). According to these results, it can be noticed that only small
amounts of Zn (1.3 g) were recuperated during the second stripping step. Therefore, one
stripping stage performed in the presence of 0.40 M of H$_2$SO$_4$ was chosen for the selective
stripping of Zn for the next experiments.
Fe removal could also be conducted by a selective stripping process. The stripping experiment was conducted by applying two sequential stripping steps. The first stripping was conducted to recover ZnSO₄ for electrodeposition and the second stripping was applied for Fe removal. The results presented in Table 8 showed that only the Zn was transferred to the stripping solution during the first stripping step performed at 0.4 M H₂SO₄. The Fe present in the organic phase was then stripped using 1.0 M of H₂SO₄ with an O/A ratio of 1 (v/v) to remove all of the Fe initially present in the organic phase. The results obtained after the second stripping stage showed that 65% of the Fe (0.29 g) was removed from the organic phase; allowing this solution to be recycled in the solvent extraction process.

Table 9 presents the concentration of metals measured in the effluent emerging from stripping steps that will be used for the electrodeposition of Zn. According to Haghighi et al. (2015), the concentration of Co and Ni should not be greater than 0.5 and 1.0 mg/L, respectively, in order to attain reasonable costs for the Zn electrodeposition process. For iron, it should not be greater than 20 mg/L. For Cd, it should be less than 1 mg/L. The concentration of Mn greater than 10 g/L would affect the Zn electrodeposition efficiencies (decrease of the faradic yield due to electrochemical parasitic reactions) and costs (increase of the frequency of electrodes cleaning).

From our experiment results presented in Table 10, it could be noticed that the concentration of Co was equal to 1.1 mg/L while Ni was not detected. The concentration of Mn was equal to only 0.17 g/L. The concentrations of Cd (2.9 mg/L) and Fe (98 mg/L) were higher than the concentrations recommended by Haghighi et al. (2015). From the previous reason, the scrubbing stage was highly recommended to remove the Cd from the organic phase and an additional step is recommended to remove Fe by precipitation method.
Mass balance of the solvent extraction process

Table 10 presents the mass balance performed for the solvent extraction experiments including both solvent extraction and stripping steps. The determination of the mass balance of a solvent extraction system is important to ensure that there is no accumulation, contamination or loss of metals during the different steps (extraction, stripping). According to the results obtained, the mass balance ratios were closed to 1 for all the metals (between 0.99 and 1.03); indicating that the balance error didn’t exceed 3%. These results indicated that the solvent extraction process is reliable.

Zn electrodeposition

Fig. 3 summarizes the global hydrometallurgical process developed in the present study to selectively recover the Zn from the PLS, produced by the leaching process applied to unsorted spent batteries that contains huge amounts of Zn, Mn, Cd, Ni, Co, and Fe. Electrodeposition experiments were carried out on the stripping solution obtained from the experiments conducted to recover the Zn. Fig. 4 illustrates the results of the Zn electrodeposition obtained at different pH values. During the experiments, a pH drop was observed at the end of each experiment due to the production of H₂SO₄ from unreacted sulfate ions and hydrogen ions dislodged during water decomposition (Fatmehsari et al. 2009). Even if the main impurities (Mn, Co, Ni, Cd and Fe) were removed from the Zn-enriched solution using various solvent extraction and stripping steps, trace elements were still presented in the ZnSO₄ solution obtained from the stripping step. Indeed, the Zn-enriched stripping solution initially contained 9.2 g Zn/L, 0.032 g Fe/L, 0.259 g Mn/L, 0.005 g Cd/L, 0.003 g Co/L and 0.002 g Ni/L. Iron could be co-deposited with the Zn at the cathode, while Mn can be oxidized and precipitated as MnO₂ rather than being deposited on the cathode. From our results, it can be noticed that large amounts of Zn were
initially lost at pH = 3.0 due to the precipitation of this metal at pH higher than 2.5. Moreover, it appeared that an increase of the retention time from 0 to 180 min led to an increase of the amount of Zn deposited independent of the initial pH of the Zn-enriched stripping solution. According to our results, Zn electrodeposition efficiencies were equal to 63.5%, 82.4%, and 47.5% for the experiments carried out at pH = 2.0, 2.5 and 3.0, respectively after 180 min. The current efficiencies were also calculated according to the Equation 7 and were estimated at 51.3%, 40.3% and 22.3% for pH = 2.0, 2.5 and 3.0, respectively. These results indicated that parasite reactions related to the decomposition of water were more important at higher pH values. From these results, the highest Zn electrodeposition rate was obtained at pH = 2.5; indicating that this pH was more favorable for the electrodeposition of Zn. The deposit obtained was characterized using an ICP-AES to determine its composition and a MEB-EDS to confirm if there were a present of some impurities or not. The result from the ICP-AES and EDS analysis (Fig. 5) showed that the metallic powder was mainly composed of Zn with the presence of some impurities (< 1% of Fe, Cd, Mn).
CONCLUSIONS

In this study, the Zn initially present in a PLS$_s$ or PLS$_r$ containing huge amounts of Mn, Cd, Ni, Co, and Fe was successfully and selectively extracted and recovered as a metallic deposit. According to our results, the selective precipitation of Zn as hydroxides or carbonates from the PLS was not efficient. Cyanex 272 was proven to be an effective solvent to separate Zn from the other metals (Mn, Cd, Co and Ni) present in the leaching solution. The influence of the operating conditions of the solvent extraction process was studied, and the optimal conditions were determined in the present study. According to our results, an organic phase composed of 30% vol. Cyanex 272 and 2% vol. TBP in kerosene could be used to extract 97.6% of Zn from the PLS using the following operating conditions: two extraction stages, O/A ratio = 2/1 (v/v), residence time = 10 min and $T = 50^\circ C$. Under these solvent extraction conditions, large amounts of Fe and small amounts of Mn, Ni and Cd were co-extracted in the organic phase. The use of a diluted solution of $H_2SO_4$ (0.40 M) seemed to be highly efficient to selectively strip the Zn from the organic phase after only one stripping stage, with 81.8% of Zn stripping efficiency. The Zn can then be efficiently recovered from the Zn-enriched stripping solution by electrodeposition, with electrodeposition efficiencies reaching 82.4% after 180 min of electrodeposition at pH = 2.5. The selective recovery of other metals such as Mn, Ni, Co and Cd from the PLS using D2EHPA and/or Cyanex 272 extraction steps has been studied in another work and the results seemed promising. The possibility to transfer this process from laboratory to the commercial scale is considered as a difficult task, requiring additional works. For example, the preparation of spent batteries should be improved to obtain the maximum metals yields during the leaching step. Before the Zn electrodeposition step, Zn should be concentrated in the aqueous phase by the use of a stripping step with higher O/A ratios in order to improve the performance of the
electrodeposition (increase of Faraday yield). The impurities such as Cd and Fe should be removed using some additional processes to improve the quality of Zn deposit and reduce electrochemical parasitic reactions. The difficulty of social acceptability of this process due to the use of organic solvent was also encountered. However, green alternative solvent could be used to replace the current solvent used when they will be commercially available.

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REFERENCES


F I G U R E C A P T I O N L I S T

Fig. 1  Residual concentrations of Zn, Mn, Cd and Ni (a., c.) and Co and Fe (b., d.) present in the sulfate solution after precipitation in the presence of NaOH (a., b.) or NaOH+Na₂CO₃ (c., d.) at 25°C

Fig. 2  Amounts of Zn, Mn, Cd, Co and Ni extracted in the organic phase after solvent extraction using Cyanex 272 (20%, v/v) at different pHs (single extraction stage; T = 50°C, O/A ratio = 2/1, [TBP] = 2% (v/v), residence time = 10 min)

Fig. 3  Schematic flow diagram of the solvent extraction process developed for the selective recovery of Zn from the PLS emerging from a leaching process applied to unsorted spent batteries

Fig. 4  Kinetic of Zn electrodeposition observed at different pH values (current density = 360 A/m², agitation rate = 300 rpm, T = 25°C, residence time = 180 min)

Fig. 5  Composition of the metallic powder emerging from the electrodeposition process using MEB-EDS
Table 1  Characteristics of unsorted spent batteries pregnant leaching solution and synthetic solution used for precipitation and solvent extraction assays, respectively

Table 2  Selective recovery of Fe from a solution containing Zn (19.9 ± 1.8 g/L), Mn (27.5 ± 2.4 g/L), Cd (3.71 ± 0.24 g/L), Ni (3.51 ± 0.30 g/L), Fe (0.53 ± 0.05 g/L) and Co (0.26 ± 0.02 g/L) at pH = 4 in the presence of various amounts of H₂O₂

Table 3  Metal extraction efficiencies (%) from the synthetic solution using different concentrations of TBP (single extraction stage; O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; residence time = 10 min; pH = 2.2; T = 50°C, [Zn]₀ = 19.4 ± 0.84 g/L, [Mn]₀ = 23.4 ± 1.2 g/L, [Cd]₀ = 3.27 ± 0.13 g/L, [Ni]₀ = 3.19 ± 0.14 g/L and [Co]₀ = 0.25 ± 0.01 g/L)

Table 4  Effect of residence time on Zn extraction efficiencies from the synthetic solution (single extraction stage; O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.5; T = 50°C; [Zn]₀ = 19.4 ± 0.84 g/L, [Mn]₀ = 23.4 ± 1.2 g/L, [Cd]₀ = 3.27 ± 0.13 g/L, [Ni]₀ = 3.19 ± 0.14 g/L and [Co]₀ = 0.25 ± 0.01 g/L)

Table 5  Distribution coefficients and separation factors obtained for Zn, Mn and Cd (single extraction stage; O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; t = 10 min; T = 50°C; [Zn]₀ = 19.4 ± 0.84 g/L, [Mn]₀ = 23.4 ± 1.2 g/L, [Cd]₀ = 3.27 ± 0.13 g/L, [Ni]₀ = 3.19 ± 0.14 g/L and [Co]₀ = 0.25 ± 0.01 g/L)
Table 6  Amounts of metals present in the aqueous phase after different extraction stages

(O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.2;
t = 10 min; T = 50°C; [Zn]₀ = 19.4 ± 0.84 g/L, [Mn]₀ = 23.4 ± 1.2 g/L,
[Cd]₀ = 3.27 ± 0.13 g/L, [Ni]₀ = 3.19 ± 0.14 g/L and [Co]₀ = 0.25 ± 0.01 g/L)

Table 7  Residual concentrations of metals present in the aqueous phase after different
extraction stages performed on the PLS (O/A ratio = 2/1; 30% vol. Cyanex 272 in
kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C)

Table 8  Amounts of metals present in the stripped solution after two stripping stages
performed on the organic phase emerging from the extraction process applied to
the PLS (one stripping stage; O/A ratio = 2/1; 0.15 and 0.40 M H₂SO₄; t = 10 min;
T = 50°C) for the recovery of Zn followed by a second stripping step (O/A
ratio = 2/1; 1.00 M H₂SO₄; t = 10 min; T = 50°C) for the recovery of Fe

Table 9  Concentration of metals present in the stripped solution after the 1ˢᵗ stripping
stage performed on the organic phase emerging from the extraction process
applied to the PLS (one stripping stage; O/A ratio = 2/1; 0.15 M H₂SO₄;
t = 10 min; T = 50°C) for the recovery of Zn

Table 10  Mass balance of metals (unity = g) performed on one kilogram of battery powder
for the Cyanex272 extraction stage (O/A ratio = 2/1; 30% vol. Cyanex 272 in
kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C) and stripping stage (1ˢᵗ
stripping stage: O/A ratio = 2/1; 0.15 and 0.40 M H₂SO₄; t = 10 min; T = 50°C,
2ⁿᵈ stripping stage: O/A ratio = 2/1; 1.00 M H₂SO₄; t = 10 min; T = 50°C)
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Table 2  
Selective recovery of Fe from a solution containing Zn (19.9 ± 1.8 g/L), Mn (27.5 ± 2.4 g/L), Cd (3.71 ± 0.24 g/L), Ni (3.51 ± 0.30 g/L), Fe (0.53 ± 0.05 g/L) and Co (0.26 ± 0.02 g/L) at pH = 4 in the presence of various amounts of H$_2$O$_2$.

<table>
<thead>
<tr>
<th>Mass of H$_2$O$_2$ (added)</th>
<th>1xS*</th>
<th>1.25xS</th>
<th>2xS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>6.85 ± 1.40</td>
<td>4.29 ± 1.73</td>
<td>6.70 ± 4.15</td>
</tr>
<tr>
<td>Mn</td>
<td>7.83 ± 0.12</td>
<td>3.30 ± 1.44</td>
<td>5.24 ± 2.60</td>
</tr>
<tr>
<td>Cd</td>
<td>7.23 ± 1.55</td>
<td>3.14 ± 1.59</td>
<td>5.02 ± 2.80</td>
</tr>
<tr>
<td>Ni</td>
<td>6.49 ± 1.21</td>
<td>2.72 ± 1.51</td>
<td>4.66 ± 2.22</td>
</tr>
<tr>
<td>Minor metals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>69.3 ± 12.3</td>
<td>92.4 ± 1.8</td>
<td>87.6 ± 5.6</td>
</tr>
<tr>
<td>Co</td>
<td>5.51 ± 1.41</td>
<td>2.78 ± 1.23</td>
<td>5.13 ± 2.68</td>
</tr>
</tbody>
</table>

* S: Stoichiometric value of H$_2$O$_2$ required to oxidize all the Fe$^{2+}$ ions present in the PLS to Fe$^{3+}$ ions.
<table>
<thead>
<tr>
<th>TBP concentration (%)</th>
<th>Extraction efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

**Major metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Extraction Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>54.4 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>59.7 ± 6.1</td>
</tr>
<tr>
<td></td>
<td>49.2 ± 2.1</td>
</tr>
<tr>
<td>Mn</td>
<td>2.98 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>9.20 ± 4.45</td>
</tr>
<tr>
<td></td>
<td>6.26 ± 2.04</td>
</tr>
<tr>
<td>Cd</td>
<td>3.05 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>9.96 ± 4.47</td>
</tr>
<tr>
<td></td>
<td>7.22 ± 2.06</td>
</tr>
<tr>
<td>Ni</td>
<td>2.98 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>9.66 ± 4.38</td>
</tr>
<tr>
<td></td>
<td>6.91 ± 2.22</td>
</tr>
</tbody>
</table>

**Minor metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Extraction Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>2.17 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>10.9 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>5.73 ± 1.67</td>
</tr>
</tbody>
</table>
Table 4  Effect of residence time on Zn extraction efficiencies from the synthetic solution (single extraction stage; O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.5; T = 50°C, \([\text{Zn}]_0 = 19.4 \pm 0.8 \text{ g/L, } [\text{Mn}]_0 = 23.4 \pm 1.2 \text{ g/L, } [\text{Cd}]_0 = 3.27 \pm 0.13 \text{ g/L, } [\text{Ni}]_0 = 3.19 \pm 0.14 \text{ g/L and } [\text{Co}]_0 = 0.25 \pm 0.01 \text{ g/L})

<table>
<thead>
<tr>
<th>Residence time (min)</th>
<th>Extraction efficiencies from the synthetic solution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Major metals</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>62.6 ± 4.4</td>
</tr>
<tr>
<td>Mn</td>
<td>12.1 ± 10.6</td>
</tr>
<tr>
<td>Cd</td>
<td>11.3 ± 11.0</td>
</tr>
<tr>
<td>Ni</td>
<td>11.8 ± 11.0</td>
</tr>
<tr>
<td>Minor metals</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>11.8 ± 9.6</td>
</tr>
</tbody>
</table>
Table 5  Distribution coefficients and separation factors obtained for Zn, Mn and Cd (single extraction stage; O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; t = 10 min; T = 50°C; [Zn]₀ = 19.4 ± 0.8 g/L, [Mn]₀ = 23.4 ± 1.2 g/L, [Cd]₀ = 3.27 ± 0.13 g/L, [Ni]₀ = 3.19 ± 0.14 g/L and [Co]₀ = 0.25 ± 0.01 g/L)

<table>
<thead>
<tr>
<th>pH</th>
<th>D₉n</th>
<th>D₉m</th>
<th>D₉Cd</th>
<th>β₉n/M₉m</th>
<th>β₉n/Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.33</td>
<td>0.01</td>
<td>0.01</td>
<td>56.9</td>
<td>61.1</td>
</tr>
<tr>
<td>2.0</td>
<td>1.54</td>
<td>0.00</td>
<td>0.01</td>
<td>353</td>
<td>110</td>
</tr>
<tr>
<td>2.5</td>
<td>2.35</td>
<td>0.04</td>
<td>0.07</td>
<td>57.4</td>
<td>34.2</td>
</tr>
<tr>
<td>3.0</td>
<td>40.5</td>
<td>0.08</td>
<td>0.06</td>
<td>538</td>
<td>643</td>
</tr>
<tr>
<td>3.5</td>
<td>330</td>
<td>0.90</td>
<td>0.77</td>
<td>366</td>
<td>431</td>
</tr>
</tbody>
</table>
Table 6  
Amounts of metals present in the aqueous phase after different extraction stages (O/A ratio = 2/1; 20% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C; \([\text{Zn}]_0 = 19.4 \pm 0.8 \text{ g/L, } [\text{Mn}]_0 = 23.4 \pm 1.2 \text{ g/L, } [\text{Cd}]_0 = 3.27 \pm 0.13 \text{ g/L, } [\text{Ni}]_0 = 3.19 \pm 0.14 \text{ g/L and } [\text{Co}]_0 = 0.25 \pm 0.01 \text{ g/L})

<table>
<thead>
<tr>
<th>Number of stages</th>
<th>Amounts of metals present in the aqueous phase (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td><strong>Major metals</strong></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>6.14 ± 0.96</td>
</tr>
<tr>
<td>Mn</td>
<td>23.4 ± 1.2</td>
</tr>
<tr>
<td>Cd</td>
<td>3.22 ± 0.16</td>
</tr>
<tr>
<td>Ni</td>
<td>3.03 ± 0.16</td>
</tr>
<tr>
<td><strong>Minor metals</strong></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.241 ± 0.012</td>
</tr>
</tbody>
</table>
Table 7  Residual concentrations of metals present in the aqueous phase after different extraction stages performed on the PLSr (O/A ratio = 2/1; 30% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C)

<table>
<thead>
<tr>
<th>Nb of extraction stage</th>
<th>Initial</th>
<th>Residual concentration in aqueous phase (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

**Major metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial</th>
<th>Residual</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>19.9 ± 1.8</td>
<td>4.99 ± 0.80</td>
<td>0.29 ± 0.13</td>
</tr>
<tr>
<td>Mn</td>
<td>27.5 ± 2.4</td>
<td>26.0 ± 1.6</td>
<td>25.9 ± 0.5</td>
</tr>
<tr>
<td>Cd</td>
<td>3.71 ± 0.24</td>
<td>2.86 ± 0.28</td>
<td>2.86 ± 0.28</td>
</tr>
<tr>
<td>Ni</td>
<td>3.51 ± 0.30</td>
<td>3.04 ± 0.19</td>
<td>3.10 ± 0.31</td>
</tr>
</tbody>
</table>

**Minor metals**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Initial</th>
<th>Residual</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.530 ± 0.047</td>
<td>0.317 ± 0.025</td>
<td>0.043 ± 0.023</td>
</tr>
<tr>
<td>Co</td>
<td>0.260 ± 0.023</td>
<td>0.255 ± 0.014</td>
<td>0.256 ± 0.020</td>
</tr>
</tbody>
</table>
Table 8

Amounts of metals present in the stripped solution after two stripping stages performed on the organic phase emerging from the extraction process applied to the PLSr (one stripping stage; O/A ratio = 2/1; 0.15 and 0.40 M H$_2$SO$_4$; t = 10 min; T = 50°C) for the recovery of Zn followed by a second stripping step (O/A ratio = 2/1; 1.00 M H$_2$SO$_4$; t = 10 min; T = 50°C) for the recovery of Fe

<table>
<thead>
<tr>
<th>[H$_2$SO$_4$]</th>
<th>Initial amount in organic phase</th>
<th>Metal amounts in the stripping solution (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.15 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40 M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.00 M</td>
</tr>
<tr>
<td>Zn</td>
<td>19.55</td>
<td>12.93 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.00 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>0.441</td>
<td>n.a.*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19 ± 0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.10 ± 0.00</td>
</tr>
</tbody>
</table>

*n.a.: In this case, metal concentration was not investigated.
Table 9  Concentration of metals present in the stripped solution after the 1st stripping stage performed on the organic phase emerging from the extraction process applied to the PLSr (one stripping stage: O/A ratio = 2/1; 0.15 M H₂SO₄; t = 10 min; T = 50°C) for the recovery of Zn

<table>
<thead>
<tr>
<th></th>
<th>Concentration measured in stripped solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals (g/L)</strong></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>8.28 ± 0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.17 ± 0.04</td>
</tr>
<tr>
<td><strong>Metals (mg/L)</strong></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>98 ± 20</td>
</tr>
<tr>
<td>Cd</td>
<td>2.9 ± 0.9</td>
</tr>
</tbody>
</table>
Table 10  Mass balance of metals (unity = g) performed on one kilogram of battery powder for the Cyanex272 extraction stage (O/A ratio = 2/1; 30% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C) and stripping stage (1st stripping stage: O/A ratio = 2/1; 0.15 and 0.40 M H₂SO₄; t = 10 min; T = 50°C, 2nd stripping stage: O/A ratio = 2/1; 1.00 M H₂SO₄; t = 10 min; T = 50°C)

<table>
<thead>
<tr>
<th>Metals</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Mass balance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic phase</td>
<td>Aqueous phase</td>
<td>Organic phase</td>
<td>Aqueous phase</td>
<td>Organic phase</td>
</tr>
<tr>
<td>Zn</td>
<td>183</td>
<td>180</td>
<td>2.7</td>
<td>29.5</td>
<td>151</td>
</tr>
<tr>
<td>Cd</td>
<td>252</td>
<td>14.7</td>
<td>238</td>
<td>11.1</td>
<td>3.58</td>
</tr>
<tr>
<td>Mn</td>
<td>34.0</td>
<td>7.80</td>
<td>26.2</td>
<td>7.79</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>2.40</td>
<td>0.00</td>
<td>2.30</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Co</td>
<td>32.2</td>
<td>3.80</td>
<td>28.4</td>
<td>3.76</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe</td>
<td>4.90</td>
<td>4.50</td>
<td>0.39</td>
<td>4.47</td>
<td>0.00</td>
</tr>
</tbody>
</table>

A = Initial (leachate)
B = Extractions stage
C = 1st stripping stage
D = 2nd stripping stage

Mass balance ratios = Grey cases in B (aqueous phase) + C (aqueous phase) + D (organic phase)/A
Fig. 1
Fig. 2
* C272: Cyanex 272 – Solvent extraction conditions: two extraction stage; O/A ratio = 2/1; 30% vol. Cyanex in kerosene, 2% vol. TBP, pH = 2.2, t = 10 min and T = 50°C

Fig. 3
Fig. 4
Fig. 5
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Publication Title: Journal of Environmental Engineering

Manuscript Title: Recovery of Zn from unsorted spent batteries using solvent extraction and electrodeposition

Author(s) – Names, postal addresses, and e-mail addresses of all authors
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Date: July 19, 2017

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Date: July 19, 2017

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July 19, 2017
Date

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Manuscript MS EEENG-4240

Reviewers' comments:

Reviewer #1: Overall Remark

The authors have shown the challenging task of the selective removal of one metal species (in this case Zn) from a concentrated solution containing several metals and the successful separation of Fe and Zn from the rest of the metals using two technologies of precipitation and solvent extraction.

Specific Comment:
Perform a mass balance for all metal species [Fe, Co, Zn, Mn, Cd, Ni] for precipitation and solvent extraction. Show the mass balance for the cumulative removal of all metal species using both removal technologies [precipitation and solvent extraction]. This can be shown in a Table or in a Figure using histograms.

Response: The mass balance was performed for the solvent extraction process and the results were added in the Table 9 in the section “Results and Discussion > solvent extraction > Mass balance of the solvent extraction process”. The following sentences were added in Page 29.

“Mass balance of the solvent extraction process

Table 10 presents the mass balance performed for the solvent extraction experiments including both solvent extraction and stripping steps. The determination of the mass balance of a solvent extraction system is important to ensure that there is no accumulation, contamination or loss of metals during the different steps (extraction, stripping). According to the results obtained, the mass balance ratios were closed to 1 for all the metals (between 0.99 and 1.03); indicating that
the balance error didn’t exceed 3%. These results indicated that the solvent extraction process is reliable.”

Table 10  Mass balance of metals (unity = g) performed on one kilogram of battery powder for the Cyanex272 extraction stage (O/A ratio = 2/1; 30% vol. Cyanex 272 in kerosene; 2% vol. TBP; pH = 2.2; t = 10 min; T = 50°C) and stripping stage (1st stripping stage: O/A ratio = 2/1; 0.15 and 0.40 M H₂SO₄; t = 10 min; T = 50°C, 2nd stripping stage: O/A ratio = 2/1; 1.00 M H₂SO₄; t = 10 min; T = 50°C)

<table>
<thead>
<tr>
<th>Metals</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Mass balance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic phase</td>
<td>Aqueous phase</td>
<td>Organic phase</td>
<td>Aqueous phase</td>
<td>Organic phase</td>
</tr>
<tr>
<td>Zn</td>
<td>183</td>
<td>180</td>
<td>2.7</td>
<td>29.5</td>
<td>151</td>
</tr>
<tr>
<td>Cd</td>
<td>252</td>
<td>14.7</td>
<td>238</td>
<td>11.1</td>
<td>3.58</td>
</tr>
<tr>
<td>Mn</td>
<td>34.0</td>
<td>7.80</td>
<td>26.2</td>
<td>7.79</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>2.40</td>
<td>0.00</td>
<td>2.30</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Co</td>
<td>32.2</td>
<td>3.80</td>
<td>28.4</td>
<td>3.76</td>
<td>0.00</td>
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<tr>
<td>Fe</td>
<td>4.90</td>
<td>4.50</td>
<td>0.39</td>
<td>4.47</td>
<td>0.00</td>
</tr>
</tbody>
</table>

A = Initial (leachate)  
B = Extractions stage  
C = 1st stripping stage  
D = 2nd stripping stage  
Mass balance ratios = Grey cases in B (aqueous phase) + C (aqueous phase) + D (organic phase)/A

We didn’t perform the mass balance for Fe precipitation as some information related to the composition of precipitation sludge and the amount produced are missing. Moreover, these information are less important than those related to the solvent extraction as we decided to use selective stripping process to separate Fe from Zn.
Reviewer #2: This important and interesting paper is overall of good quality, well written and presented. I recommend its publication in Journal of Environmental Engineering.

Major comments:

None.

Minor comments:

1. I am interested in knowing about what to be done with the leaching solution following recovery. It is technically still hazardous waste containing very high concentrations of some potentially toxic elements including Cd as well as organics (actually it seems worse than disposing the batteries as solid hazardous waste). What is the proposed route for further manipulation/disposal? This should be mentioned. This is also one aspect that deserves studying in parallel with the main recovery process as it may impede the commercialization of the overall project.

Response:

After the recovery of Zn from the leachate, the residual metals present in the leachate will be recovered using additional steps:

- D2EHPA organic solvent extraction will be used to recover Cd from the Zn-depleted leachate.
- Cyanex 272 solvent extraction will be also applied recover Co and Ni at higher pH values from the Zn- and Co-depleted leachate.

The following sentences were added in the Conclusion to clarify this point:

“The selective recovery of other metals such as Mn, Ni, Co and Cd from the PLS using D2EHPA and/or Cyanex 272 extraction steps has been studied in another work and the results seemed promising. The possibility to transfer this process from laboratory to the commercial scale is considered as a difficult task, requiring additional works. For example, the preparation of spent batteries should be improved to obtain the maximum metals yields during the leaching step. Before the Zn electrodeposition step, Zn should be concentrated in the aqueous phase by the use
of a stripping step with higher O/A ratios in order to improve the performance of the electrodeposition (increase of Faraday yield). The impurities such as Cd and Fe should be removed using some additional processes to improve the quality of Zn deposit and reduce electrochemical parasitic reactions. The difficulty of social acceptability of this process due to the use of organic solvent was also encountered. However, green alternative solvent could be used to replace the current solvent used when they will be commercially available.”

Due to the limitation of natural resources, the recovery of metals from wastes is becoming essential even if their disposal in landfill sites might be cheaper. The landfilling of spent batteries may contaminate the groundwater and may be hazardous to the aquatic life. From the previous reasons, we are seeking the method that could be economical feasible and at the same time have a less hazardous effect on the environment. Technically, solvent extraction was proven as an economical beneficial method to selectively recover metals of interest from highly contaminated solutions due to the long duration life of organic solution and the possibility to reuse them several times. However all economic analysis was predicted to be analyse in the further study. Additional experiments should be performed to recover Co, Mn, Ni and Cd from the leachate in order to recycle these elements.

2. Introduction: We already know, as the authors suggested, that some organic solvents including Cyanex 272 can be effectively used to extract Zn under certain conditions. Similar parameters as in the cited references were used in the present paper. The originality of the study (which is clear to me) is not obvious in the introduction for the reader and therefore should be clearly stated. Currently it may seem to some as taking what parameters work and duplicating what is already done.

Response: The originality of this project was related to the recovery of valuable metals from a mixture of spent batteries using two different organic solvents and to improve the performances of metals recoveries compared to actual studies which focused their attention on only one metal or one type of spent batteries. The approach used in the present study was different from the existing processes. Indeed, the experimental conditions used in this study and the form under which metals are recovered were different from the other studies. For example, Innocenzi and
Veglio (2012) used an O/A ratio of 1/1 while an O/A ratio of 2/1 was applied in our study. Also in their study, the experiments were performed at pH 2 while in our study, the pH was fixed at approximately 2.2 due to the different composition of our samples. The composition of PLS was also different from the other studies, highlighting the necessity to develop/optimize a process train allowing the recovery of Zn since the PLS solution used in our study contained huge amounts of various metals. From the previous statement, it is much more difficult to separate each metal from another one as they are present in high concentrations. The following sentence were added in the Introduction to highlight the originality of this study (Page 7).

“The originality of the present study is based on the use of a Cyanex 272 solvent extraction to selectively recover Zn from a PLS emerging from the recycling of unsorted spent batteries (alkaline, Zn-C, Li-ion, Ni-Cd, Ni-MH and Li-M). This PLS contained huge amounts of metals (Zn, Fe, Cd, Mn, Ni, Co, etc.), requiring the development of a purification process train to selectively recover Zn while minimizing the loss of the other valuable metals that could be recovered from the PLS. The present work was focused on the selective recovery of Zn from the PLS by comparing the performances of the selective precipitation and solvent extraction. The influence of solvent extraction parameters (pH, phase modifier concentration, reaction time, etc.) was also investigated. This study aims to:

- Selective recover the Zn from the PLS by comparing the performances of the selective precipitation and solvent extraction (Cyanex 272 was used as an organic solvent);
- Investigate the influence of solvent extraction parameters (pH, phase modifier concentration, reaction time, etc.) on the recovery of Zn;
- Investigate the recovery of Zn by electrodeposition.

The recovery of residual metals (Mn, Cd, Ni, etc.) from the leaching solution will be also investigated in future work using other type of organic solvents.”
3. Materials and methods: Did the research team develop their own protocols by themselves or did they directly use/improve some previously developed protocols? I don't see any source cited for a number of detailed protocols presented there (must be cited if there are any). Otherwise, it needs much more detailed explanation for protocol details (maybe in supplementary material). Parameter selections should be justified whenever needed; e.g. 45 min contact of black powder with leaching solution on p.12. why exactly 45 min? This is just one example.

Response:

The leaching experiment conditions were obtained from a previous study. This study aimed to determine the optimal leaching conditions to simultaneously solubilize the valuable metals from unsorted spent batteries. The reference (Tanong et al., 2017) was added to this publication to explain the selection of leaching parameters. Some of the experiments were performed in our laboratory using our own protocol combed with the protocol obtained from the Company Cytec (Cytec 2008) and the literature review. For the solvent extraction processes, some experimental details came from personal contact with Cytec Company. For the solvent extraction, some experimental conditions (pH, number of stripping steps, etc.) were determined by varying some parameters to obtain the best results. The amount of organic solvent was calculated from the stoichiometry value of Zn present in the PLS. Some sentences of the “Methodology” were modified according the suggestion of the reviewer.

Page 12: “The optimal leaching conditions were obtained from a previous work (Tanong et al., 2017).”

Page 13: “For the first series of solvent extraction experiments, Fe was selectively removed from the PLSr by precipitation after the addition of H2O2 to oxidize Fe2+ ions to Fe3+ ions and the addition of NaOH until pH = 4.00 to precipitate Fe as Fe(OH)3. Indeed, according to the Pourbaix diagram, the precipitation of iron is better at pH 4.00 once oxidized in its trivalent form.”

Page 14: “Solvent extraction experiments were carried out in 250-mL beakers at 50°C (Cytec, 2008).”
Page 14: “The first set of extraction experiments, performed in triplicate, successively determined the influence of different parameters, such as pH (1.5, 2.0, 2.5, 3.0 and 4.0) (Cytec, 2008), equilibration time (5, 10, 20, 30 and 60 min) and [TBP] (0, 2 and 5% (v/v)) (Cytec, 2008) on the selective extraction of Zn from the PLSs.”

Page 17: “The aqueous samples were analyzed by ICP-AES (Inductively coupled plasma - atomic emission spectroscopy, Varian 725-ES) (Tanong et al., 2017).”

4. Results and discussion: Would potential co-deposition/co-precipitation of other elements present in the solution in trace concentrations together with Zn be problematic? What purity of Zn is needed for that to be commercially viable (if there is such an expectation/standard)? What is the sensitivity of MEB-EDS. Is detection capability high enough to draw the brief conclusion presented on p.29 that 'there was only Zn' in the metallic powder? Deserves a longer discussion than one sentence.

Response
The following sentences were added in the Section “Results and Discussion > solvent extraction > stripping experiment” to present the potential metals that can be problematic for the electrodeposition of Zn and the concentration tolerated based on the study performed by Haghighi et al. (2015).

“Table 9 presents the concentration of metals measured in the effluent emerging from stripping steps that will be used for the electrodeposition of Zn. According to Haghighi et al. (2015), the concentration of Co and Ni should not be greater than 0.5 and 1.0 mg/L, respectively, in order to attain reasonable costs for the Zn electrodeposition process. For iron, it should not be greater than 20 mg/L. For Cd, it should be less than 1 mg/L. The concentration of Mn greater than 10 g/L would affect the Zn electrodeposition efficiencies (decrease of the faradic yield due to electrochemical parasitic reactions) and costs (increase of the frequency of electrodes cleaning). From our experiment results presented in Table 10, it could be noticed that the concentration of Co was equal to 1.1 mg/L while Ni was not detected. The concentration of Mn was equal to only 0.17 g/L. The concentrations of Cd (2.9 mg/L) and Fe (98 mg/L) were higher than the
concentrations recommended by Haghighi et al. (2015). From the previous reason, the scrubbing stage was highly recommended to remove the Cd from the organic phase and an additional step is recommended to remove Fe by precipitation method.”

Table 9 Concentration of metals present in the stripped solution after the 1st stripping stage performed on the organic phase emerging from the extraction process applied to the PLSr (one stripping stage: O/A ratio = 2/1; 0.15 M H2SO4; t = 10 min; T = 50°C) for the recovery of Zn

<table>
<thead>
<tr>
<th>Metals (g/L)</th>
<th>Concentration measured in stripped solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>8.28 ± 0.02</td>
</tr>
<tr>
<td>Mn</td>
<td>0.17 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metals (mg/L)</th>
<th>Concentration measured in stripped solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>98 ± 20</td>
</tr>
<tr>
<td>Cd</td>
<td>2.9 ± 0.9</td>
</tr>
</tbody>
</table>

To determine the impurities present in the Zn metallic powder, a powder sample was dissolved in 5 % HNO3 and an ICP analysis was conducted to determine the amount of impurities. The purity of the Zn deposit was estimated at 99% based on the composition of the results emerging from the ICP-AES analysis. An MEB-EDS analysis was only performed to confirm/infirm that there was some impurities present in the metallic powder.

The following sentence were added/modified to clarify this point:

“The deposit obtained was characterized using an ICP-AES to determine its composition and a MEB-EDS to confirm if there were a present of some of impurities or not. The result from the
ICP-AES and EDS analysis (Fig. 5) showed that the metallic powder was mainly composed of Zn with the presence of some impurities (< 1% of Fe, Cd, Mn).”

5. Results and discussion: It would be very interesting to know where are we exactly after this study regarding the industrial/commercial feasibility of the protocol (if possible). What challenges are addressed in terms of extraction process and what remains? Alternatively, this could rather be briefly mentioned in Conclusions. if preferred (see the next comment).

Response: The following sentences were added in the conclusion according to the suggestion of the reviewer:

“The selective recovery of other metals such as Mn, Ni, Co and Cd from the PLS using D2EHPA and/or Cyanex 272 extraction steps has been studied in another work and the results seemed promising. The possibility to transfer this process from laboratory to the commercial scale is considered as a difficult task, requiring additional works. For example, the preparation of spent batteries should be improved to obtain the maximum metals yields during the leaching step. Before the Zn electrodeposition step, Zn should be concentrated in the aqueous phase by the use of a stripping step with higher O/A ratios in order to improve the performance of the electrodeposition (increase of Faraday yield). The impurities such as Cd and Fe should be removed using some additional processes to improve the quality of Zn deposit and reduce electrochemical parasitic reactions. The difficulty of social acceptability of this process due to the use of organic solvent was also encountered. However, green alternative solvent could be used to replace the current solvent used when they will be commercially available.”

6. Conclusions: What one question did this study successfully answer, in one sentence. as a summary? It is important to see that at the very end of this section. I also strongly recommend the research team to address further specific research recommendations at the end. Is there a need/opportunity to extend this to a larger scale? What needs to be specifically done next from the scientific standpoint (must be mentioned) as well as in terms of industrial/commercial feasibility (if possible)?
Response: The following sentences were added in the conclusion to clarify what should be done in order to allow the commercialisation of the process developed.

“The selective recovery of other metals such as Mn, Ni, Co and Cd from the PLS using D2EHPA and/or Cyanex 272 extraction steps has been studied in another work and the results seemed promising. The possibility to transfer this process from laboratory to the commercial scale is considered as a difficult task, requiring additional works. For example, the preparation of spent batteries should be improved to obtain the maximum metals yields during the leaching step. Before the Zn electrodeposition step, Zn should be concentrated in the aqueous phase by the use of a stripping step with higher O/A ratios in order to improve the performance of the electrodeposition (increase of Faraday yield). The impurities such as Cd and Fe should be removed using some additional processes to improve the quality of Zn deposit and reduce electrochemical parasitic reactions. The difficulty of social acceptability of this process due to the use of organic solvent was also encountered. However, green alternative solvent could be used to replace the current solvent used when they will be commercially available.”